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(21) International Application Number: PCT/EP92/00318 (22) International Filing Date: 14 February 1992 (14.02.92) (71) Applicant (for AT only): SANDOZ-ERFINDUNGEN VERWALTUNGSGESELLSCHAFT M.B.H. [AT/AT]; Brunner Strasse 59, A-1230 Vienna (AT). (71) Applicant (for DE only): SANDOZ-PATENT-GMBH [DE/DE]; Humboldtstrasse 3, D-7850 Lörrach (DE). (71) Applicant (for all designated States except AT DE): SANDOZ LTD. [CH/CH]; Lichtstrasse 35, CH-4002 Basle (CH). (72) Inventors: ELLENBERGER, Peter ; Rebbergstrasse 97, CH-8706 Feldmeilen (CH). SCHMITT, Heinz, W. ; Tüfistrasse 98, CH-8107 Buchs (CH). VALENTI, Salvatore ; Im Rehwechsel 37, CH-4102 Binningen (CH). YANG, Qiwei ; Furkastrasse 16, CH-8048 Zürich (CH).		(74) Common Representative: SANDOZ LTD.; Lichtstrasse 35, CH-4002 Basle (CH). (81) Designated States: AU, CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LU, MC, NL, SE). Published <i>With international search report.</i>
(54) Title: PRODUCTION OF CEMENT-MORTAR DRY MIX (57) Abstract A storable cement-mortar dry mix, which comprises the components cement, aggregate, reaction resin and hardener in a single mixture, wherein the hardener is present as the reaction product of the hardener with an organic acid or a functional derivative thereof.		

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PRODUCTION OF CEMENT-MORTAR DRY MIX

This invention relates to a process for the production of a storable cement-mortar dry mix containing a reaction resin and hardener therefor.

It is known from German Patent application DE 35 23 479 that, in the production of cement-mortar dry mixes which contain a reactive resin, it is desirable to have available a storable dry mix which contains all the components (except water) and only has to be mixed with water at the place of use. This problem was solved, according to DE 35 23 479, by mixing some of the components to form a preliminary mix A, and, if necessary, mixing the remaining components to form a preliminary mix B, and mixing these preliminary mixes with water at the place of use. Thus, at least two preliminary mixes have to be mixed with water; there is mentioned the possibility of making a single dry mix containing all the components except water in a storable mixture, but this apparently was not followed through.

It has now been found that it is possible to produce a cement-mortar dry mix comprising a reactive resin and hardener therefor, which contains all the components except water, and which is storable, which remains fluid over a long period of time and which does not harden prematurely. This is achieved by reacting the hardener with an organic acid or a functional derivative thereof, to form an anhydrous product, prior to its addition to the dry mix.

The invention therefore provides a process for the production of a cement-mortar dry mix, which comprises cement, aggregate, reactive resin and hardener in a single mixture, characterized in that the hardener is added in the form of a dry reaction product with an organic acid or a functional derivative thereof. The dry mixes thus produced can be stored for an unlimited period, and only at the place of use need they be mixed with water, after which they harden over

time periods typical for equivalent conventional compositions to produce building materials with excellent strength.

The reaction products of the hardener (generally an amino group-containing compound) with an organic acid or a functional derivative thereof, should be dry, that is, they should be powdery or granular solids and not aqueous fluids. They may be dry per se or they may be mixed with amorphous admixed materials such that are absorbed and converted to dry form and they can be added in this dry powder form. These reaction products are generally salts or amides, which hydrolyze in an alkaline medium. Thus, if the dry mix is brought into contact with water, the amine hardener is released and reacts with the reactive resin.

This invention also provides a hardener composition for reactive resins which is the reaction product of a hardener and an organic acid or functional derivative thereof, and which is a dry powder or a granular solid.

It is preferred that, when the hardener is an amino group-containing compound, the relative proportions of hardener and acid or functional derivative thereof are such that at least 30%, more preferably 40% and most preferably from 50-90% of the amino groups are reacted.

It is preferable to use carboxylic acids, polycarboxylic acids or functional derivatives of the acids, e.g. lactones or mixtures of carboxylic acids or polycarboxylic acids, which, after reacting with the hardener, yield a dry powder which readily hydrolyzes in an alkaline medium. Specific examples of such acids are gluconic acid or the lactone thereof, lactic acid, aminosulphonic acid and oxalic acid, oxalic acid being especially preferred. Superplasticizers which contain acidic groups may also be used, e.g. copolymers of styrene and maleic acid. However, if the reaction product is liquid at ambient temperature, for example, as occurs when formic acid is used, it is advantageous firstly to mix it with an amorphous admixed material so that a dry powder is obtained. This can then be easily incorporated into the dry mix according to the invention.

The reaction product of the hardener and the organic acid may be prepared by a suitable method known to the art. The choice of method will depend on the natures of the materials involved (as the final product must be a dry powder or granular solid, different techniques will be needed, for example, depending on whether the reaction product is liquid or solid). The skilled man will readily be able to determine the most appropriate method for any given set of circumstances.

During the preparation of the cement-mortar dry mix, the reactive resin should not come into contact with the cement, but initially with an amorphous admixed material, so that during the mixing operation, the reactive resin and hardener are separated not only from each other but also from the cement, and no premature reaction can take place between the resin and hardener, nor can the solidifying properties of the cement be affected. Such admixed materials are non-crystalline materials, usually containing silicon, and which because of their large specific surface have an affinity for the reactive resin, but do not have the same hydraulic effect as cement. Examples of such materials are fly ash, trass, ground blast-furnace slag, silica fume and bentonite. Materials such as lampblack and active silicic acid may also be used, provided that their colour or price is acceptable for the application envisaged. The only proviso is that the grain size of these materials does not exceed 0.05 mm, and that their specific surface is greater than 0.2 m²/g. The smaller the grain size and the greater the specific surface of these admixed materials, the smaller the quantity which will be needed.

Preferred amorphous admixed materials for the process according to the invention are fly ash and silica fume. These may be used alone or mixed.

The mixing procedure according to the invention is preferably carried out such that firstly the aggregate (e.g. sand) is mixed with the reaction resin, and then secondly with the special admixed material and with the cement to give a first preliminary mix. The reaction

product of the hardener, given powder form where necessary by separate mixing with amorphous admixed material, is mixed with any further required admixtures and/or additives to give a second preliminary mix. The two preliminary mixes are finally combined to form a dry mix. Alternatively, the reactive resin may also be initially mixed with amorphous admixed material, and then all the components may be combined in one mixing operation.

The reactive resin suitable for use in this invention may be one of the polymerisable compounds which are known for this purpose and which are crosslinkable by means of an amine hardener. These are available commercially as so-called 2-component resins. Examples of such resins are epoxy resins. The corresponding hardeners are usually (and preferably) compounds containing amino groups.

The cements which are useful in this invention are the known hydraulic binding agents such as Portland cement, iron Portland cement, blast-furnace cement and trass cement. The preferred binding agent is Portland cement, and in particular Portland cement which is low in aluminates, such as so-called PCHS (Portland cement with high sulphate resistance).

The aggregate materials used are either natural stone, e.g. quartz sand, sea gravel, pit gravel, or artificial aggregates, e.g. blast-furnace slag, coal ashes, cinders and granulates, pumice from various base materials, calcined aluminous aggregates or organic aggregate materials. For certain applications, reinforcing materials, such as fibres of steel, glass and plastics, can additionally be used.

There may also be used in the compositions of this invention polymer additives and cement admixtures. These are materials, which, used in small quantities, influence the properties of the finished cement mixes. The additives are usually organic in nature. Examples are defoamers, corrosion inhibitors, degassing agents, adhesion improvers, dispersing agents and pigments. The admixtures alter the workability, the ability to withstand frost or de-icing salt, absorption of water, solidifying times, etc., of the cement mix and are very well known to

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and widely used by the art. Examples of such admixtures are plasticizers and superplasticizers, air entraining agents, concrete sealing materials, solidifying retardants, solidifying accelerators, compression aids and stabilizers.

A preferred dry mix contains, in addition to Portland cement, various constituents in the following quantities:

	<u>preferably</u>	more <u>preferably</u>	most <u>preferably</u>	
- reactive resin	2-25 %	5-20 %		
- hardener	2-25 %	5-20 %		
- fly ash	10-200 %	10-100 %	30-100 %	30-80 %
- aggregate	50-500 %	100-400 %		
- cement admixtures	0-20 %	0.5-10 %	0.5-5 %	1-3 %
- additives	0-20 %	0-10 %	0.5-10 %	1-6 %

whereby all percentages refer to the weight of the cement, the hardener being present in the form of an anhydrous reaction product with an organic acid or functional derivative thereof.

The dry mixes obtained, which contain reactive resin, may be used in many applications. As mortar (with sand as the aggregate), they may be used in building restoration, especially those attacked to a great extent by frost/salt, or to produce floors and coatings. With the incorporation of coarser aggregates, they may be used as construction material. Such dry mixes are also suitable for spraying.

In the following examples, all parts are understood to be parts by weight. The percentages are by weight and the temperatures are given in degrees Celsius.

Example 1**Preparation of a dry powder hardener**

5.263 parts of "Beckopox" (trade mark) EH 623 (amine hardener ex Hoechst) are prepared and heated to 75-80°. 1500 parts of water are added at this temperature and the mixture is stirred for 60-90 minutes until a homogeneous mixture is obtained. Subsequently, 834 parts of oxalic acid are measured in over the course of 2-3 hours at the same temperature. The reaction mixture is dried over 2 - 2½ hours at 110° in a vacuum drying chamber, and pulverized. The dried powder has a melting point of 123-127°.

Example 2**Preparation of a dry powder hardener**

40 parts of "Rütapox" (trade mark) ECC-4000-B amine hardener (from Bakelite GmbH) are added to a kettle, followed by 54.5 parts of water, and the mixture heated to 75°-80°C and maintained at this temperature until a homogeneous blend is achieved (this takes no more than one hour). The blend temporarily becomes milky. To this blend is added 9.5 parts of hydrated oxalic acid ($C_2H_2O_4 \cdot 2H_2O$), the addition being gradual such that the temperature remains in the range of 80°-85°C.

The product is a 45% (wt) solution of hardener which is converted to a dry powder by spray drying. The temperature at which spray drying is carried out should not exceed 80°C.

Example 3**Preparation and testing of a cement-mortar dry mix**

The following materials and quantities were used:

	<u>parts</u>
1. mixed quartz sand 0.1-0.75 mm	53.75
2. "Rütapox" ECC-4000 K.A. epoxy resin	1.143
3. "TiONA" (trade mark) RCL-535 TiO_2 pigment	1.00
4. EFA FILLER fly ash	18.00
5. Portland cement	25.00
6. Hardener (from Example 2)	1.107

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Materials 1 and 2 are mixed and then materials 3, 4, 5 and 6, are added to this mixture in that order, blending of an added material being completed before the next material is added.

The dry mortar was tested after storing for six months. Fresh mortar is produced according to DIN 18,555 part 1. The mortar is mixed for 3 minutes using 15% mixing water.

Control of the fresh mortar is carried out according to DIN 18,555 part 2.

Prisms of 4/4/16 cm are produced with the fresh mortar according to DIN 18,555. After one day, they are uncovered and stored for 6 days in a climate of 20°/95% relative humidity and for 21 days at normal climate of 20°/50% relative humidity according to DIN 50,014. The tests for flexural-bending strength and compressive strength are similarly carried out according to DIN 1,164. The bonding tensile strength is determined according to ZTV-SIB 87.

In all cases, the values found correspond to the normal values determined with freshly prepared mixtures.

P a t e n t C l a i m s

1. Process for the production of a storable cement-mortar dry mix, which comprises the components cement, aggregate, reactive resin and hardener in a single mix, characterized in that the hardener is added in the form of a dry reaction product with an organic acid or a functional derivative thereof.
2. Process according to claim 1, characterized in that the reaction product of the hardener with an organic acid or a functional derivative thereof is used as a dry powder or a granular solid.
3. Process according to claim 1 or claim 2, characterized in that the reactive resin is firstly brought into contact with an amorphous admixed material, prior to its being mixed with other materials of the composition.
4. Process according to claim 3, characterized in that fly ash and/or silica fume is used as the amorphous admixed material.
5. Process according to claim 1 or claim 2, characterized in that the aggregate is first mixed with the reactive resin and subsequently with the amorphous admixed material and the cement in succession to give a first preliminary mixture, the reaction product is mixed, optionally separately, with the amorphous admixed material and with possible further admixtures and/or additives to give a second preliminary mixture, and the two preliminary mixtures are combined together to form a dry mix.
6. Process according to claim 5, characterized in that the reactive resin is first of all brought into contact with the amorphous admixed material, and afterwards all the components are combined in a single mixing operation.

7. An amine hardener for reactive resins, obtained by reacting the hardener with an organic acid or a functional derivative thereof, the amine hardener being in the form of a dry powder or a granular solid.
8. An amine hardener according to claim 7, wherein the quantities of hardener and acid reacted are such that at least 30%, preferably at least 40%, more preferably from 50 to 90% of the amine groups are reacted.
9. An amine hardener according to claim 7, characterized in that it is a dry powder or granular solid.
10. An amine hardener according to claim 7, characterized in that the organic acid is oxalic acid.
11. A storable cement-mortar dry mix which comprises cement and the following ingredients in the following proportions expressed by weight of the cement:

- reactive resin	2-25 %
- hardener	2-25 %
- fly ash	10-100 %
- aggregate	50-500 %
- cement admixtures	0-20 %
- additives	0-20 %

the hardener being present in the form of its anhydrous reaction product with an organic acid or functional derivative thereof.

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12. A dry mix according to claim 11, wherein the proportions of ingredients are:

- reactive resin	5-20 %
- hardener	5-20 %
- fly ash	10-100 %
- aggregate	100-400 %
- cement admixtures	0.5-10 %
- additives	0-10 %

13. A dry mix according to claim 11, wherein the proportions of fly ash, cement admixtures and additives are from 30-100%, from 0.5-5% and from 0.5-10% respectively.

14. A dry mix according to claim 11, wherein the proportion of fly ash, cement admixtures and additives are from 30-80%, from 1-3% and from 1-6% respectively.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 92/00318

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁴		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁵ : C 04 B 28/04, C 08 G 59/50, C 04 B 24/28		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁵	C 04 B, C 08 G	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁶		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁸		
Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	EP, A1, 0 409 787 (SANDOZ LTD.) 23 January 1991 (23.01.91), see totality.	1-6, 11-14
X	EP, A2, 0 207 473 (MAROHN) 07 January 1987 (07.01.87), see totality.	1, 3-6
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X	JP, A, 54-111 599 (MITSUBISHI PETROCHEMICAL	7-10
⁴ Special categories of cited documents: ¹⁰ "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 doubt 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 "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 "Z" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
04 May 1992	21. 05. 92	
International Searching Authority	Signature of Authorizing Officer	
EUROPEAN PATENT OFFICE	Natalie Weinberg	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
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ANHANG

ANNEX

NNEXE

zum internationalen Recherchen-
bericht über die internationale
Patentanmeldung Nr.

to the International Search
Report to the International Patent
Application No.

au rapport de recherche inter-
national relatif à la demande de brevet
international n°

PCT/EP 92/00318 SAE 56245

In diesem Anhang sind die Mitglieder
der Patentfamilien der im obenge-
nannten internationalen Recherchenbericht
angeführten Patentdokumente angegeben.
Diese Angaben dienen nur zur Unter-
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This Annex lists the patent family
members relating to the patent documents
cited in the above-mentioned inter-
national search report. The Office is
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La présente annexe indique les
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dans le rapport de recherche inter-
national visée ci-dessus. Les renseigne-
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JP A 5620025		keine - none - rien	