



(86) **Date de dépôt PCT/PCT Filing Date:** 2011/07/27
(87) **Date publication PCT/PCT Publication Date:** 2013/01/31
(45) **Date de délivrance/Issue Date:** 2018/03/27
(85) **Entrée phase nationale/National Entry:** 2014/01/23
(86) **N° demande PCT/PCT Application No.:** EP 2011/062932
(87) **N° publication PCT/PCT Publication No.:** 2013/013714

(51) **Cl.Int./Int.Cl. C09C 1/30** (2006.01)
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(54) **Titre : PROCÉDE POUR PRODUIRE DES CORPS MOULES HYDROPHOBES THERMO-ISOLANTS**
(54) **Title: METHOD FOR PRODUCING HYDROPHOBIC, HEAT-INSULATING MOULDINGS**

(57) **Abrégé/Abstract:**

Process for hydrophobizing a microporous thermal insulation molding comprising hydrophilic silica, in which the molding is treated with at least one organosilane and in which one or more organosilanes which are gaseous under the reaction conditions are introduced into a chamber containing the microporous thermal insulation molding comprising hydrophilic silica until the pressure difference Δp is ≥ 20 mbar.

Abstract

5 Process for hydrophobizing a microporous thermal insulation molding comprising hydrophilic silica, in which the molding is treated with at least one organosilane and in which one or more organosilanes which are gaseous under the reaction conditions are introduced into a chamber containing the microporous thermal insulation molding comprising hydrophilic silica until the pressure difference Δp is ≥ 20 mbar.

Method for producing hydrophobic, heat-insulating mouldings

The invention relates to a process for producing hydrophobic, thermally insulating moldings under defined pressure conditions.

5 DE-A-3037409 discloses making thermal insulation materials composed of foamed perlites water-repellent by means of stearates, siliconates, waxes and fats. This is attributable to coating of the surface with these materials. Although the thermal insulation materials which have been treated this way repel liquid water, they absorb water vapor in the form of atmospheric moisture. This leads to a deterioration in the insulation properties.

10 DE-A-4221716 discloses reacting pyrogenic silicas with organosilanes and thereby making them water-repellent. However, such hydrophobic silica cannot be compressed sufficiently and is therefore not pressable. Pressing of a mixture provided with hydrophobic silica also does not lead to acceptable results.

15 EP-A-1988228 describes a process for pressing to form hydrophobic, microporous thermal insulation moldings by addition of organosilanes during a mixing process. A disadvantage of this process can be considered to be that pressing to form stable plates is possible only with very great difficulty, in particular when gaseous products are formed in the hydrophobization.

20 It was therefore a technical object of the invention to provide a process which minimizes the disadvantages occurring in the hydrophobization of thermal insulation materials and is also simple and economical to carry out.

The invention provides a process for hydrophobizing a microporous thermal insulation molding comprising hydrophilic silica, in which the molding is treated with at least one organosilane, wherein one or more organosilanes which are
25 gaseous under the reaction conditions are introduced into a chamber containing the microporous thermal insulation molding comprising hydrophilic silica until the pressure difference Δp is ≥ 20 mbar.

-2-

$\Delta p = p_2 - p_1$, where p_1 = pressure in the chamber before introduction of the organosilane, p_2 = pressure in the chamber at which the introduction of the organosilane is stopped. The process of the invention is carried out so that preferably $50 \text{ mbar} \leq \Delta p \leq 5 \text{ bar}$, particularly preferably $100 \text{ mbar} \leq \Delta p \leq 500$
5 mbar, very particularly preferably $200 \text{ mbar} \leq \Delta p \leq 400 \text{ mbar}$.

For the purposes of the present invention, a hydrophilic silica is a silica which on its surface bears no organic groups such as alkyl groups which could give it a hydrophobic, water-repellent character. Rather, the groups present on the surface should consist largely or entirely of Si-OH and Si-O-Si groups. Mention may be
10 made by way of example of the preparation of pyrogenic silicas by flame hydrolysis, in which a gaseous silicon compound is burnt in a hydrogen/oxygen flame. This pyrogenic silica is hydrophilic.

The chamber merely has to meet the requirement that it can maintain the pressures required in the process of the invention.

15 In a particular embodiment of the invention, the process is carried out so that the pressure in the chamber before introduction of the organosilane is less than atmospheric pressure. In particular, it is advantageous when $0.1 \text{ mbar} \leq p_1 \leq$ atmospheric pressure. Particular preference is given to a variant in which $1 \leq p_1 \leq 500 \text{ mbar}$. In this preferred embodiment, the organosilane is thus introduced into
20 an evacuated chamber. In this subatmospheric pressure process, the organosilane is itself "sucked" into the finest pores of the hydrophilic molding and optimally distributed therein.

In a further preferred embodiment of the invention, the process is carried out with the pressure in the chamber before introduction of the organosilane being
25 atmospheric pressure or above. In this case, it is advantageous when atmospheric pressure $\leq p_1 \leq 10 \text{ bar}$. In this superatmospheric pressure process, the organosilane is "pushed" into the pores of the hydrophilic thermal insulation molding and thereby optimally distributed.

As microporous, hydrophilic silica in the process of the invention, preference is given to using a pyrogenic silica and/or a silicon dioxide aerogel.

Silicon dioxide aerogels are produced by specific drying processes from aqueous silicon dioxide gels. They likewise have a very high porosity and are therefore
5 highly effective insulation materials.

Pyrogenic silicas are produced by flame hydrolysis of volatile silicon compounds such as organic and inorganic chlorosilanes. In this process, a hydrolyzable silicon halide in vaporized or gaseous form is reacted with a flame formed by combustion of hydrogen and an oxygen-containing gas. The combustion flame provides water
10 for the hydrolysis of the silicon halide and sufficient heat for the hydrolysis reaction. A silica prepared in this way is referred to as pyrogenic silica. In this process, primary particles which are virtually free of internal pores are firstly formed. These primary particles fuse during the process via "sintering necks" to form aggregates. Owing to this structure, pyrogenic silica is an ideal thermal
15 insulation material since the aggregate structure brings about sufficient mechanical stability, minimizes heat transfer by solid-state conductivity via the "sintering necks" and produces a sufficiently high porosity.

The organosilanes used react with the silanol groups of the hydrophilic silica and in this way make the thermal insulation molding water-repellent.

20 For the process of the invention, one or more organosilanes can preferably be selected from the group consisting of $R_n\text{-Si-X}_{4-n}$, $R_3\text{Si-Y-SiR}_3$, $R_n\text{Si}_n\text{O}_n$, $(\text{CH}_3)_3\text{-Si-(O-Si(CH}_3)_2)_n\text{-OH}$, $\text{HO-Si(CH}_3)_2\text{-(O-Si(CH}_3)_2)_n\text{-OH}$, where $n = 1-8$; $R = \text{-H, -CH}_3, \text{-C}_2\text{H}_5$; $X = \text{-Cl, -Br, -OCH}_3, \text{-OC}_2\text{H}_5, \text{-OC}_3\text{H}_8$, $Y = \text{NH, O}$.

Explicit mention may be made of $(\text{CH}_3)_3\text{SiCl}$, $(\text{CH}_3)_2\text{SiCl}_2$, CH_3SiCl_3 ,
25 $(\text{CH}_3)_3\text{SiOC}_2\text{H}_5$, $(\text{CH}_3)_2\text{Si(OC}_2\text{H}_5)_2$, $\text{CH}_3\text{Si(OC}_2\text{H}_5)_3$, $(\text{CH}_3)_3\text{SiNHSi(CH}_3)_3$,
 $(\text{CH}_3)_3\text{SiOSi(CH}_3)_3$, $(\text{CH}_3)_8\text{Si}_4\text{O}_4$ [octamethyltetracyclosiloxane], $(\text{CH}_3)_6\text{Si}_3\text{O}_3$
[hexamethyltricyclosiloxane] and $(\text{CH}_3)_3\text{Si(OSi(CH}_3)_2)_4\text{OH}$ [low molecular weight polysiloxanol]. Preference is given to using $(\text{CH}_3)_3\text{SiCl}$, $(\text{CH}_3)_2\text{SiCl}_2$, CH_3SiCl_3 ,
 $(\text{CH}_3)_3\text{SiNHSi(CH}_3)_3$ and $(\text{CH}_3)_8\text{Si}_4\text{O}_4$.

The process of the invention is, inter alia, characterized in that the organosilane is gaseous under the reaction conditions prevailing in the chamber. The organosilane itself can be introduced in liquid or vapor form into the chamber. When introduced in liquid form, for instance by spraying in, it should go over into
5 the vapor state in the chamber. Preference is given to introducing an organosilane in vapor form.

The process can also be carried out by introducing polar substances into the chamber during or after the introduction of the organosilane. These substances can preferably be water, alcohols and hydrogen halides.

10 The microporous thermal insulation molding comprising hydrophilic silica which is used in the process of the invention can additionally contain opacifiers, fibers and/or finely divided inorganic additives.

Possible opacifiers are titanium oxides, zirconium oxides, ilmenite, iron titanate,
15 iron oxides, zirconium silicate, silicon carbide, manganese oxide and carbon black. These opacifiers preferably have a maximum in the range from 1.5 to 10 μm in the infrared spectrum. The particle size of these particles is preferably 0.5–15 μm . They are present in the total mixture in a proportion of preferably from 5 to 20% by weight.

20 For reinforcement, i.e. for mechanical strengthening, fibers are used. These fibers can be inorganic or organic in nature and make up up to 12% by weight of the mixture. Examples of inorganic fibers which can be used are glass wool, rock wool, basalt fibers, slag wool and ceramic fibers consisting of melts of aluminum
25 and/or silicon dioxide, and also further inorganic metal oxides. Pure silicon dioxide fibers are, for example, silica fibers. Examples of organic fibers which can be used are cellulose fibers, textile fibers or polymer fibers. The diameter of the fibers is preferably 1-12 μm , particularly preferably 6-9 μm , and the length is preferably 1-25 mm, particularly preferably 3-10 mm.

Furthermore, inorganic filler materials can be added in the process of the invention. Use can be made of various, synthetically produced modifications of silicon dioxide, e.g. precipitated silicas, electric arc silicas, SiO₂-containing fly dusts which are formed by oxidation of volatile silicon monoxide and are formed in the electrochemical preparation of silicon or ferrosilicon. Silicas produced by leaching of silicates such as calcium silicate, magnesium silicate and mixed silicates such as olivine with acids are likewise suitable. It is also possible to use naturally occurring SiO₂-containing compounds such as diatomaceous earths and kieselguhrs. Thermally expanded minerals such as perlites and vermiculites, finely divided metal oxides such as aluminum oxide, titanium dioxide, iron oxide can likewise be added.

In a particular embodiment of the invention, the microporous thermal insulation molding containing hydrophilic silica contains 45-95% by weight, preferably 55-90% by weight, of pyrogenic silicon dioxide and/or silicon dioxide aerogel, 5-20% by weight, preferably 7-15% by weight, of opacifiers, 5-35% by weight, preferably 10-30% by weight, of finely divided inorganic additives and 0-12% by weight, preferably 1-5% by weight, of fibers.

To accelerate the process, the thermal insulation molding to be treated can additionally be perforated. The perforation channels enable the organosilanes used in each case to be brought more quickly and in a targeted manner into the thermal insulation molding. Any excesses or reaction products to be removed can likewise be removed again in an accelerated manner through the perforation channels. The perforation can be carried out by needling the thermal insulation molding to be treated, preferably by means of needle grippers during actual pressing of the thermal insulation molding. Primarily in the case of thermal insulation boards, perforation can be carried out on one side but preferably on both sides. The hole depth depends on the thickness of the hydrophilic thermal insulation molding and can be in the range from 5 mm to all the way through, preferably about 2/3 of the thickness of the hydrophilic thermal insulation molding. To avoid heat bridges, two-sided perforation with an offset pattern of holes should preferably be carried out with the hydrophilic thermal insulation molding not being

punctured all the way through. The diameter of a perforation channel should be in the range from 0.1 mm to 3.0 mm, preferably from 0.5 mm to 1.0 mm. The spacing of the perforation channels can be in the range from 5 mm to 200 mm, and in the case of one-sided perforation the spacing of the channels should preferably be as
5 great as the needle depth and in the case of two-sided perforation should preferably be twice the needle depth.

It can be advantageous for the temperature in the chamber to be from 20°C to 300°C. The treatment time can be controlled by means of this. Depending on the type of organosilane used, it can be particularly advantageous to select a
10 temperature in the range from 50 to 200°C.

It can likewise be advantageous to leave the microporous thermal insulation molding containing hydrophilic silica in the chamber for from 1 minute to 1 hour, particularly preferably from 2 to 20 minutes, from the point in time at which the organosilane is added.

15 After the treatment is complete, any excess organosilanes and reaction products can be removed from the now hydrophobic molding by heating. To effect mechanical stabilization and to improve handling, including dust-free handling, the hydrophobic molding can be enclosed in nonwovens and films, preferably shrink films.

20 The invention further provides for the use of the hydrophobized thermal insulation molding produced by the process of the invention for producing insulation in hollow building blocks, core insulation in multilayer building blocks, core insulation for composite thermal insulation systems for interior and exterior insulation of buildings, insulation in cavity wall masonry, insulation in furnace construction and
25 vacuum insulation panels.

Fields of use for these hydrophobic thermal insulation moldings produced by the process of the invention are, inter alia, all applications in which the insulation materials are exposed to moisture or wetness.

Examples

- Example 1: A microporous thermal insulation panel having a size of 250 x 250 x 20 mm and a weight of 184.4 g, corresponding to an overall density of 147.5 kg/m³, and a composition of 87.0% by weight of pyrogenic silica having a BET surface area of 300 m²/g, 9.0% by weight of flame black and 4.0% by weight of short chopped viscose fibers (\varnothing 9 μ m; L 6 mm) is present in a desiccator heated to about 100°C. The pressure in the desiccator is reduced to 15 mbar by means of a water pump. Hexamethyldisilazane in vapor form is subsequently introduced into the desiccator until the pressure increases to 300 mbar.
- Example 2: A microporous thermal insulation panel having a size of 250 x 250 x 20 mm and a weight of 189.3 g, corresponding to an overall density of 151.4 kg/m³, and a composition of 87.0% by weight of pyrogenic silica having a BET surface area of 300 m²/g, 9.0% by weight of flame black and 4.0% by weight of short chopped viscose fibers (\varnothing 9 μ m; L 6 mm) is present in a desiccator heated to about 100°C. The pressure in the desiccator is reduced to 15 mbar by means of a water pump. Dimethyldichlorosilane in vapor form is subsequently introduced into the desiccator until the pressure increases to 300 mbar.

The plates obtained as per examples 1 and 2 are completely water-repellent, have good mechanical stability and an unchanged low thermal conductivity.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for hydrophobizing a microporous thermal insulation molding comprising hydrophilic silica, in which the molding is treated with at least one organosilane, wherein at least one organosilane which is gaseous under the reaction conditions is introduced into a chamber containing the microporous thermal insulation molding comprising hydrophilic silica until the pressure difference is $\Delta p \geq 20$ mbar,
wherein the microporous thermal insulation molding comprising hydrophilic silica is perforated,
wherein $\Delta p = p_2 - p_1$, where
 p_1 is the pressure in the chamber before introduction of the organosilane,
and
 p_2 is the pressure in the chamber at which the introduction of the organosilane is stopped, and
wherein the pressure in the chamber before introduction of the organosilane is atmospheric pressure or above.
2. The process as claimed in claim 1, wherein a pyrogenic silica and/or a silicon dioxide aerogel is used as hydrophilic silica.
3. The process as claimed in claim 1 or 2, wherein the organosilane is $R_n\text{-Si-X}_{4-n}$, $R_3\text{Si-Y-SiR}_3$, $R_n\text{Si}_n\text{O}_n$, $(\text{CH}_3)_3\text{-Si-(O-Si(CH}_3)_2)_n\text{-OH}$, or $\text{HO-Si(CH}_3)_2\text{-(O-Si(CH}_3)_2)_n\text{-OH}$;
wherein n is 1-8; R is -H, -CH₃, or -C₂H₅; X is -Cl, -Br, -OCH₃, -OC₂H₅, or -OC₃H₈; and Y is NH, or O.
4. The process as claimed in any one of claims 1 to 3, wherein the organosilane is introduced in liquid or vapor form into the chamber.
5. The process as claimed in any one of claims 1 to 4, wherein water, an

alcohol or a hydrogen halide, or any combination thereof, is introduced simultaneously with, or subsequent to, the addition of the organosilane.

6. The process as claimed in any one of claims 1 to 5, wherein the microporous, hydrophilic thermal insulation molding used further comprises an opacifier, fibers or a finely divided inorganic additive, or any combination thereof.

7. The process as claimed in any one of claims 1 to 6, wherein the microporous thermal insulation molding containing hydrophilic silica contains 45-95% by weight of pyrogenic silicon dioxide and/or silicon dioxide aerogel; 5-20% by weight of an opacifier; 5-35% by weight of a finely divided inorganic additive; and 0-12% by weight of fibers.

8. The process as claimed in any one of claims 1 to 6, wherein the microporous thermal insulation molding containing hydrophilic silica contains 55-90% by weight of pyrogenic silicon dioxide and/or silicon dioxide aerogel; 7-15% by weight of an opacifier; 10-30% by weight of a finely divided inorganic additive; and 1-5% by weight of fibers.

9. The process as claimed in any one of claims 1 to 8, wherein the temperature in the chamber is from 20 to 300°C.

10. The process as claimed in any one of claims 1 to 9, wherein the microporous thermal insulation molding containing hydrophilic silica which is used is left in the chamber for from 1 minute to 1 hour from the point in time at which the organosilane is added.

11. The process as claimed in any one of claims 1 to 10, wherein the perforation is carried out by needling.

12. The process as claimed in claim 11, wherein the needling is carried out by means of needle grippers during actual pressing of the thermal insulation

molding.

13. The process as claimed in any one of claims 1 to 12, wherein the hole depth of the perforation is about $2/3$ of the thickness of the thermal insulation molding comprising hydrophilic silica.

14. The process as claimed in any one of claims 1 to 13, wherein the diameter of a perforation channel is in the range of 0.1 mm to 3.0 mm.