

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
5 June 2003 (05.06.2003)

PCT

(10) International Publication Number
WO 03/045872 A1

(51) International Patent Classification: **C04B 28/02**

(21) International Application Number: PCT/EP02/12483

(22) International Filing Date:
7 November 2002 (07.11.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0128438.9 28 November 2001 (28.11.2001) GB

(71) Applicant (*for all designated States except US*): **MBT HOLDING AG** [CH/CH]; Vulkanstrasse 110, CH-8048 Zürich (CH).

(72) Inventor; and

(75) Inventor/Applicant (*for US only*): **ANGELSKAAR, Terje** [NO/CH]; Honeretshof 6, CH-8962 Bergdietikon (CH).

(74) Agent: **MCSTEA, John, Anthony**; Vulkanstrasse 110, CH-8048 Zürich (CH).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

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.

(54) Title: CEMENT ACCELERATOR AND METHOD

(57) Abstract: An alkali-free accelerator for sprayed cementitious composition, such as concrete, is prepared by dissolving aluminium sulphate in water and amorphous aluminium hydroxide in water optionally containing amine, and adding at least one stabiliser which is glycolic acid, and optionally at least one defoaming agent.



WO 03/045872 A1

Cement Accelerator and Method

This invention relates to cementitious compositions and to accelerators for use therein, particularly for sprayed concrete.

5

The application of a cementitious material such as concrete to a substrate by spraying from a nozzle is a well-established technology, and it is widely used in such applications as the lining of tunnels. It is important that the sprayed concrete set very rapidly on the substrate, and this is achieved by the addition to the concrete at the nozzle
10 of an accelerator. These accelerators are quite different from those used with conventional concrete and have traditionally included such materials as alkali metal hydroxides, aluminates and silicates.

The highly alkaline nature of these materials has given handling problems. It also
15 means that their use in confined spaces such as tunnels has led to very unpleasant working atmospheres. Recent attempts to avoid such materials have involved the use of aluminium compounds and typical examples may be found in European Patents 0 076 927, 0 775 097 and 0 742 179, Australian Patent 706917 and European Applications 0 812 812 and 0 946 451.

20

It has now been found that it is possible to prepare an accelerator for sprayed concrete by a simple process, which accelerator performs especially well. The invention therefore provides a method of preparing an accelerator for sprayed cementitious material consisting essentially of the steps of

25

- (i) dissolving aluminium sulphate and aluminium hydroxide in water, which optionally contains at least one amine dissolved therein, to give a clear solution; and
- 30 (ii) optionally adding at least one defoaming agent;

the proportions of ingredients present being such that the final product contains from 3%-12% by weight of aluminium sulphate (measured as Al_2O_3), up to 30% by weight of

amorphous aluminium hydroxide, up to 15% by weight amine, up to 3% by weight defoaming agent and up to 1.5 mol/kg. stabiliser, the stabiliser being glycolic acid.

The invention additionally provides an accelerator for use with sprayed
5 cementitious material preparable by such a method.

The invention additionally provides an accelerator for cementitious material consisting essentially of a solution of aluminium sulphate, amorphous aluminium hydroxide and glycolic acid, optionally containing amine and defoaming agent, the
10 accelerator containing from 3%-12% by weight of aluminium sulphate (measured as Al_2O_3), up to 30% by weight of amorphous aluminium hydroxide, up to 15% by weight amine, up to 3% by weight defoaming agent and up to 1.5 mol/kg. glycolic acid.

The aluminium sulphate used may be any commercially-available material.
15 Aluminium sulphates differ in their purity and constitution, the most common being so-called "17%" because it contains 17% of Al_2O_3 . In practical terms, the weight percentage of 17% aluminium sulphate, $\text{Al}_2(\text{SO}_4)_3 \cdot 14.3 \text{ H}_2\text{O}$, which should be used in the process according to the invention lies in the range of from 30% to 60%, preferably from 40%-
54%.

20

The aluminium hydroxide may be any commercially-available amorphous aluminium hydroxide. Although all such aluminium hydroxides will give satisfactory results, it is generally true that the more recent the date of manufacture, the better the result. In addition, aluminium hydroxides which, as a result of their particular manner of
25 manufacture, contain a small proportion of aluminium carbonate (up to 5%) are easier to dissolve and are preferred materials. This behaviour is not obtained by simply adding aluminium carbonate to pure aluminium hydroxide. Although very small quantities of aluminium hydroxide may be used (less than 0.1% is possible), a significant improvement is observed at 5% or more. The preferred range of weight proportions is from 4-25%,
30 preferably from 6-18%.

There must also be present a stabiliser, which may be added at the end of the process. This is a material which prevents the aluminium hydroxide/aluminium sulphate

solution either from precipitating or from forming a gel. Without stabiliser, the solution will function well as an accelerator, but it will lack stability and therefore shelf life, necessitating its use very shortly after manufacture, something usually not practical.

- 5 The stabiliser for use in this invention is glycolic acid (hydroxyacetic acid). It has been previously proposed to use hydroxycarboxylic acids as stabilisers in International Application PCT/EP00/12216, but there was no specific mention of glycolic acid and the preferred acid in that application was citric acid. It has been found surprisingly that glycolic acid gives outstanding stability, far better than other hydroxycarboxylic acids.
- 10 Preferably the stabiliser is present to the extent of from 0.1 –1 mol./kg. As a general rule, the more glycolic acid present, the better the stability. However, there comes a point when addition of further glycolic acid brings no improvement. Thus, although the stated maximum of 1.5 mol./kg. can be exceeded, this brings no benefit. The best results are obtained by using quantities in the region of 1 mol./kg.

15

The properties of the accelerators provided by this invention can be considerably enhanced by the use of one or both of two optional, but preferred, components.

- 20 The first of these is amine. This must be water-soluble, otherwise there is no restriction on the choice of amine. Preferred amines are alkanolamines, such as diglycolamine, diethanolamine and triethanolamine, diethanolamine being particularly preferred. Up to 12% by weight amine may be used, but the preferred quantity is from 1 - 4%.

- 25 The second preferred additional component, defoaming agent, may be any such material known to the art. Most of these are proprietary commercial materials whose precise composition is never revealed, but any such material known to the art is suitable. Typical examples include silicone types such as AGITAN (trade mark) and fatty acid polyether types such as LUMITEN (trade mark) EL.

30

The defoaming agent may be used at a rate out up to 5% (solids by weight of the whole composition), preferably from 0.5%-3%. The use of defoaming agent makes the use of less fresh aluminium hydroxides easier. It is believed, without restricting the scope

of the invention in any way, that its presence helps in the removal of carbon dioxide which accumulates on the surface of the aluminium hydroxide over time. Surprisingly, provided that the defoamer contains no silicone and that it is not present to the extent of more than 3%, it gives an appreciable improvement in setting time over that of an
5 identical composition without defoaming agent or with silicone types.

The process of the invention is readily carried out with standard equipment, and the skilled person will have no difficulty in doing so. It will be appreciated that in order to achieve solutions at the various stages, some heating may be necessary, typically to about
10 50-60°C.

In the process, the clear solution can be produced by any convenient method. It is possible to add the aluminium sulphate and aluminium hydroxide sequentially in any order to water. It is also possible to add them together to water, or to dissolve or disperse
15 them individually in two different quantities of water and then combine these quantities.

Preferably, the aluminium sulphate and the aluminium hydroxide are added sequentially to water. Preferably the aluminium sulphate is first dissolved in water; aluminium sulphate will dissolve with heating. To this solution the aluminium hydroxide
20 is then added. A clear solution is obtained.

It is possible, although less preferable, first to add the aluminium hydroxide to the water. Aluminium hydroxide does not dissolve readily in water, but gives a fine suspension. To this suspension the aluminium sulphate is added. A clear solution is
25 obtained. The stabiliser is added to this solution and stirred in.

The precise nature of the product of the process is not known. It is certainly not a mere mixture of the original components (the fact that the product is a clear or slightly turbid solution and not an opaque suspension typical of aluminium hydroxide is evidence
30 of this), and without restricting the invention in any way, it is believed to be oligomeric or polymeric in nature.

The accelerator thus prepared gives excellent results when used as an accelerator for

sprayed cementitious material, especially concrete. Sprayed concrete treated with this accelerator hardens rapidly and has good final strength. The accelerator has a long shelf-life, is resistant to changes in temperature and is completely non-alkaline, thus leading to better working environments.

5

The invention therefore also provides a method of applying a cementitious composition to a substrate by spraying, comprising the conveying of the composition to a spray nozzle, there being added at the nozzle an accelerating composition of the kind hereinabove described.

10

The invention is further illustrated by the following non-limiting examples.

An accelerator is made from the following ingredients:

15	aluminium sulphate (17%)	42 parts (weight)
	aluminium hydroxide	18 "
	glycolic acid	4 "
	diethanolamine	1 "
	water	35 "

20

The water is heated to 55° - 60°C, and the aluminium sulphate is added with stirring. When it has dissolved, the aluminium hydroxide is added, followed by the glycolic acids and the amine. The mixture is then allowed to cool. The final solution is a pale yellow, slightly turbid solution.

25

This accelerator composition is called Accelerator A.

Another accelerator (Accelerator B) is prepared in the same manner, but substituting formic acid, a well-known stabiliser, for glycolic acid. The quantity of water
30 is reduced, so that more formic acid can be added - the quantity of formic acid in Accelerator B is twice that of glycolic acid in Accelerator A.

Both accelerators are subjected to long-term stability testing at 5°C, 20°C and 40°C.

The particular test period is 70 days. The assessment criteria and the results are as follows:

- 5 a) Change in turbidity Both accelerators show no change over the entire period at 5° and 20°. However, at 40°, Accelerator A shows a turbidity change (indicating the onset of instability) at 31 days, whereas Accelerator B showed this change at 13 days.
- 10 (b) Gelling A gelled accelerator cannot be used. Both accelerators show no gelling over the whole period at 5° and 20°, but Accelerator A gelled at 59 days and Accelerator B at 27 days.
- (c) Separation The separation of the accelerator solution into discrete liquid layers indicates that it can no longer be used. Both accelerators show no separation over the period.
- 15 (d) Sedimentation Excessive sedimentation (in excess of 1mm) means that an accelerator can no longer be used. Neither accelerator has excessive sedimentation over the period of the test.
- 20 The performance of Accelerator B is typical of a high-performance commercial accelerator. It can readily be seen that Accelerator A according to the invention has a significant edge in stability performance, even though it has only half of the quantity of stabiliser. 40°C is typical of the temperatures commonly encountered in tunnels, and it is often required that accelerators ready for use be stored in such conditions. The
- 25 improvement in performance shown by Accelerator B is therefore of major commercial significance, as it saves the need for less stable accelerators to be stored in cooler conditions and then brought in on demand.

Claims

1. A method of preparing an accelerator for sprayed cementitious composition,
consisting essentially of the steps of
 - (i) dissolving aluminium sulphate and aluminium hydroxide in water, which
optionally contains at least one amine dissolved therein, to give a clear
solution; and
 - (ii) optionally adding at least one defoaming agent;
- the proportions of ingredients present being such that the final product contains
from 3%-12% by weight of aluminium sulphate (measured as Al_2O_3), up to 30% by
weight of amorphous aluminium hydroxide, up to 15% by weight amine, up to 3%
by weight defoaming agent and up to 1.5 mol/kg. stabiliser, the accelerator
additionally containing a stabiliser which is glycolic acid.
2. A method according to claim 1, wherein there is additionally present in the water
at least one water-soluble amine.
3. A method according to claim 3, wherein there is added at least one defoaming
agent.
4. A method according to claim 3, wherein the defoaming agent contains no silicone
and is present to a maximum extent of 3%.
5. A method according to claim 1, wherein the clear solution is prepared by the steps
of
 - (i) dissolving aluminium sulphate in water, optionally containing at least one
amine dissolved therein;
 - (ii) dissolving amorphous aluminium hydroxide in the solution of (i) until a clear

solution is obtained; and

(iii) adding glycolic acid to the clear solution.

- 5 6. A method according to claim 5, wherein there is added to the clear solution at least one defoaming agent.
7. An accelerator for use with sprayed cementitious composition, consisting essentially of a solution of aluminium sulphate, amorphous aluminium hydroxide
10 and glycolic acid, optionally containing amine and defoaming agent, the accelerator containing from 3%-12% by weight of aluminium sulphate (measured as Al_2O_3), up to 30% by weight of amorphous aluminium hydroxide, up to 15% by weight amine, up to 3% by weight defoaming agent and up to 1.5 mol/kg. glycolic acid.
- 15 8. An accelerator for use with sprayed cementitious composition, preparable by a process that consists of the steps of
- (i) dissolving aluminium sulphate and aluminium hydroxide in water, which optionally contains at least one amine dissolved therein, to give a clear
20 solution; and
- (ii) optionally adding at least one defoaming agent;
- the proportions of ingredients present being such that the final product contains
25 from 3%-12% by weight of aluminium sulphate (measured as Al_2O_3), up to 30% by weight of amorphous aluminium hydroxide, up to 15% by weight amine, up to 3% by weight defoaming agent and up to 1.5 mol/kg. stabiliser, the accelerator additionally containing a stabiliser which is glycolic acid.
- 30 9. A method of applying a cementitious composition to a substrate by spraying, comprising the conveying of the composition to a spray nozzle, there being added at the nozzle an accelerator according to any one of claims 6 to 8.

Internal Application No.

PCT/EP 02/12483

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C04B28/02

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 7 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)

EPO-Internal, WPI Data, 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	WO 01 42165 A (HOFMANN THOMAS ;MBT HOLDING AG (CH)) 14 June 2001 (2001-06-14) cited in the application the whole document ---	1-8
Y	EP 0 465 991 A (SIKA AG) 15 January 1992 (1992-01-15) claims 1,4 ---	1-8
Y	EP 0 508 158 A (SIKA AG) 14 October 1992 (1992-10-14) claims 1-3 ---	1-8

	---/---	



Further documents are listed in the continuation of box C.



Patent family members are listed in 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

5 May 2003

Date of mailing of the international search report

14/05/2003

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 _____

Andriollo, G

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/12483

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96 05150 A (SANDOZ LTD ;SANDOZ AG (DE); SANDOZ AG (AT); LEIKAUF BERNHARD (CH)) 22 February 1996 (1996-02-22) claims & EP 0 775 097 A 28 May 1997 (1997-05-28) cited in the application -----	1-8
A	EP 0 076 888 A (FREUDENBERG CARL FA) 20 April 1983 (1983-04-20) claims 1,2 -----	1-8

INTERNATIONAL SEARCH REPORT

Inter Application No

PCT/EP 02/12483

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 0142165	A	14-06-2001	AU 2671901 A	18-06-2001
			BR 0016261 A	20-08-2002
			CA 2393458 A1	14-06-2001
			CN 1407954 T	02-04-2003
			WO 0142165 A2	14-06-2001
			EP 1237827 A2	11-09-2002
			NO 20022662 A	08-08-2002
			US 2002195026 A1	26-12-2002
EP 0465991	A	15-01-1992	CH 680730 A5	30-10-1992
			AT 130285 T	15-12-1995
			CA 2046500 A1	10-01-1992
			DE 59106895 D1	21-12-1995
			DK 465991 T3	04-03-1996
			EP 0465991 A1	15-01-1992
			ES 2030377 T1	01-11-1992
			GR 92300022 T1	26-08-1992
			GR 3018463 T3	31-03-1996
			JP 4342450 A	27-11-1992
EP 0508158	A	14-10-1992	CH 681720 A5	14-05-1993
			AT 136529 T	15-04-1996
			DE 59205931 D1	15-05-1996
			DK 508158 T3	19-08-1996
			EP 0508158 A2	14-10-1992
			ES 2086568 T3	01-07-1996
			GR 3019647 T3	31-07-1996
WO 9605150	A	22-02-1996	AT 174887 T	15-01-1999
			AU 701619 B2	04-02-1999
			AU 3257895 A	07-03-1996
			DE 69506881 D1	04-02-1999
			DE 69506881 T2	02-06-1999
			WO 9605150 A1	22-02-1996
			EP 0775097 A1	28-05-1997
			ES 2125644 T3	01-03-1999
			FI 970551 A	07-02-1997
			JP 10504273 T	28-04-1998
			US 5968256 A	19-10-1999
EP 0076888	A	20-04-1983	DE 3140784 A1	28-04-1983
			AU 553566 B2	24-07-1986
			AU 8465882 A	21-04-1983
			DD 202107 A5	31-08-1983
			DE 3279227 D1	29-12-1988
			EP 0076888 A2	20-04-1983
			ES 8400860 A1	16-02-1984
			FI 821599 A ,B,	15-04-1983
			JP 58076434 A	09-05-1983
			NO 821896 A ,B,	15-04-1983
			US 4559243 A	17-12-1985
			YU 110682 A1	31-12-1984