

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
31 May 2007 (31.05.2007)

PCT

(10) International Publication Number
WO 2007/060237 A1

(51) International Patent Classification:
C08L 61/06 (2006.01) **D04H 1/64** (2006.01)

(21) International Application Number:
PCT/EP2006/068934

(22) International Filing Date:
27 November 2006 (27.11.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
102005056792.4
28 November 2005 (28.11.2005) DE

(71) Applicant (for all designated States except US): **SAINT-GOBAIN ISOVER** [FR/FR]; Les Miroirs - 18 Avenue D'Alsace, F-92400 Courbevoie (FR).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **WAGNER, Eva** [DE/DE]; Dalbergstrasse 23, 67122 Altrip (DE). **HÜNIG, Hagen** [DE/DE]; Dr Albert Reinmann Strasse 20, 68526 Ladenburg (DE).

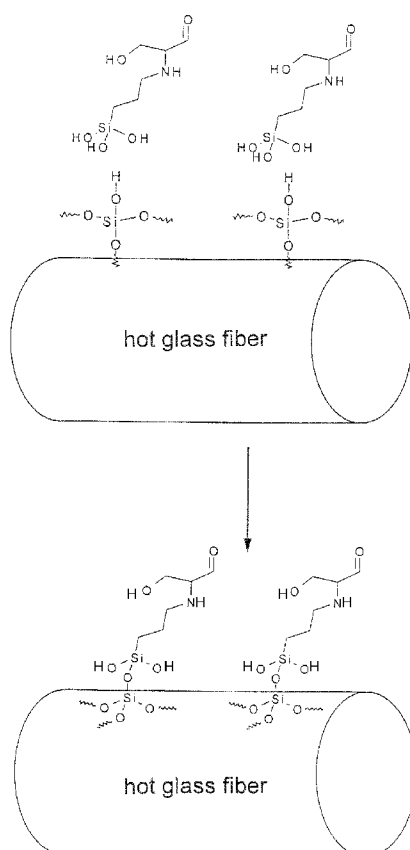
(74) Agent: **JAMET, Vincent**; Saint-Gobain Recherche, Industrial Property Department, 39 Quai Lucien Lefranc, F-93300 Aubervilliers (FR).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: FORMALDEHYDE-FREE PHENOLIC RESIN BINDER.



(57) Abstract: The present invention concerns a composition containing: an aqueous dispersion of at least one phenol-formaldehyde resin; at least one amine compound, wherein the molecular mass of the amine compound does not exceed approximately 20 000 g/mole, at least one activated silane, as well as at least one aromatic hydroxyl compound. The composition may be employed as a formaldehyde-free binder for the manufacture of mineral wool.



Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

FORMALDEHYDE-FREE PHENOLIC RESIN BINDER

The present invention concerns a formaldehyde-free composition comprising
5 a phenolic resin to be used for the manufacture of insulation products made of mineral wool, a binder for mineral wool, a method for the manufacture of mineral wool bound in a formaldehyde-free manner, as well as the bound mineral wool product thus obtained.

In the manufacture of bound mineral wool products from a molten glass or
10 mineral material it has for a long time been accepted practice to apply, following fiberization of the molten material, a binder on the basis of phenol-formaldehyde resin on the fibers while they are still hot. This preferably takes place in the chute following fiberization, e.g. in accordance with the blast drawing process according to DE 35 09 426 A1.

15 Here a phenol-formaldehyde resin, being the best-known binder of the prior art, is preferably sprayed onto the fibers in the form of an aqueous solution, or dispersion, wherein the phenol-formaldehyde resin then begins to polymerize on the fiber surface owing to the still relatively high temperatures of the fibers, and connects the single fibers with each other as a result of the polymerization process,
20 particularly at crossing points of fibers, inasmuch as the fibers lying on top of each other at a crossing point are more or less embedded there by solidified droplets of resin, and thus the relative mobility of the single fibers is initially impeded and later on prevented entirely upon curing by means of hot gases, for instance inside a tunnel furnace.

25 A like binder is described, e.g., in US 3,231,349. For reasons of protection of the environment as well as for reasons of workplace safety, more and more attempts are meanwhile being undertaken to replace the conventional phenolic resin binders with alternative, formaldehyde-free binders because of their formaldehyde content and their formaldehyde emission.

Thus for example EP 0 583 086 B2 describes a curable, formaldehyde-free, aqueous binder composition for glass fibers on the basis of polymer polyacids containing at least two carboxylic acid groups or anhydride groups, which comprises a polyol containing at least two hydroxyl groups and a phosphorus-containing catalyst, wherein a ratio of the number of equivalents of COOH group to OH group must be from 0:0.01 to 1:3.

A polymer polyacid described in EP 0 583 086 B2 is, for instance, polyacrylic acid.

A preferably used polyol is β -hydroxyalkylamide, e.g., [N,N-di(β -hydroxyethyl)]-adipamide, however it is also possible to use, e.g., ethylene glycol, glycerol, pentaerythritol, trimethylol propane, sorbitol, sucrose, glucose, resorcinol, catechol, pyrogallol, glycolated ureas, 1,4-cyclohexane diol, diethanolamine or triethanolamine.

Similar binder compositions for mineral fibers are, e.g., also known from US 6,331,350 B1, EP 0 990 727 A1, EP 0 990 728 A1, and EP 0 990 729 A1. The listed documents of the prior art also use a polyacrylic acid as a polymer polyacid. By way of a polyol, alkanolamines as well as glycols are also used there.

In addition, EP 0 882 074 B1 describes binder compositions for mineral fibers on the basis of polyacrylic acids and glycols as polyols.

All of the binder compositions of the prior art constituting an alternative for phenol-formaldehyde resins are, however, currently only conditionally suited for the manufacture of mineral wool products, mainly due to their lack of water resistance, so that, for example, the binders based on polyacrylate resins have hitherto generally been barred from practical use for the manufacture of mineral wool products.

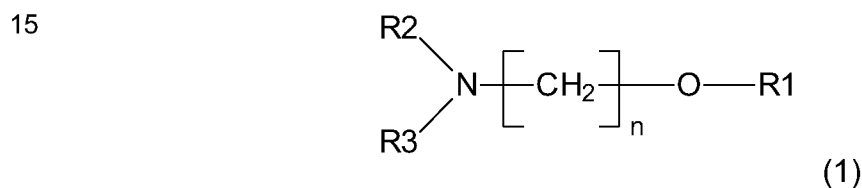
The chemical industry has meanwhile furnished pre-condensated phenol-formaldehyde resins that do - in a sense - already present a reduced content of free formaldehyde, however still have to be subsequently crosslinked with additional formaldehyde in order to improve the properties of resin and binder, particularly water resistance. As a result, emissions of formaldehyde due to its

high vapor pressure and the relatively slow crosslinking reaction between polymer chains are nearly unavoidable.

Starting out from the prior art of the commercially available phenolic resin binders reduced in formaldehyde, the applicant has set itself the task for the purposes of mineral wool manufacture in the development of novel,
 5 environmentally compatible binders to arrive at formaldehyde-free binders with the classical phenol-formaldehyde resins despite their formaldehyde content.

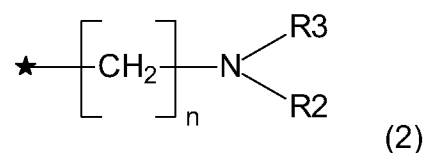
According to the present invention, this object is achieved through a formaldehyde-free composition comprising an aqueous dispersion of a phenol-
 10 formaldehyde resin, a binder comprising said composition and a method for the manufacture of mineral wool bound in a formaldehyde-free manner.

In particular, the present invention concerns a composition containing:
 an aqueous dispersion of at least one phenol-formaldehyde resin;
 at least one amine compound of the general formula (1)



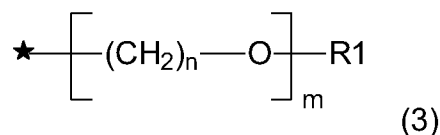
wherein:

R1, R2 and R3 independently of each other, equal or not equal,
 20 corresponds to H and R1 of the general formula (2):



with a value for n of 2-10, and

R2 and R3, independently of each other, are equal or not equal to H or correspond to the general formula (3):



wherein m may assume a value of 1-50,

and the molecular mass of the amine compound does not exceed approximately 20 000 g/mole;

5 at least one activated silane,

which may be obtained by a conversion of a silane, selected from the group: mono-, di- and trialkoxysilanes having one C₁ to C₈ alkoxy group, wherein the alkoxysilane carries at least one C₂ to C₁₀ aminoalkyl group or a C₂ to C₁₀ N-aminoalkyl group; 3(2-aminoethylamino)propyltrimethoxysilane; (MeO)₃-Si-(CH₂)₃-NH-(CH₂)₃-Si-(OMe)₃; 3-aminopropylsilanetriol; aminosilane with ethoxylated nonylphenolate; phenyl-CH₂-NH-(CH₂)₃-NH-(CH₂)₃-Si-(OMe)₃*HCl; as well as mixtures thereof;

15 with an enolizable ketone having at least one carbonyl group or a ketone having at least one OH group, wherein the ketone contains 3 to 12 C atoms, as well as

at least one aromatic hydroxyl compound selected from the group consisting of: dihydroxybenzenes and their hydroxymethylated compounds; trihydroxybenzenes and their mono- and dihydroxymethylated compounds; C-alkylated compounds of phenol or of resorcin; autocondensation products of the hydroxymethylated compounds; activated heterocycles and their mono- or dialkylated compounds or their anellated derivatives; di- and trihydroxy derivatives of naphthalene; as well as mixtures thereof or mixtures containing these substances.

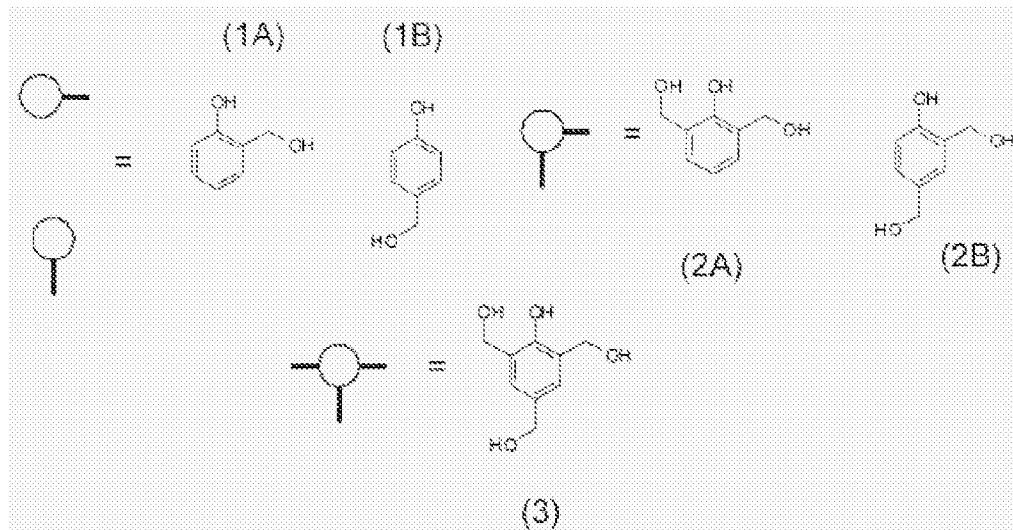
Particularly due to the fact that the composition of the invention contains at least one aromatic hydroxyl compound, it is possible to trap free formaldehyde

from the used resin and chemically convert it non-reversibly under the given conditions into such molecules which themselves are not capable of participating in the crosslinking reaction of the resin. Thanks to this measure it is one the one hand not necessary any more to add additional formaldehyde for subsequent crosslinking, and on the other hand free formaldehyde contained in the phenolic resin is bound chemically. Thus free formaldehyde is present neither in the resin nor in a mineral wool product bound by it.

As aromatic hydroxyl compounds those are suited which are in particular selected from the group consisting of: dihydroxybenzenes, particularly 1,3-dihydroxybenzene, 1,2-dihydroxybenzene or 1,4-dihydroxybenzene, as well as their hydroxymethylated compounds, in particular hydroxymethylated derivatives of resorcin or benzocatechin, such as 2,4-dihydroxyphenylmethanol or 2,3-dihydroxyphenylmethanol, but also multihydroxymethylated derivatives of these activated aromatic substances, e.g., 2,3-dihydroxy-4-hydroxymethylphenylmethanol or 4,5-dihydroxy-2-hydroxymethylphenylmethanol; trihydroxybenzenes, particularly 1,3,5-trihydroxybenzene or 1,2,3-trihydroxybenzene, their mono- and dihydroxymethylated compounds, such as 2,3,4-trihydroxyphenylmethanol or 2,4,6-trihydroxyphenylmethanol; C-alkylated compounds of phenol or of resorcin, e.g., 1-hydroxy-2-methylbenzene, 1-hydroxy-3-methylbenzene, 1-hydroxy-4-methylbenzene or 2-methylresorcin; autocondensation products of the hydroxymethylated compounds, such as bis-2,4-dihydroxyphenylmethane; activated heterocycles, e.g., pyrrole, thiophene, their mono- or dialkylated compounds or their anellated derivatives, such as indole or thioindole; di- and trihydroxyderivatives of naphthalene. It is, of course, also possible to use mixtures of these substances and mixtures containing them.

The modification on a complex multi-substance mixture - such as a phenol-formaldehyde resin or a binder produced therefrom for mineral wool with different additives - constitutes a difficult set of problems, particularly inasmuch as the resin constitutes a very unstable intermediate product. Depending on the usually unknown origin of this preparation, the reactive components are present in various concentrations and thus critically influence the material properties of the finished product. The main constituents of a typical phenol-formaldehyde resin and their effect as a polymer constitutional unit are shown in the following schematic

formulae:



Depending on the ratio of the single constituents, a resin polymer having various properties is formed.

- 5 It is possible to discern various cases of polymerization and thus of the resulting polymers having different properties, which are represented schematically in the following:

Case 1:

- Where predominantly only simple constitutional units are present, a chain-type polymer having few linking sites between the single chains is built up, i.e., the simple constitutional units polymerize with themselves, which fact may be represented schematically by the following schematic formulae by using the above defined formula abbreviations:

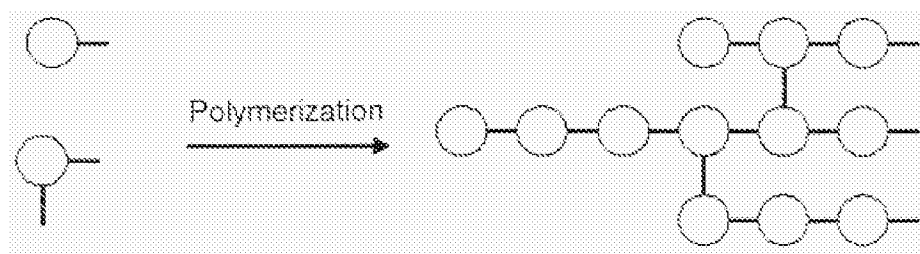


- 15 In the prior art such essentially linear and hardly branched polymer chains were subsequently crosslinked with formaldehyde in order to achieve an enhanced water resistance. The inventors intend to avoid this addition of formaldehyde. Particularly the reason for this is that formaldehyde is a volatile substance, and that the latter has a tendency to desorption under the production conditions of an elevated temperature rather than entering the
- 20

comparatively slow crosslinking reaction with the polymer chains.

Case 2:

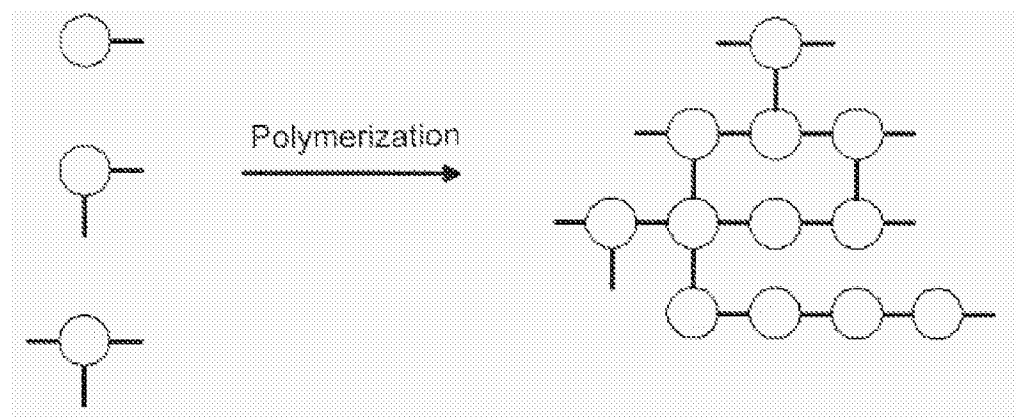
Where a mixture of simple- and double-substituted constitutional units exists which polymerize with themselves, one obtains a polymer having more
5 strongly reticulated chains, which may be represented schematically by the following schematic formulae by using the above defined formula abbreviations:



The resistance of such binder resins and of mineral wool products thereby
manufactured against swelling processes due to moisture, such as on the
10 construction site during bad weather or in the outdoor range, is enhanced in
comparison with the non-crosslinked polymer chains.

Case 3:

In the third case, three simple-, double- and triple-substituted compounds
are present in parallel which polymerize with themselves, which may be
15 represented schematically by the following schematic formulae by using the
above defined formula abbreviations:



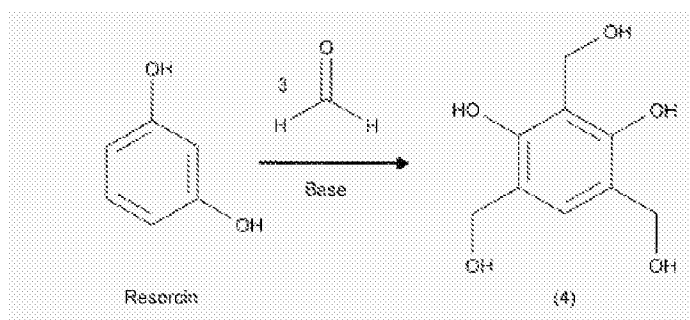
The resistance of such a plastic material against swelling is very high.

Nevertheless, the storing capability and the processing time may be reduced depending on the concentration of the higher-substituted constitutional units depending on the pH value and the concentration of formaldehyde or of compounds releasing it, respectively,

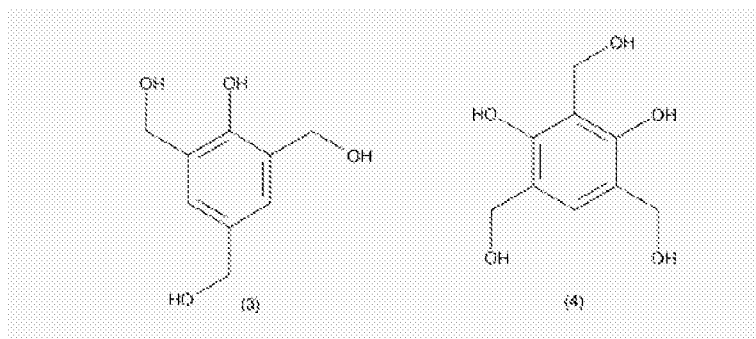
- 5 When viewed globally, however, a resin in accordance with Case 3 is desirable, yet in the prior art this could only be achieved with formaldehyde-containing phenolic resins which still release small quantities of formaldehyde.

As a result of the addition of at least one aromatic hydroxyl compound it is on the one hand possible to trap excess formaldehyde that is contained in the used resin, so that its liberation is prevented, and on the other hand the compounds resulting from the reaction of the formaldehyde with the aromatic hydroxide form molecules that are very similar to the molecule species of Case 3, which shall be shown in the following by the example of resorcin:

Chemical trapping of free formaldehyde:



From the following schematic formulae it may be seen that the polymer constitutional unit (3) has a high similarity with the molecule species (4) resulting from the trapping reaction:



20 Due to this similarity, the molecule species (4) may in addition to the chemical

fixation of free formaldehyde furthermore participate in the desirable crosslinking reactions and thus lastly result in formaldehyde-free phenolic resins as well as binders therefrom for mineral wool.

It is accordingly also possible to employ commercially available aromatic
5 hydroxyl compounds that were in a certain part already reacted with formaldehyde, in order to further push the crosslinking.

It is preferred to employ such commercially available phenolic resins having at the most approx. 8% (mass), particularly less than approx. 3% (mass), preferably less than approx. 2% (mass) and more preferably less than approx. 1%
10 (mass) of free formaldehyde.

As a phenolic resin, particularly resins with monomer constitutional units of the benzyl alcohol type are suited, which may also contain chain-type and/or cyclic, oligomer alkyl-bridged aromatic multinuclear compounds having a molecular mass of up to 3000 g/mole.

15 The composition in accordance with the invention may additionally contain a carboxylic acid, particularly hydroxycarboxylic acid, preferably hydroxyacetic acid (glycolic acid).

It is one preferred embodiment of the present invention to select the amine from the group consisting of C₂ to C₁₀ alkanolamine, particularly ethanolamine,
20 diethanolamine and triethanolamine.

One preferred silane of the composition in accordance with the invention is 3-aminopropyltriethoxysilane. It is commercially available at a low cost.

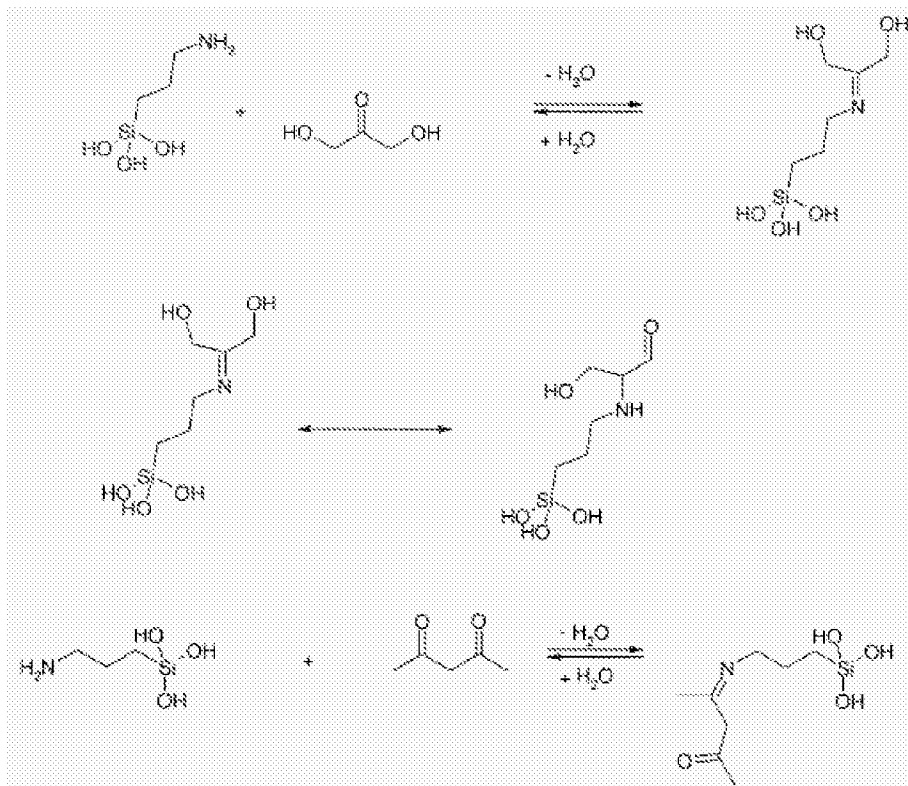
As ketones for the manufacture of the activated silane, dihydroxyacetone or acetylacetone are preferably employed due to their easy availability, however the
25 activated silane may also be produced with an enolizable ketone having at least one carbonyl group or a ketone having at least one OH group, wherein the ketone contains 3 to 12 C atoms.

Furthermore it is frequently desirable for the composition to additionally contain at least one crosslinking agent, with those being preferred that are

selected from the group consisting of: glycerol, polyols, neopentylglycol, trimethylallylamine, 1,3,5-triallyl-2-methoxybenzene, 1,1,1-tris(4-hydroxyphenyl)-ethane, triallylneopentylether, pentaerythrite, sugars, sugar molasse, particularly turnip molasse; as well as mixtures thereof.

- 5 It is particularly preferred if the composition in accordance with the invention has a pH value in the range of approx, 7.0 to 10, particularly 8 to 9. Hereby it is on the one hand ensured that conduits and nozzles, particularly spraying nozzles, are less subjected to corrosion. On the other hand compositions in the preferred pH range do by far not attack the mineral or glass fiber to the extent as the prior-art
10 compositions on polyacrylate basis that are distinctly more acidic.

Without being bound thereto, the activation of the silane with the carbonyl compound possibly appears to unfold in accordance with the following reaction scheme, as is shown by two different carbonyl compounds:



- 15 As a result of the activation of the silane - in the above reaction scheme by way of the example of the γ -aminopropylsilanetriol having resulted from hydrolysis von 3-aminopropyltriethoxysilane - by reaction with an enolizable ketone having at

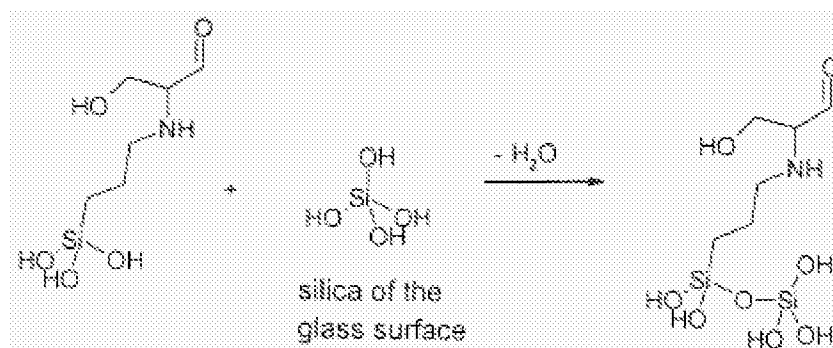
least one carbonyl group or a ketone having at least one OH group, wherein the ketone contains 3 to 12 C atoms, there is formed on the activated molecule a "resin side" which is formed by the N part, in addition to a glass side formed by the Si part.

- 5 In the prior art, the amino group of the silane was reacted with formaldehyde into a Schiff's base which in turn reacted with the phenol-formaldehyde resin.

Thus a formaldehyde content of the binder as required in the prior art is not necessary any more because the activated silane carries an N-containing molecule portion which is capable of coupling to the resin - in accordance with the invention
10 to the phenolic resin or to amine functions of nitrogen-containing polymers - which is thus bound via the silane linker to the glass surface of the hot fiber.

Crosslinking thus takes place both through the described molecule species (4) and through the silane linker.

The reactions of the activated silanes used in accordance with the invention
15 at the glass surface - presently represented by a silica tetrahedron - are in the following shown schematically and exemplarily without being bound thereby:



These hydrolytic linkings take place even more rapidly on the fiber while still hot.

- 20 Further advantages and features of the present invention become evident from the description of practical examples as well as from the drawings, wherein:

Fig. 1: is a schematic view of silanes coupled to a glass fiber via the Si portion of an activated silane; and

Fig. 2: is a schematic view of a resin bound to a glass surface on a fiber via an activated silane.

The overall context of the composition in accordance with the invention and binder in connection with the manufacture of mineral or glass fibers is once again
5 visualized in Fig. 1 and Fig. 2.

Here the represented molecular arrangement should merely be understood in a schematic manner. Crosslinking reactions will, of course, moreover still take place within the resin such as phenolic resin, in accordance with the above description, for instance with the molecule species (4) as well as the alkanolamine
10 or further additional crosslinking agents.

It is, of course, also possible for unintended secondary reactions to occur, as is true with any polymerization. The contents of Figs. 1 and 2 may therefore merely be considered to be a model concept which is, however, helpful for an understanding of the invention.

15 The composition in accordance with the invention is excellently suited as a binder for mineral wool. On the one hand it is thus possible to manufacture positively formaldehyde-free mineral wool products, and on the other hand the cured binders of the invention and thus, of course, also the mineral wool products are water-resistant.

20 In order to manufacture mineral wool bound in a formaldehyde-free manner by means of the binder of the invention, the binder is applied, following fiberization of a molten mineral material, on the fibers while they are still hot, and the mineral wool product with the applied binder is subjected to a curing process.

Here the binder is applied on the fibers in the chute by spraying the fibers
25 attenuated from the molten mineral material, in particular sprayed on.

A bound mineral wool product manufactured in accordance with the method of the invention satisfies any mechanical and chemical requirements just like a mineral wool product bound by using classical phenol-formaldehyde resin.

Practical examples

The commercially available phenolic resins reduced in formaldehyde were tested on the finished product in accordance with current testing methods. The results were compared with those of a standard phenolic resin. The approaches chosen
5 here shall be set forth by way of the following examples and only represent a small selection of the test results. As will readily be evident to the person having skill in the art, the used substances may be varied in an extraordinary breadth; what is important for the trapping of formaldehyde are solely the pH value and the reactivity of the aromatic substances used. The used resorcin may very easily be
10 replaced with similarly reactive systems such as pyrocatechol, pyrrole or thiophene. Reactivity may conveniently be controlled through the acid-base ratio. Activation of the silane is possible both through the intermediary of carbonyl compounds and heterocyclic Systems such as phthalimide. By the addition of replenishable raw materials such as molasse it is possible to additionally improve
15 the processing friendliness of the resins.

In the named binders a target concentration of approx. 40% total solid matter was generally aspired.

Comparative example

Binder 1 - Standard comparative example: A typical alkali-catalyzed phenolic resin
20 having a total solid matter content of 44% was used. Composition: 150 kg of phenolic resin; 35.5 kg of urea; 1.0 kg of ammonium sulfate; 2.0 kg of ammonia solution (25%); 25.8 kg of 3-aminopropyltriethoxysilane (2%); 44.6 kg of water. The free formaldehyde content 6 hours after addition of the urea was approx. 0.5% (mass).

Activation of the silane

In the following practical examples of the invention, the following general prescription for the representation of an activated silane is valid:

In a vat including a mechanical stirrer of a suitable size, a part of the dilution water is initially charged. Then the corresponding quantity of the carbonyl compound is
30 added and stirred until complete dissolution. In the case of compounds poorly

soluble in water, careful heating is performed, or a dispersant is added under vigorous stirring. The silane is added to the solution, and then stirring is continued until a distinct change of color of the solution. A more intense coloration indicates the formation of the imine as activated silane. The silane thus activated is added to the binder batch. Following homogeneization, the binder is ready for use.

Example 1

Binder 2: A commercially available, non-neutralized phenolic resin having a total solid matter of 43.5% and a proportion of free formaldehyde of approx. 1% (mass) was used.

Composition: 150 kg of phenolic resin; 4.7 kg of resorcin; 0.2 kg of glycolic acid; 0.3 kg of ethanolamine; 0.4 kg of 3-aminopropyltriethoxysilane; 0.2 kg of dihydroxyacetone; 21.3 kg of water.

The pH value of the finished binder is approx. 8.

Example 2

Binder 3: A commercially available, non-neutralized phenolic resin having a total solid matter of 46.5% and a proportion of free formaldehyde of approx. 2% (mass) was used.

Composition: 150 kg of phenolic resin; 11.7 kg of resorcin; 0.4 kg of phloroglucin; 0.2 kg of glycolic acid; 0.7 kg of ethanolamine; 0.4 kg of 3-aminopropyltriethoxysilane; 0.2 kg of dihydroxyacetone; 43.2 kg of water.

The pH value of the finished binder is approx. 8.

Example 3

Binder 4: A commercially available, non-neutralized phenolic resin having a total solid matter of 46.5% and a proportion of free formaldehyde of approx. 2% was used.

Composition: 150 kg of phenolic resin; 11.2 kg of resorcin; 0.4 kg of phloroglucin; 27.9 kg of turnip molasse; 0.2 kg of glycolic acid; 0.8 kg of ethanolamine; 0.5 kg of

3-aminopropyltriethoxysilane; 0.3 kg of dihydroxyacetone; 68.1 kg of water.

The pH value of the finished binder is approx. 8.

Performance of quality tests

1. Laboratory tests

5 **1.1 Decrease of the free formaldehyde content**

Initially, the decrease of free formaldehyde following the addition of phloroglucin and resorcin, respectively, is shown in the binders 2 - 4 in comparison with the standard binder 1 (Table 1).

Table 1: Decrease of the free formaldehyde content

Binder	Starting concentration of free formaldehyde [% (mass)]	Concentration of free formaldehyde after 10 min. [% (mass)]	Concentration of free formaldehyde after 60 min. [% (mass)]
1 [Comparison]	8.5 (without urea)	5.0 (after addition of urea)	0.5 (6h after addition of urea)
2	1.0	0.1	not detectable
3	2.0	0.5	not detectable
4	1.8	0.4	not detectable

10 **2. Tests with mineral wool product manufactured with the binders in accordance with the invention**

With the above binders in accordance with Examples 1 to 3, mineral wool products were manufactured wherein the binder is sprayed in the usual manner, following fiberization of the molten material, e.g. in accordance with the blast drawing process, inside the chute on the fibers while they are still hot.

The obtained products were then subjected to a series of examinations that are described in the following. What was generally tested was a façade insulation board having a target bulk density of 75 kg/m³ and a target loss due to burning of 3.7%.

2-1 Adhesion strength of insulation materials in accordance with German Industrial Standard [DIN] 52274 / EN 1607 before and after autoclaving

From a finished product, parallelepipedic test samples are cut with an edge length of 200 x 200 mm. Half of the test samples thus obtained are bonded between two steel plates provided with eyelets and torn apart by means of a suitable apparatus. The other part is aged in air saturated with water vapor during 15 min. at 105°C and subsequently torn apart in the same way. The measured tearing forces provide an indication of the strength of the overall system glass fibers-resin after manufacture and of its resistance under normal conditions of use. In the case of standard products of this class without hydrophobizing agents, residual strengths around 60% after autoclaving are normal. The results are summarized in Table 2.

Table 2: Adhesion strength of insulation materials in accordance with DIN 52274 / EN 1607 before and after autoclaving

Binder	Tearing strength after manufacture (in kPa)	Tearing strength after autoclaving (in kPa)	Residual strength (in %)
1 [Comparison]	103.5	67.3	65
2	139.2	108.6	78
3	157.1	133.6	85
4	142.7	99.9	70

2.2 Adhesion strength in accordance with DIN 52274 / EN 1607 of insulation materials according to Nordtest

For performing these tests, test samples having an edge length of 200 x 200 mm are cut from a finished product. One part of the test samples is torn in analogy with the autoclave test before ageing. The other part is stored in accordance with the provision of the Nordtest during 7 days at 70°C and 95% relative humidity, Following re-drying, the strength of the aged sample bodies is determined by tearing apart. An accurately manufactured insulation material should have a residual strength of at least 50% after this very drastic ageing method. The results are represented in Table 3.

Table 3: Adhesion strength in accordance with DIN 52274 / EN 1607 of insulation materials according to Nordtest

Binder	Tearing strength after manufacture (in kPa)	Tearing strength according to Nordtest (in kPa)	Residual strength (in %)
1 [Comparison]	111.4	62.4	56
2	135.8	88.3	65
3	165.2	119.0	72
4	145.5	98.9	68

Thus the performed tests confirm that the composition in accordance with the invention is not only fundamentally suited as a formaldehyde-free binder for the manufacture of mineral wool, but also practically applicable in accordance with determined product quality, processing capability, and economy. The existing
5 machine equipment need not be modified.

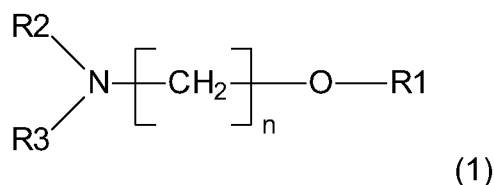
CLAIMS

1. A composition containing:

an aqueous dispersion of at least one phenol-formaldehyde resin;

at least one amine compound of the general formula (1)

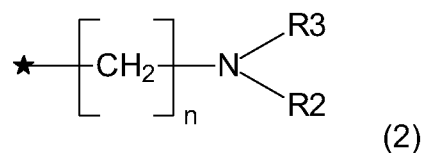
5



wherein:

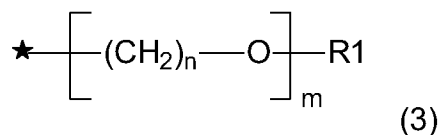
R1, R2 and R3 independently of each other, equal or not equal,
corresponds to H and R1 of the general formula (2):

10



with a value for n of 2-10, and

R2 and R3, independently of each other, are equal or not equal to H
or correspond to the general formula (3):



15

wherein m may assume a value of 1-50,

and the molecular mass of the amine compound does not exceed
approximately 20 000 g/mole;

at least one activated silane,

20

which may be obtained by a conversion of a silane, selected from the
group: mono-, di- and trialkoxysilanes having one C₁ to C₈ alkoxy
group, wherein the alkoxy silane carries at least one C₂ to C₁₀

aminoalkyl group or a C₂ to C₁₀ N-aminoalkyl group; 3(2-aminoethylamino)propyltrimethoxysilane; (MeO)₃-Si-(CH₂)₃-NH-(CH₂)₃-Si-(OMe)₃; 3-aminopropylsilanetriol; aminosilane with ethoxylated nonylphenolate; phenyl-CH₂-NH-(CH₂)₃-NH-(CH₂)₃-Si-(OMe)₃*HCl; as well as mixtures thereof;

with an enolizable ketone having at least one carbonyl group or a ketone having at least one OH group, wherein the ketone contains 3 to 12 C atoms, as well as

at least one aromatic hydroxyl compound selected from the group consisting of: dihydroxybenzenes and their hydroxymethylated compounds; trihydroxybenzenes and their mono- and dihydroxymethylated compounds; C-alkylated compounds of phenol or of resorcin; autocondensation products of the hydroxymethylated compounds; activated heterocycles and their mono- or dialkylated compounds or their anellated derivatives; di- and trihydroxy derivatives of naphthalene; as well as mixtures thereof or mixtures containing these substances.

2. The composition in accordance with claim 1, characterized in that the at least one aromatic hydroxyl compound is selected from the group consisting of : dihydroxybenzenes, particularly 1,3-dihydroxybenzene, 1,2-dihydroxybenzene or 1,4-dihydroxybenzene, as well as their hydroxymethylated compounds, in particular hydroxymethylated derivatives of resorcin or benzocatechin, such as 2,4-dihydroxyphenylmethanol or 2,3-dihydroxyphenylmethanol, but also multihydroxymethylated derivatives of these activated aromatic substances, e.g., 2,3-dihydroxy-4-hydroxymethylphenyl-methanol or 4,5-dihydroxy-2-hydroxymethylphenylmethanol; trihydroxybenzenes, particularly 1,3,5-trihydroxybenzene or 1,2,3-trihydroxybenzene, their mono- and dihydroxymethylated compounds, such as 2,3,4-trihydroxyphenylmethanol or 2,4,6-trihydroxyphenylmethanol; C-alkylated compounds of phenol or of resorcin, e.g., 1-hydroxy-2-methylbenzene, 1-hydroxy-3-methylbenzene, 1-hydroxy-4-methylbenzene or 2-methylresorcin; autocondensation products of the hydroxymethylated compounds, such as bis-2,4-dihydroxyphenylmethane; activated heterocycles, e.g., pyrrole, thiophene, their

mono- or dialkylated compounds or their anellated derivatives, such as indole or thioindole; di- and trihydroxyderivatives of naphthalene.

3. The composition in accordance with claim 1 or 2, characterized in that the phenol-formaldehyde resin contains at the most approx. 8% (mass), particularly
5 less than approx. 3% (mass), preferably less than approx. 2% (mass) and more preferably less than approx 1% (mass) of free formaldehyde.

4. The composition in accordance with any one of claims 1 to 3, characterized in that the phenol-formaldehyde resin contains monomer constitutional units of the benzyl alcohol type and/or chain-type and/or cyclic, oligomer alkyl-bridged
10 aromatic multinuclear compounds having a molecular mass of up to 3 000 g/mole.

5. The composition in accordance with any one of claims 1 to 4, characterized in that it additionally contains a carboxylic acid, particularly hydroxycarboxylic acid, preferably hydroxyacetic acid (glycolic acid).

6. The composition in accordance with any one of claims 1 to 5, characterized
15 in that the amine compound is selected from the group consisting of: a C₂ to C₁₀ alkanolamine, particularly ethanolamine, diethanolamine and triethanolamine.

7. The composition in accordance with any one of claims 1 to 6, characterized in that the silane is 3-aminopropyltriethoxysilane.

8. The composition in accordance with any one of claims 1 to 7, characterized
20 in that the ketone is dihydroxyacetone or acetylacetone.

9. The composition in accordance with any one of claims 1 to 8, characterized in that it contains at least one further crosslinking agent.

10. The composition in accordance with claim 9, characterized in that the crosslinking agent is selected from the group consisting of: glycerol, polyols,
25 neopentylglycol, trimethylallylamine, 1,3,5-triallyl-2-methoxybenzene, 1,1,1-tris(4-hydroxyphenyl)-ethane, triallylneopentylether, pentaerythrite, sugars, sugar molasse, particularly turnip molasse; as well as mixtures thereof.

11. The composition in accordance with any one of claims 1 to 10, characterized in that it has a pH value in the range of approx. 7.0 to 10, particularly 8 to 9.

12. A binder for mineral wool, containing a composition in accordance with at least one of claims 1 to 11.

13. A method for the manufacture of mineral wool bound substantially in a formaldehyde-free manner with a binder in accordance with claim 12, wherein the
5 binder is applied, following fiberization of a molten mineral material, on the fibers while they are still hot, and the mineral wool product with the applied binder is exposed to a curing process.

14. The method in accordance with claim 13, characterized in that the binder is applied on the fibers in the chute by spraying the fibers attenuated from the molten
10 mineral material.

15. A bound mineral wool product which may be obtained by a method in accordance with claim 13 or 14.

16. Use of a composition in accordance with any one of claims 1 to 11 for the manufacture of a mineral wool product bound substantially in a formaldehyde-free
15 manner.

Fig. 1

1/2

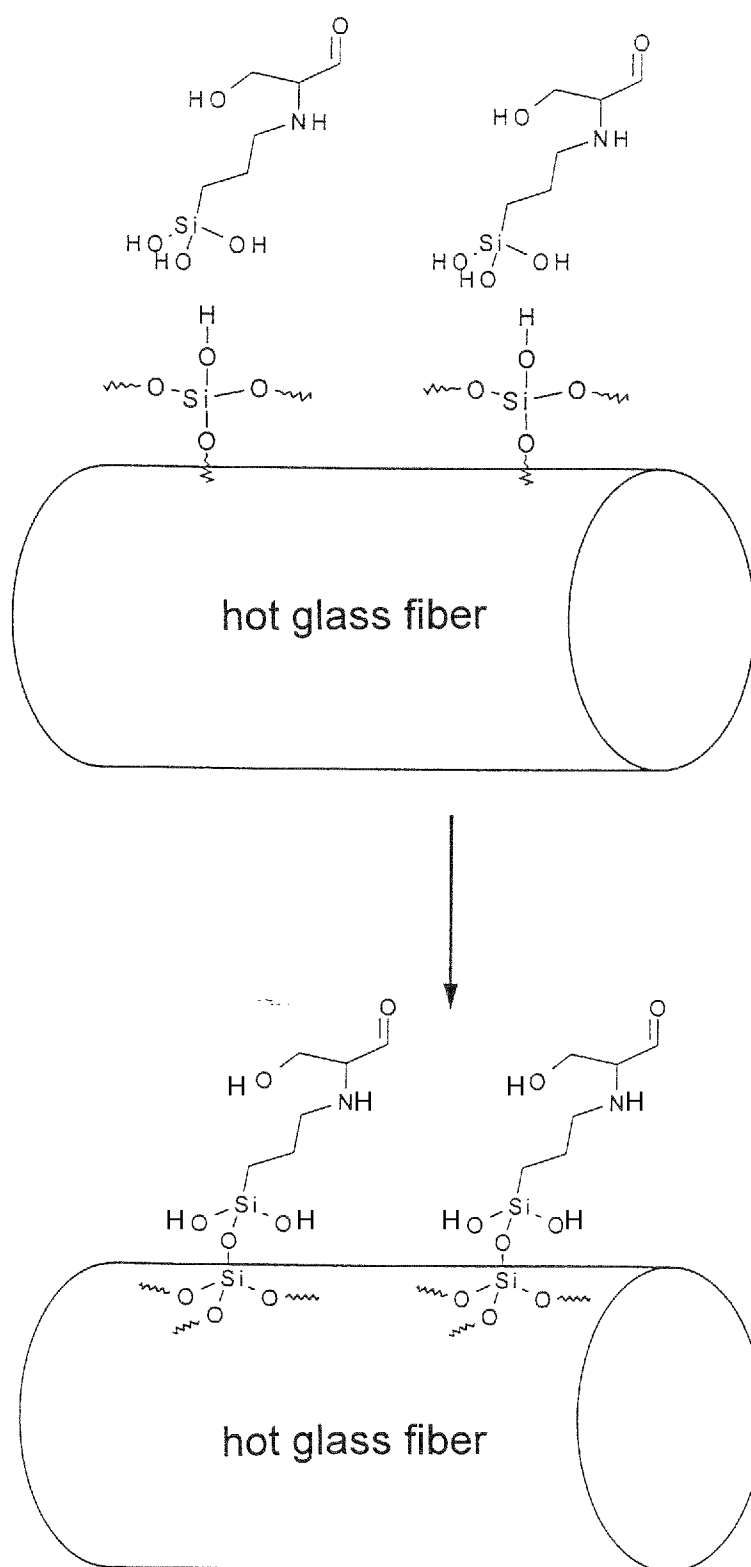
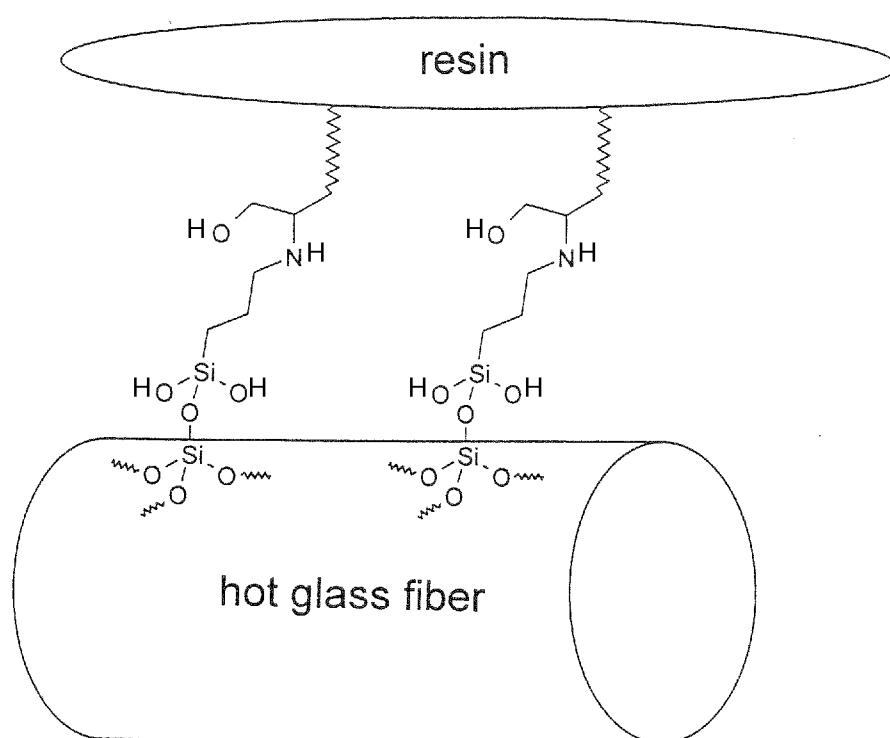


Fig. 2

2/2



INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2006/068934

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C08L61/06 D04H1/64

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 C08L D04H

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB 1 457 216 A (OWENS CORNING FIBERGLASS CORP) 1 December 1976 (1976-12-01) page 1, line 7 - page 2, line 51 page 6, lines 26-45 page 7, lines 34-40; claims; example 19	1-16
Y	US 4 832 748 A (TAWARA KUNIO [JP] ET AL) 23 May 1989 (1989-05-23) column 1, lines 5-19 column 2, line 26 - column 4, line 61 column 10, lines 1-12; claims; examples	1-16
Y	US 2004/197484 A1 (YOSHIDA YUJI [JP]) 7 October 2004 (2004-10-07) paragraphs [0005] - [0012], [0040] - [0051], [0068] - [0070]; claims; examples ----- -/--	1-16

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

9 February 2007

Date of mailing of the international search report

27/02/2007

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+31-70) 340-3016

Authorized officer

Otegui Rebollo, Juan

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2006/068934

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2003/224119 A1 (COVENTRY-SAYLOR KATHLEEN H [US]) 4 December 2003 (2003-12-04) paragraphs [0015], [0029], [0039], [0045] -----	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2006/068934

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
GB 1457216	A	01-12-1976	CA 1067226 A1	27-11-1979
			DE 2509151 A1	09-10-1975
			FR 2264845 A1	17-10-1975
			JP 50123154 A	27-09-1975
US 4832748	A	23-05-1989	DE 3735643 A1	28-04-1988
US 2004197484	A1	07-10-2004	KR 20040084772 A	06-10-2004
US 2003224119	A1	04-12-2003	NONE	