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<p>(54) Title: HARDENER FOR HARDENING SILICATE SOLUTIONS</p>		
<p>(57) Abstract</p> <p>Hardener for hardening silicate solutions comprising a silicate providing compound, capable of providing silica in amorphous or dissolved form in a silicate solution. Said silicate providing compound in the selected form amorphous silica and amorphous metal silicate. Further a silicate solution to be hardened, a method for hardening such a silicate solution and a hardened silicate material which can thus be obtained are described.</p>		

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Title: Hardener for hardening silicate solutions.

The present invention relates to hardeners for hardening silicate solutions.

In the state of the art, silicate solutions can be hardened by the addition of inorganic acids, organic acids or aluminate
5 to the silicate solutions. By addition of such components, the silicate solution hardens virtually instantaneously, however resulting in a relatively brittle product with too little inherent strength and durability.

Furthermore, it is essential in many applications, that
10 the hardening process is delayed for a predetermined period, allowing the mixture to be prepared before use, e.g. by mixing with other components which have to be transformed or shaped into a hard form, e.g. in foundries or before being sprayed onto surfaces to form a protective layer or before pumping into
15 the ground e.g. for waste fixation or grouting.

In an alternatively known technique, specially selected esters are added to silicate solutions, which hydrolyse in water, thus releasing acids, which harden the silicate solution in a slower and more controlled way. However the organic salts
20 and the alcohols formed during the hydrolysis of the expensive esters used for hardening, dilute the hardened system and weaken the bonding produced during the hardening of the silicate. Furthermore gases are generally slowly released that can cause smell, be toxic, or even form explosive gas mixtures in air
25 and consequently can not be applied in many applications for safety or environmental reasons.

Surprisingly, it has now been found that silica providing compounds, capable of providing silica in amorphous or dissolved form in a silicate solution are excellent hardeners for such
30 silicate solutions. It is known per se that by the addition of amorphous silica to a silicate solution, the molar ratio $\text{SiO}_2/\text{M}_2\text{O}$ of the silicate solution, M being an alkali metal or ammonium, can be increased.

Silicate solutions can be obtained from the market with
35 $\text{SiO}_2/\text{M}_2\text{O}$ molar ratios up to 3.3. To increase said ratio, amorphous silica is added and a solution with an $\text{SiO}_2/\text{M}_2\text{O}$ molar ratio of

4.0 can be obtained. The person skilled in the art is however aware of the fact that addition of more silica will lead to unwanted gelling of the silicate solution. The gelling point of the silicate solutions are at a $\text{SiO}_2/\text{M}_2\text{O}$ molar ratio of about 5 4.0 - 4.3, depending on the silicate content of the solution. Because of the gelling, further addition of silica has not been practised nor explored. It has now been found, that the addition of silica, or another reactive silica providing compound, see below, i.e. beyond the gelling point of the silicate solution, 10 leads to perfect hardening of the solution. Surprisingly, the reaction continues in the gel phase. This can be observed as the white silica particles, still present in the gel making the gel opaque, disappear in time, turning the soft gel into translucent hard gel, which finally after drying can become 15 a hard glass type product. It was found, that this reaction can continue until a molar ratio $\text{SiO}_2/\text{M}_2\text{O}$ (M being either sodium, potassium, lithium or ammonium) is reached in the gel of above 5.5. The maximum molar ratio which can be reached depends on time and temperature and will reach levels of around 7 at 20 slightly elevated temperatures already, as can be determined by those skilled in the art.

Furthermore, the hardening of the silicate solution with a hardener according to the present invention takes place gradually. The instantaneous hardening with known compounds 25 of the state of the art can therefore be avoided, leading to a hardened silicate solution not being brittle, but being very hard and of glassy consistency. By varying the amount of hardener according to the present invention added to the silicate solution, the reaction time needed for hardening can also be 30 varied. Thus, use of a hardener according to the present invention has the advantage of controlling the hardening time and of improving the quality of the hardened product.

Silica in amorphous form slowly dissolves in the silicate, thus acting as an acid, neutralizing the silicate and 35 consequently forming a gel which hardens in time. This is the case when sufficient amorphous silica is mixed in pure silicate liquors, giving a gel, but also when sufficient amorphous silica is mixed in suspensions comprising other ingredients like a filler material. The hardened product obtained when mixing

amorphous silica in silicate suspensions provided superior density, hardness and minimum permeability.

Consequently it was found, that amorphous silica or an amorphous alkali metal silicate form ideal hardeners, being
5 again completely inorganic and completely safe with respect to humans and the environment. It also further reduces the flammability and increases the solid content of the product obtained after hardening. An additional benefit is, that the hardened solution, using sufficient amorphous silica forms a
10 neutralised solid phase with superior adhesion and filling properties, which is very strong and substantially insoluble in water.

In the present application the silicate solutions can also comprise a filler, i.e. be a suspension.

15 Silicate solutions, suspensions comprising a hardener according to the invention are therefore suitable for applications, e.g. adhesion applications, where weatherproof properties are required, such as outside applications, construction of buildings for bonding bricks of outside walls, bonding leather
20 to be used outside like shoe soles etc. or for bonding wood for outside purposes. By using silicate solutions, suspensions hardened with the hardener according to the invention buildings, homes etc could be manufactured based on paper or other cellulosic material like woodfibres etc still having weatherproof
25 properties. Also bricks could be adhered together with such hardened solutions, no longer needing any mortar and associated drying time.

It was found, that the rate of hardening of the silicate solutions according to the invention, using amorphous silica
30 can be influenced by the choice of amorphous silica and by the amount of amorphous silica used. The use of silicas with a higher rate of dissolution in alkaline aqueous solutions increases the hardening rate.

It is therefore possible to control the hardening (setting)
35 rate by choosing the type of silica, the optimum concentration and the temperature, as can be carried out by a person skilled in the art. The hardener system should be mixed in the solution shortly before use.

As a hardener, also an amorphous metal silicate can be

used. Addition of such a compound results in a spacial configuration change of the silicate in the solution by alteration of the molar $\text{SiO}_2/\text{M}_2\text{O}$ ratio thereof. Suitable metal silicates are preferably those which do not readily dissolve
5 in the silicate solution to be hardened, like e.g. magnesium silicate, calcium silicate or aluminium silicate.

Preferably, the silica providing compound is chosen from the group, consisting of amorphous silica, and amorphous metal silicate that do not readily dissolve in the silicate solution.
10 The metal silicates are preferably chosen from the group, comprising magnesium silicate, calcium silicate and aluminium silicate. These silicates do not readily dissolve in the silicate solution and therefore give rise to a gradual hardening process of the silicate solution.

15 The invention also relates to a silicate solution to be hardened, comprising a hardener according to the invention, wherein said silicate solution has a silicate content of at least 10% by weight, and preferably at least 20% by weight. A hardening solution is intended to encompass a solution, or
20 suspension, comprising the hardener according to the present invention and a silicate solution. The hardener according to the invention functions very well in hardening silicate solutions having a silicate content of at least 10% by weight, and even better when the silicate content is at least 20% by weight.
25 The higher the silicate content in the solution, the harder the hardened phase obtained.

The $\text{SiO}_2/\text{M}_2\text{O}$ molar ratio of these soluble silicates can vary from 1.0 to around 4.0 and for lithium silicate even higher. All silicate solutions are alkaline, but the alkalinity decreases
30 with increasing molar ratio. Consequently less hardener is needed to harden the solution. Furthermore silicate solutions with higher molar ratios are safer in handling, which is demonstrated by the following safety classification of the standard silicate solutions as offered on the market.

35

<u>Molar Ratio</u>	<u>Solutions offered</u>	<u>Classification</u>
<u>SiO₂/M₂O:</u>	<u>on the market as:</u>	<u>in Europe (Safety):</u>
1.0	Metasilicate	Corrosive
2.0	"Alkaline" Silicate	Highly Irritant
5	(or: "Alkaline waterglass")	
3.3	"Neutral" Silicate	Not classified
as	(or: "Neutral waterglass")	unsafe

The preferred SiO₂/M₂O ratio for most applications is therefore above 2.6 and more preferably 3.3 and higher for safety reasons. As is outlined above, it is preferred to maximize the SiO₂ content and consequently also the SiO₂/M₂O ratio to minimize the amount of hardener required.

The amount of hardener required is highly influenced by the SiO₂/M₂O molar ratio of the silicate, as for higher molar ratios less hardener is needed for neutralization. Therefore, advantageously the SiO₂/M₂O molar ratio of the aqueous silicate solution to be hardened, M being an alkali metal or ammonium, is comprised between 1 - 4.5, preferably between 2 - 4.2 and most preferably between 2.6 - 4.2.

For many applications, it is advantageous to incorporate filler material in the silicate solution to be hardened. As filler material, zeolites as zeolite 4A, zeolite P, zeolite X and zeolite Y, fine particulate or fibres amorphous inorganic material being relatively inert in an alkaline aqueous solution, like amorphous alkali metal alumino silicate, a fine particulate of graphite or carbon black or mixtures thereof can be used.

It is advantageous when the filler material has an average particle size between 0.8 - 15 µm with a specific weight of below 2.75 kg/l. It is however to be noted that filler material with other properties, i.e. with a smaller particle size, may be suitable as well, depending on the intended use of the hardening solution.

Preferably the filler material comprises a zeolite, in particular of the P-type.

The present invention further relates to a method for hardening a silicate solution, wherein a hardener according to the present invention is added to the silicate solution in an amount exceeding the amount of hardener, needed to gel the

solution.

The preferred amount of hardener can be either calculated or predetermined by those skilled in the art. The best results with respect to hardness are obtained, when the maximum amount of hardener, i.e.: reactive (amorphous) silica is added, which can react with the silicate used under the conditions applied in the application, which can be observed as the opaque amorphous silica then has disappeared. This will generally be reached, when the final molar ratio $\text{SiO}_2/\text{M}_2\text{O}$ of the silicate present in the gel is 4.4 - 5.5 at ambient temperature, but can reach higher values of up to 7, when the hardening takes place at elevated temperatures.

As outlined above, by adding a hardener according to the present invention, amorphous silica is added to the silicate containing solution, leading to an increase of the $\text{SiO}_2/\text{M}_2\text{O}$ ratio which results in gelling and subsequently, to hardening of the solution. The gelling point of the silicate solutions upon adding hardener lies around 4.1 - 4.3. Hardening takes place at higher molar ratios.

The present invention will now be illustrated with the following examples.

EXAMPLES

Materials used :

25

A. Commercial name : Crystal 0070 (Crosfield Eijsden (NL))
Product : Neutral sodium-silicate liquor
Dry solid content : 35.06 %
 SiO_2 content : 26.81 %
30 Na_2O content : 8.25 %
Density (20 °C) : 1355 g/l
Viscosity : 51 cP

C. P-type zeolite in dry powder form

35

Commercial name : Zeocros CG180 (Crosfield Eijsden)
Dry solid content*) : 90 %
Particle size **) : 0.7 - 3 micrometer
Average particle size **) : 0.92 micrometer

D50 : 1.22 micrometer
 Effective density***) : 2480 g/l.

L Lucilite.

5 A commercially available, synthetically produced amorphous Silica (hydrogel), marketed and produced by Crosfield, Warrington, UK.

Dry Solid content *) : 34.78 %

10 M. Gasil HP 250

A commercially available amorphous Silica, synthetically produced and marketed by Crosfield, Warrington, UK.

Dry Solid content *) : 93.49 %

Average Particle size: 4.8 - 6.2 micrometer (Mastersizer)

15

N. Microsil ED

A commercially available amorphous Silica, synthetically produced and marketed by Crosfield, Warrington, UK.

Dry Solid content *) : 89.37 %

20

Q. Stabifix Super

A commercially available amorphous Silica, synthetically produced and marketed by Crosfield, Warrington UK.

Dry Solid content *) : 94.6 %

25 Average Particle size: 10.3 maximum micrometer (Mastersizer)

*) Measured by heating at 800 °C during 30 minutes

**) Measured by the sedimentation technique using

30 Sedigraph type 5100, marketed by Micromeritics

***) Measured by immersion in water.

EXAMPLE 1

Addition of amorphous Silica to a neutral Sodium-silicate liquor.

35 Materials used:

	Material	Dry Solid
	Nr.:	content (wt.%)
Neutral Sodiumsilicate liquor	A	35.06
Amorphous Silica: Lucilite	L	34.78

Amorphous Silica: Gasil HP250	M	93.49
Amorphous Silica: Microsil ED	N	89.37
Amorphous Silica: Stabifix Super	Q	94.6

5 Neutral silicate liquor (A) was introduced into a beakerglass of 600 ml.

A range of suspensions was made in which varying quantities of silica were added under intensive stirring to the silicate liquor.

10 It was not possible to produce suspensions adding more than approximately 15 % by weight on a dry basis of silica.

Suspensions Produced and behaviour during Storage:

(The SiO₂ and Sodiumsilicate contents of the suspensions are
15 expressed on bone dry basis)

Material	L				M			N		Q			
Sample Nr.	L1	L2	L3	L4	M1	M2	M3	N1	N2	N3	Q1	Q2	Q3
SiO ₂ (wt. %)	4.4	7.8	10.5	12.7	4.7	9	12.9	4.7	9	12.8	4.7	9	12.9
20 Silicate (wt.%)	:31	27	25	22	33	32	30	33	32	30	33	32	30
Gelling Time(h)	<1/2	<1/2	<1/2	<3/4	15	<15	<15	>48	24	20	15	<15	<<15
Gel type,1 day*)	: s	h	h	mh	l	s	s	l	s	s	l	s	h
Gel type,2 days	: s	h	h	h	l	s	s	l	s	h	l	s	h
Gel type,4 days	: s	h	h	h	l	h	h	s	h	h	l	h	h
25 Gel appearance*)	: t	t	t	o	-	g	g	-	-	t	g	g	g

*) After 1 day, the gel was assessed visually and after 1,2 and 4 days on strength by pressing a rod manually into the gel and assessing the pressure needed.

30 Following symbols were used to characterize the gel:
l = liquid; s = very-soft; mh = medium-hard and h = hard.
t = translucent; g = greyish; o = opaque

35 **Summarizing:**

Material L (Lucilite) is a hydrogel and most soluble and most reactive, resulting in fastest and most efficient gelling. The other silicas also show different gelling efficiencies. It was observed, that at increasing silica content gelling is
40 more efficient and the gel obtained becomes harder.

It can be assumed, that the silica dissolution process

for Material L, being highly reactive will have reached its end point within 1 day, while the other silicas were still reacting further.

Sample L4 shows, that at an apparent excess level of silica the gel becomes opaque and again softer. It was concluded from this, that there is an optimal silica addition level giving maximum hardness around the 10 % Silica level. This means 40 wt.% relative to the neutral silicate (Total effective Molar Ratio: $\text{SiO}_2/\text{Na}_2\text{O}$, then being around 4.7).

10

EXAMPLE 2, 3 and 4

Addition of amorphous Silica to a neutral Sodium-silicate liquor at 50 °C. and 80 °C

In order to demonstrate the influence of temperature on the gelation time, suspensions of Silica in a neutral Sodium-silicate liquor were produced at 50 °C and at 80 °C.

Procedure:

A mortar, which was preheated at 50 °C for Examples 2 and 3 or at 80 °C for Example 4, neutral Sodium-silicate liquor (Material A) was added and brought to the same temperature, Silica was subsequently added and shortly milled in order to realize fast mixing.

The suspension obtained was quickly transferred into a beakerglass of 250 ml kept at 50 °C for Examples 2 and 3 and at 80 °C for Example 4 in a waterbath.

Materials used:

Example Nr.	:	2*)	3**)	4**)
30 Material (Silicate)	:	A	A	A
Silicate Liquor (g)	:	100	100	100
Silica Material Nr.	:	L	M	M
Silica (as is) (g)	:	28.75	10.7	10.7
Storage Temperature (°C)	:	50	50	80
35 Start of gelling (min)***)	:	2	10	3

*) Example 2 is based on the same raw materials and has the same composition as sample L2 of Example 1, which was tested at room temperature (approx. 20 °C).

Gelling of sample L2 at room temperature started after approximately 30 minutes.

**) Examples 3 and 4 are based on the same raw materials and have the same composition as sample M2 of Example 1, which was also tested at room temperature. Gelling of sample M2 at 20 °C started very slowly and a real start point could not be defined (after several hours).

***) Gelling assessment at 50 °C and 80 °C:

Gelling was visually observed as well as by regularly assessing the strength needed to enter a glass rod in the gelling suspension.

Summarizing:

1. Increasing the storage- (or "curing"-) temperature decreases the time needed for gelling or solidifying (or: "curing" or hardening).
2. Addition of amorphous silica offers an excellent means to gel (or "cure" or "harden") a silicate liquor.
3. Curing silicate liquors using amorphous silica also renders the hardened product less soluble in water, creating a more permanent "cure" even when in contact with water.

EXAMPLES 5-9

Addition of amorphous Silica to suspensions of zeolite of a P-type in a neutral silicate liquor.

Procedure:

A suspension of 15 % by weight of zeolite in neutral Sodiumsilicate liquor was prepared, following the procedure as in EXAMPLE 1 using the same beakerglass and following materials:

Zeolite in silicate suspension:

Silicate liquor (g) : 500

(Material A)

Zeolite powder (g) : 100

(Material C)

Zeolite content (wt.%): 15

(Bone dry basis)

This suspension was split up in 120 g portions to which amorphous silica was added at room temperature in a mortar.

After intensive milling in the mortar, the samples were gathered in small beaker glasses for assessment of the gelling process.

The following tests were carried out:

EXAMPLE Nr.	:	5	6	7	8	9
10 Zeolite suspension (g)	:	120	120	120	120	120
Amorphous Silica:						
- Material Nr.	:	L	L	L	M	M
- weight (as is) (g)	:	14.4	28.8	43.1	5.37	10.7
Final Composition Slurry						
15 Silicate (dry basis) (wt.%)	:	26.1	23.6	21.5	28.0	26.8
Zeolite (dry basis) (wt.%)	:	13.4	12.1	11.0	14.4	13.8
Silica (dry basis) (wt.%)	:	3.7	6.7	9.2	4.0	7.7
Water content (wt.%)	:	56.8	57.6	58.3	53.6	51.7
20 Gelling *) :						
- gelling start (min.)	:	30	30	30		
- after 1 day	:	s.g	g	h	s.g	h
- after 2 days	:	s.g	h	h	s.g	h
- after 3 days	:	s.g.	h	h	s.g	h

25

*) Gelling is specified as: s.g.= soft gel; g = gel; h = hard.

The gelled suspensions of EXAMPLES 6, 7 and 9 were harder than those of the gelled suspensions L2,L3,L4,M2 and M3 of EXAMPLE 1, showing the additional strengthening resulting from the zeolite additionally present in the suspension.

Exerting a similar force on a thin glass rod in hardened (cured) gels containing 11 - 14.4 wt. % additional zeolite reduced the penetration by a factor of roughly 3 - 4.

C L A I M S

1. Hardener for hardening silicate solutions comprising a silica providing compound, capable of providing silica in
5 amorphous or dissolved form in a silicate solution.
2. Hardener according to claim 1, characterized in that the silica providing compound is selected from the group, comprising amorphous silica and an amorphous metal silicate.
10
3. Hardener according to claim 2, characterized in that the amorphous metal silicate is selected from the group, comprising magnesium silicate, calcium silicate and aluminium silicate.
- 15 4. Silicate solution to be hardened, comprising a hardener according to one or more of the preceding claims, wherein said silicate solution has a silicate content of at least 10% by weight, preferably at least 20% by weight.
- 20 5. Silicate solution to be hardened, comprising a hardener according to one or more of claims 1-3, wherein said silicate solution has an $\text{SiO}_2/\text{M}_2\text{O}$ molar ratio, M being an alkali metal or ammonium, being comprised between 1 - 4.5, preferably between 2 - 4.2 and more preferably between 2.6 - 4.2.
25
6. Silicate solution to be hardened, comprising a hardener according to one or more of claims 1-3, wherein said silicate solution comprises a filler material.
- 30 7. Silicate solution according to claim 6, characterized in that the filler material has an average particle size of 0.8 - 15 μm and a specific weight of below 2.75 kg/l.
8. Silicate solution according to claim 6 or 7, characterized
35 in that the filler material comprises a zeolite.
9. Silicate solution according to claim 8, characterized in that the zeolite is of the P-type.

10. Method for hardening a silicate solution, wherein a hardener according to claim one or more of claims 1-3 is added to the silicate solution in an amount exceeding the amount of hardener needed to gel the solution.

5

11. Method according to claim 10, characterized in that the amount of hardener added to the silicate solution is selected such that the $\text{SiO}_2/\text{M}_2\text{O}$ molar ratio, M being an alkali metal or ammonium, of the silicate solution is increased to between 5-7.

10

12. Method according to claim 11, characterized in that the amount of hardener added to the silicate solution is selected such that the $\text{SiO}_2/\text{M}_2\text{O}$ molar ratio, M being an alkali metal or ammonium, of the silicate solution is increased to between 4.4 -

15 5.5.

13. Hardened silicate material obtainable by hardening a silicate solution according to one or more of claims 4-9.

20

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 98/01228

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C04B28/26 C04B22/06 C04B22/00

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)

IPC 6 C04B

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 94 04355 A (VETROTECH AG) 3 March 1994 see page 3, line 25-29 ---	1,2
X	DATABASE WPI Week 8510 Derwent Publications Ltd., London, GB; AN 85-059657 XP002074071 & JP 60 016 856 A (NIPPON CHEM IND CO) see abstract ---	1,3
A	EP 0 458 504 A (ACHESON INDUSTRIES INC.) 27 November 1991 see claim 1 ---	6-8
A	US 3 920 578 A (P. C. YATES) 18 November 1975 see claim 1 ---	1,2
-/--		

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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19/08/1998

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 98/01228

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Week 7420 Derwent Publications Ltd., London, GB; AN 74-37426v XP002074072 & JP 49 015 941 B (NIPPON CHEM IND CO) see abstract ---	1,2,10, 13
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