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PROCESS FOR THE WATER-REPELLENT IMPREGNATION OF PLASTER
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- (56) Prior Art Documents
US 5136805
US 4975122
FR 2308602
- (57) Claim

1. Water-repellent plaster compositions including as constituents

- a) 100 parts by weight of gypsum plaster,
- b) from 0.05 to 50 parts by weight of inorganic species chosen from the group comprising oxides of alkali metals, oxides of alkaline earth metals, hydroxides of alkali metals, hydroxides of alkaline earth metals or combinations thereof,
- c) from 0.05 to 20 parts by weight of organopolysiloxane which has hydroxyl groups or alkoxy groups or both hydroxyl groups and alkoxy groups bonded to silicon atoms, the organopolysiloxane being liquid at 25°C and having a viscosity of from 0.5 to 3000 mPa.s.

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**ORIGINAL
COMPLETE SPECIFICATION
STANDARD PATENT**

Application Number:

Lodged:

Invention Title:

PROCESS FOR THE WATER-REPELLENT IMPREGNATION OF
PLASTER

The following statement is a full description of this invention, including the
best method of performing it known to us :-

Process for the water-repellent impregnation of plaster

5 The invention relates to water-repellent plaster compositions comprising oxide and/or hydroxide of alkali and/or alkaline earth metals and organopolysiloxane which has hydroxyl and/or alkoxy groups bonded to silicon atoms, and a process for the water-repellent treatment of
10 plaster.

 It is known from US-A-3,455,710 that plaster can be given water-repellent properties by impregnation with organosiloxanes containing Si-bonded hydrogen atoms (H-siloxanes). This reference also describes the impreg-
15 nation of mixtures of plaster and calcium hydroxide with H-siloxanes. However, the water-repellent action of the H-siloxanes is unsatisfactory. Furthermore, the H-siloxanes are very expensive and evolve hydrogen on contact with water.

20 US-A-4,411,702 describes water-repellent shaped articles which are produced from the constituents calcium sulphate dihydrate, slag and calcium hydroxide and in the production of which part of the constituents is treated with a polydimethylsiloxane liquid. However the water-
25 repellent action of the polydimethylsiloxane liquid is unsatisfactory.

 It is an object of the present invention to provide low-cost and easy-to-process water-repellent
30 plaster compositions and shaped articles which can be produced therefrom.

 The invention provides water-repellent plaster compositions comprising the constituents

- (A) 100 parts by weight of gypsum plaster,
- (B) from 0.05 to 50 parts by weight of oxide and/or
35 hydroxide of alkali and/or alkaline earth metals,
- (C) from 0.05 to 20 parts by weight of organopoly-siloxane which has hydroxyl and/or alkoxy groups

bonded to silicon atoms.

The water-repellent plaster compositions can comprise any type of calcium sulphate. Among the types of calcium sulphate, preference is given to plaster (CaSO₄·H₂O) in the form of, for example, building plaster, stucco plaster or insulation plaster and plaster of Paris (CaSO₄·1/2 H₂O). Other types of plaster such as screed plaster, marble plaster and anhydrite can also be used. The calcium sulphate formed in flue gas desulphurization is also well suited.

As oxide and/or hydroxide of alkali and/or alkaline earth metals (B), preference is given to CaO, MgO, Ca(OH)₂, Mg(OH)₂ and NaOH, in particular Ca(OH)₂, CaO and NaOH.

Preference is given to using, based on 100 parts by weight of gypsum plaster (A), from 0.1 to 35, in particular from 0.5 to 25 parts by weight of oxide and/or hydroxide (B).

The organopolysiloxane (C) is preferably made up of units of the general formula (I)



where

- R are identical or different, unsubstituted or halogen-substituted C₁-C₁₈-hydrocarbon radicals,
- R' are identical or different C₁-C₄-alkyl radicals or hydrogen atoms,
- a is 0, 1, 2 or 3, on average from 0.1 to 2.5 and
- b is 0, 1, 2, 3 or 4, on average from 0.1 to 3.5.

Examples of unsubstituted radicals R are alkyl radicals such as the methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-pentyl, iso-pentyl, neo-pentyl, tert-pentyl radical, hexyl radicals such as the n-hexyl radical, heptyl radicals such as the n-heptyl radical, octyl radicals such as the n-octyl radical and iso-octyl radicals such as the 2,2,4-trimethylpentyl radical, nonyl radicals such as the n-nonyl radical, decyl radicals such as the n-decyl radical, dodecyl radicals such as the n-dodecyl radical, octadecyl radicals such as the n-octadecyl radical; alkenyl

radicals such as the vinyl and the allyl radical; cycloalkyl radicals such as cyclopentyl, cyclohexyl, cycloheptyl radicals and methylcyclohexyl radicals; aryl radicals such as the phenyl, naphthyl and anthryl and phenanthryl radicals; alkaryl radicals such as the o-, m-, p-tolyl radicals, xylyl radicals and ethylphenyl radicals; aralkyl radicals such as the benzyl radical, the alpha- and the beta-phenylethyl radical.

Examples of halogen-substituted radicals R are substituted by fluorine and chlorine, such as the 3,3,3-trifluoro-n-propyl radical, the 2,2,2,2',2',2'-hexafluoroisopropyl radical, the heptafluoroisopropyl radical, and haloaryl radicals such as the o-, m- and p-chlorophenyl radical.

Preferred radicals R are unsubstituted hydrocarbon radicals, in particular those having from 1 to 8 carbon atoms, especially methyl, ethyl, propyl, n-octyl, iso-octyl, vinyl, tolyl and phenyl radicals.

Examples of radicals R' are hydrogen atoms, methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, iso-butyl and tert-butyl radicals, in particular methyl and ethyl radicals.

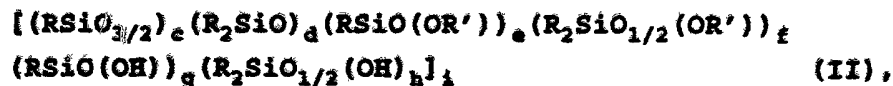
The index a preferably has an average value of from 0.3 to 2.0, in particular from 0.5 to 1.8.

The index b preferably has an average value of from 0.2 to 1.5, in particular from 0.3 to 1.3.

The organopolysiloxane (C) is preferably branched to crosslinked in a resin-like manner. The sum of a+b therefore preferably has a value of from 1.5 to 1.9.

The organopolysiloxane (C) is preferably liquid at 25°C and preferably has a viscosity of from 0.5 to 3000 mPa·s, in particular from 1 to 500 mPa·s, especially from 2 to 200 mPa·s, at 25°C.

The organopolysiloxane (C) has, in particular, the general formula (II)



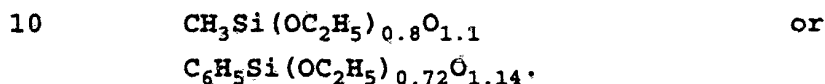
where

c has a value of from 0.5 to 0.9,

d has a value of from 0 to 0.3,
the sum of e+f+g+h has a value of from 0.1 to 0.4,
i has a value of from 2 to 100, in particular from 3
to 40, and

5 R and R' are as defined above.

Particularly preferred organopolysiloxanes (C)
are those which are obtainable by reaction of methyl-
trichlorosilane or phenyltrichlorosilane with methanol or
ethanol in water, e.g. those of the empirical formula



The organopolysiloxanes (C) can contain, owing to
the method of preparation, organosilanes such as methyl-
trimethoxysilane and methyltriethoxysilane, but prefer-
15 ably not more than 30% by weight, in particular not more
than 10% by weight.

Preference is given to using, based on 100 parts
by weight of gypsum plaster (A), from 0.1 to 8, in
particular from 0.3 to 5, parts by weight of organopoly-
20 siloxanes (C).

The water-repellent plaster compositions can also
contain further organopolysiloxanes which have no
hydroxyl and/or alkoxy groups bonded to silicon atoms.
Preferably, the amount of further organopolysiloxanes is
25 at most 30 parts by weight, in particular at most 10
parts by weight, based on 100 parts by weight of organo-
polysiloxanes (C).

The water-repellent plaster compositions can
contain further additives (D) which aid the production of
30 shaped plaster articles or improve the properties of the
shaped plaster articles. Additives are, for example,
fillers such as silicon dioxide, perlite and cellulose
fibres and reinforcing materials such as glass fibres and
glass nonwovens, accelerators such as potassium sulphate
35 and aluminium sulphate, retardants such as proteins or
tartrates, air-pore formers such as organosulphonates or
organosulphates, plasticizers for the plaster slurry, for
example lignin sulphonates, and coupling agents for
cardboard such as starch and pulp.

Preference is given to using, based on 100 parts by weight of gypsum plaster (A), at most 25, in particular at most 15, parts by weight of additives (D).

The invention also provides a process for the
5 water-repellent treatment of plaster, wherein

- (A) 100 parts by weight of gypsum plaster are mixed with
- (B) from 0.05 to 50 parts by weight of oxide and/or hydroxide of alkali and/or alkaline earth metals, and
- 10 (C) from 0.05 to 20 parts by weight of organopolysiloxane which has hydroxyl and/or alkoxy groups bonded to silicon atoms.

Oxide and/or hydroxide (B), organopolysiloxane (C) and, if desired, additives (D) are added to the
15 plaster prior to the moulding of shaped articles. The components can here be mixed in any order.

Oxide and/or hydroxide (B) and organopolysiloxane (C) can each be added as powder or as aqueous solution, suspension or emulsion. Oxide and/or hydroxide (B) and
20 organopolysiloxane (C) can be mixed with the dry plaster or with the slurry of water and plaster. Oxide and/or hydroxide (B) can also be mixed with organopolysiloxane (C) and subsequently be added with [sic] the plaster (A). Oxide and/or hydroxide (B) can also be mixed with the
25 plaster (A) and subsequently be admixed with organopolysiloxane (C).

If organopolysiloxane (C) is used as emulsion, emulsifiers known per se are employed.

Particularly suitable anionic emulsifiers are:

- 30 1. Alkyl sulphates, particularly those having a chain length of from 8 to 18 carbon atoms, alkyl and alkaryl ether sulphates having from 8 to 18 carbon atoms in the hydrophobic radical and from 1 to 40 ethylene oxide (EO) or propylene oxide (PO) units.
- 35 2. Sulphonates, particularly alkylsulphonates having from 8 to 18 carbon atoms, alkylarylsulphonates having from 8 to 18 carbon atoms, taurides, esters and half-

esters of sulphosuccinic acid with monohydric alcohols or alkylphenols having from 4 to 15 carbon atoms; if desired, these alcohols or alkylphenols can also be ethoxylated with from 1 to 40 EO units.

- 5 3. Alkali metal and ammonium salts of carboxylic acids having from 8 to 20 carbon atoms in the alkyl, aryl alkaryl or aralkyl radical.

4. Partial esters of phosphoric acid and their alkali metal and ammonium salts, particularly alkyl and alkaryl
10 phosphates having from 8 to 20 carbon atoms in the organic radical, alkyl ethers or alkaryl ether phosphates having from 8 to 20 carbon atoms in the alkyl or alkaryl radical and from 1 to 40 EO units.

Particularly suitable nonionic emulsifiers are:

- 15 5. Polyvinyl alcohol still containing from 5 to 50%, preferably from 8 to 20%, of vinyl acetate units and having a degree of polymerization of from 500 to 3000.

6. Alkyl polyglycol ethers, preferably those having from 8 to 40 EO units and alkyl radicals of from 8 to 20
20 carbon atoms.

7. Alkyl aryl polyglycol ethers, preferably those having from 8 to 40 EO units and from 8 to 20 carbon atoms in the alkyl and aryl radicals.

8. Ethylene oxide/propylene oxide (EO/PO) block
25 copolymers, preferably those having from 8 to 40 EO or PO units.

9. Fatty acids having from 6 to 24 carbon atoms.

10. Natural materials and their derivatives, such as
30 lecithin, lanolin, saponines, cellulose; cellulose alkyl ethers and carboxyalkylcelluloses whose alkyl groups in each case have up to 4 carbon atoms.

11. Linear organo(poly)siloxanes containing polar groups, in particular those containing alkoxy groups having up to 24 carbon atoms and/or up to 40 EO and/or PO groups.

5 Particularly suitable cationic emulsifiers are:

12. Salts of primary, secondary and tertiary fatty amines having from 8 to 24 carbon atoms with acetic acid, sulphuric acid, hydrochloric acid and phosphoric acids.

10 13. Quaternary alkylammonium and alkylbenzeneammonium salts, in particular those whose alkyl groups have from 6 to 24 carbon atoms, in particular the halides, sulphates, phosphates and acetates.

15 14. Alkylpyridinium, alkylimidazolinium and alkylloxazolinium salts, in particular those whose alkyl chain has up to 18 carbon atoms, especially the halides, sulphates, phosphates and acetates.

 Particularly suitable ampholytic emulsifiers are:

20 15. Long-chain substituted amino acids such as N-alkyl di(aminoethyl)glycine or N-alkyl-2-aminopropionic acid salts.

16. Betaines such as N-(3-acylamidopropyl)-N,N-dimethylammonium salts having a C₈-C₁₈-acyl radical and alkylimidazolium betaines.

25 Preferred emulsifiers are nonionic emulsifiers, in particular the polyvinyl alcohol listed above under 5. Particularly preferred polyvinyl alcohols still contain from 5 to 20%, in particular from 10 to 15%, of vinyl acetate units and preferably have a degree of polymerization of from 500 to 3000, in particular from 1200 to 2000. The aqueous emulsions of organopolysiloxane (C) preferably contain from 30 to 95% by weight, in particular from 35 to 70% by weight, especially from 45 to 60% by weight, of water. The amount of emulsifier can be from 0.1 to 15% by weight of organopolysiloxane (C).
30

It is preferably from 2 to 10% by weight.

In a preferred embodiment, a foam is produced from water, the above emulsifier and organopolysiloxane (C) and this foam is added to the slurry of water, gypsum plaster (A), oxide and/or hydroxide (B) and, if desired, additives (D). The mixture obtained can be used to produce porous shaped plaster articles.

If desired, the organopolysiloxane can be dispersed in water, which can also contain pulp, and subsequently be mixed with the gypsum plaster (A) and oxide and/or hydroxide (B) or an aqueous slurry of (A) and (B) which can, if required, also contain (D).

In a further preferred embodiment, water and organopolysiloxane (C) are mixed, if desired together with additives (D), in a long tube having turbulent flow and are subsequently added to the gypsum plaster (A) and oxide and/or hydroxide (B).

In the following examples, unless otherwise indicated,

a) all amounts are by weight;

b) all pressures are 0.10 MPa (abs.);

c) all temperatures are 25°C.

Examples

Production of the test specimens

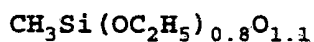
A plaster slurry was produced from x parts by weight of plaster of Paris ($\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$), 80 parts by weight of water, y parts by weight of calcium hydroxide powder and z parts by weight of any further components indicated in Table I and was poured into circular moulds to form test specimens having a diameter of 85 mm and a thickness of 6 mm. After 60 minutes, the solidified test specimens were removed from the moulds and dried for 24 hours at 40°C in a convection oven.

Water absorption in accordance with DIN 18180

The test specimens were immersed in a horizontal position in water at 23°C in such a way that there was 50 mm of water above the test surface. After storage in water for two hours, the test specimens were taken from
5 the water, the water adhering to the surface was removed and the increase in mass was determined by weighing. The water absorption in % by mass is given in Table I.

Organopolysiloxane (C)

Use was made of a liquid organopolysiloxane of
10 the empirical formula



having a viscosity of 21 mPa·s at 25°C.

Composition of the organopolysiloxane emulsion

An emulsion was produced from 240 parts by weight
15 of the above organopolysiloxane, 120 parts by weight of a 10% strength by weight aqueous solution of polyvinyl alcohol which still contained 12% of vinyl acetate units and had a degree of polymerization of 1500 and 120 parts by weight of deionized water.

Table I, Examples 1 to 9 (Examples 1 and 6 are not according to the invention)

Ex.	X	Y	Z	hydrophobicizing component	Water absorption in % by weight in accordance with DIN 18180
	1	98	2	-	43.4 %
5	2	98	2	0.5 Organo-	9.7 %
	3	98	2	2.0 poly-	3.6%
	4	96	4	0.5 siloxane	7.7 %
	5	96	4	1.0 Organopolysi- loxane emulsion	3.5 %
	6	92	8	-	41.0 %
10	7	92	8	0.5 Organopoly-	2.9%
	8	92	8	2.0 siloxane	1.6 %
	9	92	8	1.0 Organopolysi- loxane emulsion	1.5%

Example 10

4 parts by weight of a mixture of 100 parts by weight of the above organopolysiloxane and 40 parts by weight of calcium hydroxide were added to a mixture of 100 parts by weight of plaster of Paris and 80 parts by weight of water. From this slurry, test specimens were cast and dried as described above. The water absorption in accordance with DIN 18180 was 3.1%.

Example 11

From a mixture of 99 parts by weight of plaster of Paris, 1 part by weight of sodium hydroxide, 80 parts by weight of water and 1 part by weight of the above organopolysiloxane emulsion, test specimens were cast and dried as described above. The water absorption in

accordance with DIN 18180 was 3.6%.

Example 12

From a mixture of 98 parts by weight of plaster of Paris, 2 parts by weight of sodium hydroxide, 80 parts
5 by weight of water and 3 parts by weight of the above organopolysiloxane emulsion, test specimens were cast and dried as described above. The water absorption in accordance with DIN 18180 was 3.4%.

Example 13 (not according to the invention)

10 From a mixture of 90 parts by weight of plaster of Paris, 10 parts by weight of calcium hydroxide, 80 parts by weight of water and 2 parts by weight of a linear polydimethylsiloxane oil having a viscosity of
15 950 mPa·s, test specimens were cast and dried as described above. The water absorption in accordance with DIN 18180 was 47.9%.

Example 14 (not according to the invention)

Example 13 was repeated, except that only 0.5 part by weight of the linear polydimethylsiloxane oil was
20 used. The water absorption in accordance with DIN 18180 was 47.9%.

Example 15

30 parts by weight of water, 0.1 part by weight of ether sulphate (Zeliquid^R LP 2 from Hoechst AG, Germany) and 2 parts by weight of the above organopolysiloxane were mixed in a foam producer at 1200 revolutions/minute. The foam obtained was mixed with a plaster
25 slurry consisting of 90 parts by weight of plaster of Paris, 10 parts by weight of calcium hydroxide and 50 parts by weight of water. Subsequently, test specimens were cast and dried as described above. The water absorption in accordance with DIN 18180 was 2.9%.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Water-repellent plaster compositions including as constituents
 - a) 100 parts by weight of gypsum plaster,
 - b) from 0.05 to 50 parts by weight of inorganic species chosen from the group comprising oxides of alkali metals, oxides of alkaline earth metals, hydroxides of alkali metals, hydroxides of alkaline earth metals or combinations thereof,
 - c) from 0.05 to 20 parts by weight of organopolysiloxane which has hydroxyl groups or alkoxy groups or both hydroxyl groups and alkoxy groups bonded to silicon atoms, the organopolysiloxane being liquid at 25°C and having a viscosity of from 0.5 to 3000 mPa.s.
2. Water-repellent plaster compositions according to claim 1, wherein b) is chosen from the group consisting CaO, MgO, Ca(OH)₂, Mg(OH)₂ and NaOH or combinations thereof.
3. Water-repellent plaster compositions according to claim 1 or 2, wherein, based on 100 parts by weight of gypsum plaster a), from 0.1 to 35 parts by weight of inorganic species b) are used.
4. Water-repellent plaster compositions according to any one of claims 1 to 3, wherein the organopolysiloxane c) is made up on units of the general formula (I)



where

R are identical or different, unsubstituted or halogen-substituted C₁-C₁₈-hydrocarbon radicals,

R' are identical or different C₁-C₄-alkyl radicals or hydrogen atoms,

a is 0, 1, 2 or 3, on average from 0.1 to 2.5 and

b is 0, 1, 2, 3 or 4, on average from 0.1 to 3.5.



5. Water-repellent plaster compositions according to any one of claims 1 to 4, wherein, based on 100 parts by weight of gypsum plaster a), from 0.1 to 8 parts by weight of organopolysiloxanes c) are used.

6. Process for the water-repellent treatment of plaster, wherein

a) 100 parts by weight of gypsum plaster are admixed with

b) from 0.05 to 50 parts by weight of inorganic species chosen from the group comprising oxides of alkali metals, oxides of alkaline earth metals, hydroxides of alkali metals, hydroxides of alkaline earth metals or combinations thereof, and

c) from 0.05 to 20 parts by weight of organopolysiloxane which has hydroxyl groups or alkoxy groups or both hydroxyl groups and alkoxy groups bonded to silicon atoms, the organosiloxane being liquid at 25°C and having a viscosity of from 0.5 to 3000 mPa.s.

7. A process according to claim 6, wherein organopolysiloxane c) is used as emulsion.

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VAX DOC023 AU5075896.WPC : IAS/CLR/RES



Process for the water-repellent impregnation of plaster

Abstract

Water-repellent plaster compositions comprising the constituents

- (A) 100 parts by weight of gypsum plaster,
- (B) from 0.05 to 50 parts by weight of oxide and/or hydroxide of alkali and/or alkaline earth metals,
- (C) from 0.05 to 20 parts by weight of organopolysiloxane which has hydroxyl and/or alkoxy groups bonded to silicon atoms.