

Process for the production of integrally waterproofed
concrete ✓

5 This invention relates to a process for the production of
at least largely homogeneously waterproofed concrete
(integrally waterproofed concrete) by the incorporation of
aqueous emulsions containing organosilicon compounds into
uncured concrete mixes. Prior art impregnation processes
10 are known in which such emulsions are brushed onto concrete
components, so waterproofing the surface thereof (EP-B-
0538 555, EP-B-0340816, EP-A-0234024).
Although good results, for example with regard to the depth
of penetration of moisture, are achieved in this manner,
15 the process is associated with problems. One such problem
is that the user must apply the emulsions carefully to
provide a continuous layer on the concrete surface.
However, defects in the concrete are not discernible from
the outside. Nonetheless, they constitute possible points
20 of entry for destructive liquids such that protection of
the surface is no longer ensured.

Moreover, ageing of the concrete surface by exposure to
chemical, thermal and also mechanical stresses weakens the
25 hydrophobic protective layer.

This means that the layer must be renewed at regular
intervals. However, a prerequisite for this renewal is that
the surface to be treated must first be subjected to costly
cleaning, for example using a high pressure water jet.

The object of the invention is accordingly to provide a process by means of which concrete components or concrete structures may effectively be protected from corrosion without requiring costly, repeated measures to ensure this
5 protection.

Care must also be taken in this connection that incorporation of these protective chemical compounds does not degrade the workability of concrete mixes, for example
10 with regard to viscosity and, with regard to those properties influencing strength such as for example porosity, these parameters are not impaired.

The present invention provides a process for the production
15 of integrally waterproofed concrete, which process is characterised in that an aqueous emulsion containing hydrolysable organosilicon compounds is added during production or optionally thereafter to a mix containing water prepared from *per se* known inorganic and optionally
20 small proportions of organic constituents and the mix is then allowed to cure to form the concrete.

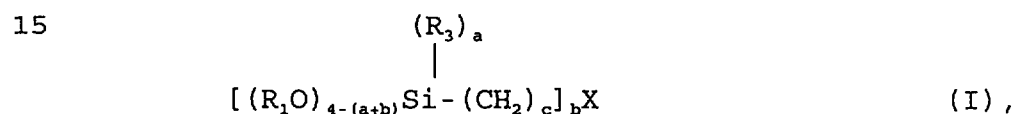
Emulsions of this type are known *per se*, but in the prior art are used only for waterproofing surfaces.

Aqueous emulsions which are suitable for the use according
25 to the invention may be found, for example, in the description of EP-A 0234 024, EP-B 0340 816 or EP-A-0616 989. The aqueous emulsions disclosed in these patent applications also constitute part of the present invention. These emulsions preferably contain hydrolysable
30 alkylalkoxysilanes of the general formula (I) in a quantity

of 1 to 70 wt.%, relative to the total quantity of the emulsion.

Further constituents are generally known nonionic or ionic emulsifiers, for example having an HLB value of 1.5 to 20, in particular stearates, oleates and optionally buffering substances. When using these emulsions, care should preferably be taken to ensure that the droplet size [sic] of the organosilicon compounds in water have a diameter of 0.5 to 10 μm . In a particularly suitable case, the average particle size is 0.30 to 1.1 μm .

In one particular embodiment, the emulsion contains 1 to 80 wt.%, preferably 1 to 60 wt.%, of at least one alkylalkoxysilane of the general formula



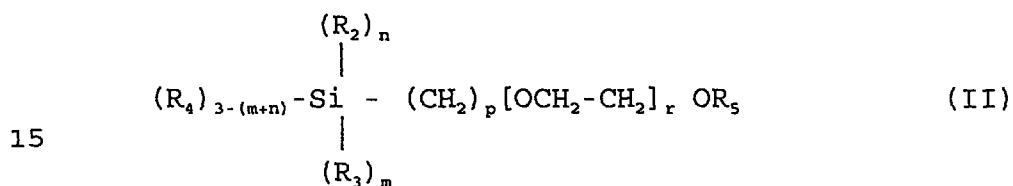
in which

- 20 R, R₁ mean C₁-C₃ alkyl, optionally branched,
 R₃ means C₁-C₂₀ alkyl, linear or branched, in particular C₁-C₁₀ alkyl, phenyl,
 a means 0 or 1,
 b means 1 or 2,
 25 c means 1 to 18,
 X means H, Cl, Br, I, NH₂, SCN, CN, N₃, NHR, N(R)₂, N(R)₃, aryl, in particular H, Cl, NH₂, SCN, NHR, N(R)₂, N(R)₃ with the meaning of R as above, phenyl, if b = 1
 30 alkenyl, in particular -CH₂-, ethylene, trimethylene or tetramethylene, if b = 2

X means S_x where $x = 1$ to 6
if $b = 2$ and $c = 1$ to 6 ,

X means without meaning,
if $b = 2$ and $c = 1$ to 12 , preferably 1 to 6 ,
5 and instead of or in addition to one of the
known surfactants in particular 1 to 20 wt.%,
preferably 1 to 5 wt.% of an organosilicon
compound of the general formula

10



in which

R_2, R_3 mean identically or differently C_1 - C_{20} alkyl, linear
or branched, in particular C_1 - C_{10} alkyl, phenyl

20 R_4 means C_1 - C_3 alkoxy,
[OCH₂-CH₂]_r OR₅,
[OCH₂-CH₂]_s-[CH₂-CHO]_t-[CH₂-CH₂O]_sH
|
CH₃

25 where $s = 3-50$, $t = 3-25$

R_5 means H, C_1 - C_{20} alkyl, C_2 - C_{36} alkenyl, C_5 - C_8
cycloalkyl, C_7 - C_{36} aralkyl, if $p = 0$ [sic] and
 $r = 0$ corresponds to OR₅:

30 -[OCH₂-CH₂]_s-[CH₂-CHO]_t-[CH₂-CH₂O]_sH

m means 0, 1, 2;

n means 0, 1, 2 providing that $(m+n) = 1$ or 2, if
p = 0, where p $\neq$ 0 $(m+n) = 0, 1$ or 2 applies,
p means 0, 1, 2, 3,
r means an integer between 0 and 50,
5 and water in a quantity from 1 to 95 wt.%,
preferably from 1 to 75 wt.%, wherein the
quantities by weight add up to 100%, and the
mix is then allowed to cure to form the
concrete.

10

Preferably, n-octyltriethoxysilane and hexadecyltriethoxy-
silane are used as compound (I).

In addition to the compounds of the formula (I), the
15 emulsions may also contain the partial condensation
products thereof, for example dimers, trimers or other
oligomers thereof, as are generally known to the person
skilled in the art.

The pH value of the emulsion is preferably adjusted to
20 approx. 7.5.

In a particular embodiment, a buffer substance is added to
the emulsion in a quantity of 0.1 to 5 wt.%, relative to
the total quantity of the emulsion.

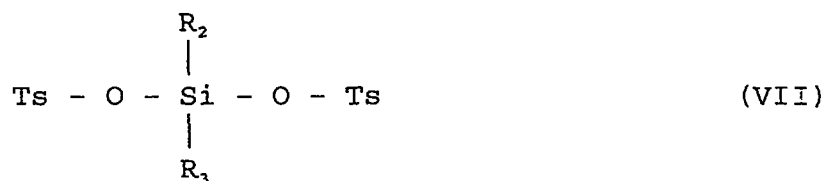
The buffer substance is, for example, sodium hydrogen
25 carbonate, sodium carbonate or trisodium phosphate.

In a preferred embodiment, 0.2 to 8.0 wt.%, relative to the
total weight of the emulsion, of one or more known anionic
surfactants are also added to the emulsion.

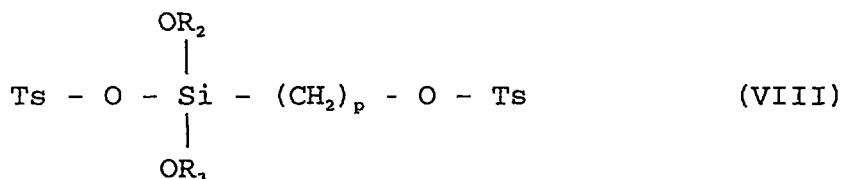
The disperse phase advantageously has an average particle or droplet diameter of 0.30 to 1.1 μm .

The emulsion according to the invention optionally also contains 0.1 to 1.0 wt.% of a known thickener, for example from the class of cellulose or starch derivatives, likewise relative to the total quantity of the emulsion.

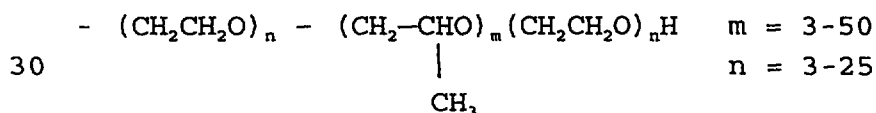
In one specific embodiment of the invention, silicon- functional surfactants of the general formulae



or



in which R_2 , R_3 and p have the meaning as above and Ts corresponds to:



are used.

In a preferred embodiment, in particular also in the case of emulsions containing short-chain silanes, for example containing C₃ and C₄ alkylene groups, an acidic catalyst is added shortly before use which is capable of breaking the Si-O bonds, but not the Si-C bonds, in the claimed alkoxy-silanes, in order to improve through [sic] the effectiveness of the silanes on neutral, weakly acidic or alkaline, in particular problematic, surfaces.

10 A homogeneous distribution of the emulsion used according to the invention in the concrete mix has, of course, proved to be most successful. However, ideal conditions cannot always be assumed under real conditions of use on construction sites.

15 It has, however, been found that the advantages of the waterproofed concrete produced according to the invention are achieved even in the event of largely homogeneous mixing of the concrete constituents with the organosilicon compounds according to the invention.

20

The emulsions used according to the invention are advantageously added to the finely divided inorganic and optionally organic constituents of the concrete mix together with the water necessary for the production of this mix.

The concentration of the emulsions amounts to 0.1 to 10, in particular 0.5 to 7 wt.%, relative to the cement present in the concrete mix.

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It has been found that the use according to the invention of the emulsions containing organosilicon compounds does not merely waterproof the concrete throughout its mass, ideally homogeneously. Even during working of the fresh
5 concrete mix, advantages are achieved relating to better flow behaviour in comparison with a standard mix without organosilicon compounds.

The liquefying action of the emulsions may in certain cases
10 be used to reduce the water content in the concrete mix to be produced, which has an additional advantageous effect on the development of strength and density.

In one important use, the concrete mixes produced according
15 to the invention are applied in the form of shotcrete onto load-bearing members, in particular made from concrete.

Destructive salts do not penetrate though this protective layer into the structural concrete.

20

The structural concrete may be optimally tailored to its supporting function since the protective function is assumed by the surfacing layer.

25 Subsequent application of this surfacing layer may, however, also be of significance, if, for example due to a change in use, a structure is subjected to an unforeseen exposure to a destructive substance.

30 There are also important applications which demand waterproofing through the mass of the concrete components.

Such applications include, for example, bridge decks, tunnel entrances and exits or waste water pipes.

- 5 Once cured, the concrete mixes produced according to the invention exhibit distinctly lower water absorption coefficients and considerably greater resistance to chloride penetration than untreated concrete.
- 10 Unlike improvements achieved by external treatment, these properties are durable as they are not determined by wear phenomena at the surface.

Integral waterproofing, as described in this document, has
15 not hitherto been considered by the person skilled in the art because, according to the prior art, the organosilicon compounds used would have been expected to be hydrolysed or condensed due to the strongly alkaline conditions in the concrete mix so greatly impairing the effectiveness of the
20 waterproofing compounds.

Applications are also conceivable in which the hydrophobic characteristics of the concrete produced according to the invention are strengthened by a prior art (DE-PS 2751714,
25 US-PS 4,661,551) external treatment with organosilicon compounds or the emulsions described.

The cited patent applications are a constituent part of the disclosure of the application.

5 Silane type A: octyltriethoxysilane (50 wt.% of the
 emulsion)
 silane surfactant according to the
 formula (II) (EP-B-0538555)
 (1 wt.% of the emulsion)

10 Silane type B: hexadecyltriethoxysilane (50 wt.% of
 the emulsion)
 silane surfactant according to the
 formula (II) (EP-B-0538555)
 (1 wt.% of the emulsion)

15

2. Testing of the concrete articles was performed in accordance with the methods specified by the Swiss association of engineers and architects: SIA 162 (1993) SIA 162/1 (1989, concrete structures: materials testing).

3. Composition of the concrete mix

Sand, 0-4 mm [kg/m ³]	829
Aggregate, 4-8 mm [kg/m ³]	368
Aggregate, 8-16 mm [kg/m ³]	645
Portland cement, CEM I 42.5 [kg/m ³]	350
Water [kg/m ³]	175
Silane emulsion (active content 51%)	10.5

Table 1

4. Properties of fresh concrete

Test no.		Slump [cm]	Air content [%]	Density [kg/dm ³]
1	Silane emulsion, type A	39.5	2.80	2373
2	Silane emulsion, type B	41.5	3.0	2375
3	Standard concrete	36	3.2	2383

Table 2

Slump, which characterises flow properties, shows that concrete mixes 1 and 2 produced according to the invention flow better and are thus more readily workable than the standard mix without silane emulsion. The mixes according to the invention also exhibit a lower air content, such that the concrete produced therefrom is less porous.

5. Resistance to chloride penetration

Resistance to chloride penetration is tested with a 3% NaCl solution. To this end, four sides of a concrete cube are coated with epoxy resin.

An uncoated side of this cube is then immersed for 24 hours in the salt solution and capillary liquid absorption measured.

The test cubes are then dried for 24 hours at 50°C.

This sequence is performed repeatedly until a virtually constant value is achieved. After 15 days, the untreated concrete article exhibited absorption of approx. 9 kg/m², while the impregnated concrete had absorbed only approx. 1 kg/m².

6. Water absorption coefficient of concrete

Test no.		Water absorption coefficient [kg/m ² h ^{0.5}]
1	Silane emulsion, type A	0.084
2	Silane emulsion, type B	0.112
3	Standard concrete	1.31

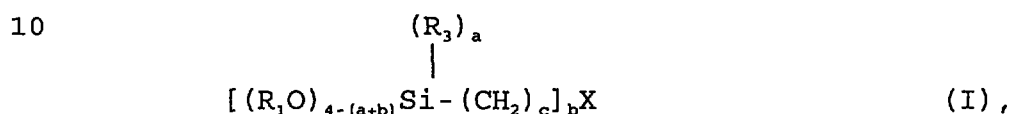
Table 3

10 The water absorption coefficient of the concrete article produced according to the invention is distinctly lower than that of the standard mix.



Patent Claims

- 5 1. Process for the production of integrally waterproofed concrete,
characterised in that an
emulsion containing an aqueous organosilicon compound
of the general formula



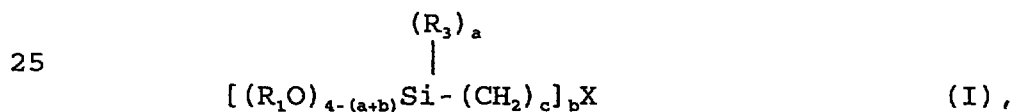
- and optionally the partial condensation products
thereof is added during production or optionally
15 thereafter to a mix containing water prepared from *per se* known inorganic and optionally small proportions of organic constituents, wherein

- R, R₁ mean C₁-C₃ alkyl, optionally branched,
20 R₃ means C₁-C₂₀ alkyl, linear or branched, in particular C₁-C₁₀ alkyl, phenyl,
a means 0 or 1,
b means 1 or 2,
c means 1 to 18,
25 X means H, Cl, Br, I, NH₂, SCN, CN, N₃, NHR, N(R)₂, N(R)₃, aryl, in the latter case in particular phenyl, if b = 1
alkenyl, in particular having 1 to 6 C atoms, if b = 2
30 X means S_x where x = 1 to 6
if b = 2 and c = 1 to 6,

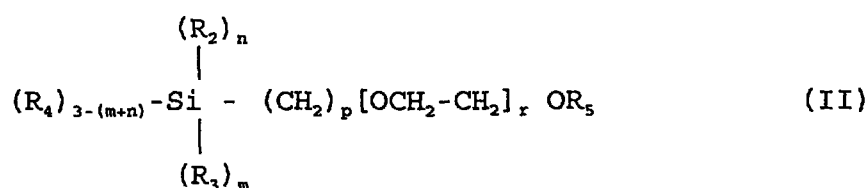


X means without meaning
if $b = 2$ and $c = 1$ to 12 ,
preferably 1 to 6 ,
and the mix is then allowed to cure to form the
concrete.

2. Process according to claim 1,
characterised in that
the emulsion contains hydrolysable organosilicon
compounds and ionic or nonionic surfactants
(emulsifiers).
3. Process according to claims 1 or 2,
characterised in that
an emulsion is used, the disperse phase of which has an
average particle size of 0.3 to $1.1 \mu\text{m}$ and a width of
the particle size distribution of ≤ 1.3 .
4. Process according to claims 1 to 3,
characterised in that
an emulsion is added which contains 1 to $80 \text{ wt.}\%$,
preferably 1 to $60 \text{ wt.}\%$, of at least one alkoxysilane
of the general formula



and optionally the partial condensation products
thereof and instead of or in addition to one of the
known surfactants in particular 1 to $20 \text{ wt.}\%$,
preferably 1 to $5 \text{ wt.}\%$ of an organosilicon compound of
the general formula



5

in which

R_2, R_3 mean identically or differently C_1 - C_{20} alkyl, linear or branched, in particular C_1 - C_{10} alkyl, phenyl,

10 R_4 means C_1 - C_3 alkoxy,
 $[\text{OCH}_2 - \text{CH}_2]_r \text{OR}_5$,
 $[\text{OCH}_2 - \text{CH}_2]_s - [\text{CH}_2 - \text{CHO}]_t - [\text{CH}_2 - \text{CH}_2\text{O}]_5\text{H}$
 $\quad \quad \quad |$
 $\quad \quad \quad \text{CH}_3$

15

where $s = 3-50$, $t = 3-25$

R_5 means H, C_1 - C_{20} alkyl, C_2 - C_{36} alkenyl, C_5 - C_8 cycloalkyl, C_7 - C_{36} aralkyl, if $p = 0$ [sic] and $r = 0$ corresponds to OR_5 :
 $-[\text{OCH}_2 - \text{CH}_2]_s - [\text{CH}_2 - \text{CHO}]_t - [\text{CH}_2 - \text{CH}_2\text{O}]_5\text{H}$

20 m means 0, 1, 2;

n means 0, 1, 2 providing that $(m+n) = 1$ or 2, if $p = 0$, where $p \neq 0$ $(m+n) = 0, 1$ or 2 applies,

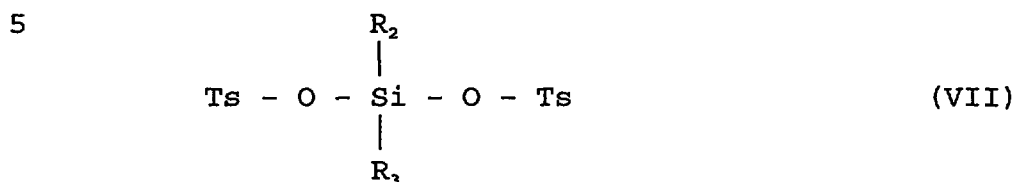
p means 0, 1, 2, 3;

25 r means an integer between 0 and 50,
 and water in a quantity from 1 to 95 wt.%, preferably from 1 to 75 wt.%, wherein the quantities by weight add up to 100%.

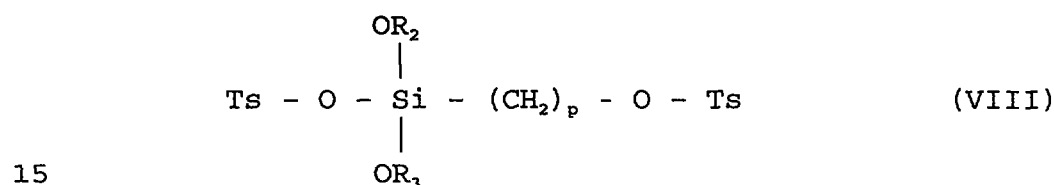
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5. Process according to claim 4,
characterised in that
an emulsion is used which contains silicon-functional
surfactants of the general formulae



10 or



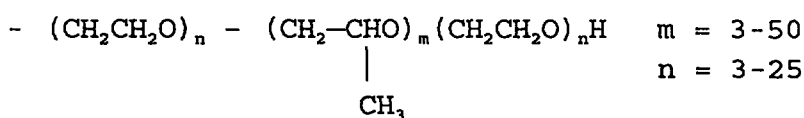
in which R_2 , R_3 and p have the meaning as above and Ts
corresponds to:



20



25



6. Process according to claims 1 to 5,
characterised in that
an emulsion is used which contains 0.2 to 8.0 wt.%,
relative to the total weight of the emulsion, of one or
more known anionic surfactants.



7. Process according to claims 4 to 6,
characterised in that
an acidic catalyst is added to the emulsion before use.
- 5 8. Process according to one or more of the preceding
claims,
characterised in that
the emulsion is added to the concrete mix in a quantity
of 0.1 to 10 wt.%, preferably of 0.5 to 7 wt.%,
10 relative to the cement.
9. Process according to one or more of the preceding
claims,
characterised in that
15 the emulsion is added to the concrete mix together with
the water.
10. Process according to claim 1,
characterised in that
20 a concrete mix containing the aqueous emulsion
containing organosilicon compounds is produced, the mix
is worked, allowed to cure and the surface is then
provided with a prior art waterproofing treatment.
- 25 11. Concrete mixes which contain *per se* known inorganic and
optionally organic constituents and the aqueous
emulsions according to claim 1.
12. Use of concrete mixes
30 according to claim 11 as shotcrete for the production
of surfacing layers.



13. Use of concrete mixes
according to claim 11 for the production of structural
components.