

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(10) International Publication Number
WO 2021/096445 A1

(43) International Publication Date
20 May 2021 (20.05.2021)

(51) International Patent Classification:

C04B 24/00 (2006.01) C04B 28/28 (2006.01)

(21) International Application Number:

PCT/TR2019/050945

(22) International Filing Date:

13 November 2019 (13.11.2019)

(25) Filing Language:

English

(26) Publication Language:

English

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(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— as to the identity of the inventor (Rule 4.17(i))

Published:

— with international search report (Art. 21(3))
— with amended claims (Art. 19(1))

(54) Title: A NOVEL PROCESS FOR HIGH-PERFORMANCE CEMENTS

(57) Abstract: The present invention relates to a novel process for manufacturing high performance cements, a novel grinding aid composition comprising an ester and/or ether polycarboxylate, to method for producing such composition and to use of such composition in the production of cement with or without other additives. The present invention provides a novel aqueous composition for use as grinding aid in the production of high-performance cement, wherein the composition comprises at least one polycarboxylate polymer and at least one surfactant.

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A NOVEL PROCESS FOR HIGH-PERFORMANCE CEMENTS

TECHNICAL FIELD

The present invention relates to a novel process for manufacturing high performance cements,
5 a novel grinding aid composition comprising an ester and/or ether polycarboxylate, to method
for producing such composition and to use of such composition in the production of cement
with or without other additives.

BACKGROUND OF THE INVENTION

For the production of common cements, preferably portland cement, clinker is firstly
10 produced by pulverizing at high heat a mixture of silica, alumina and limestone containing
materials in a rotary kiln. Said high heat is more than 1.400°C. Then, cements are produced
by grinding clinker and gypsum in a suitable mill. 27 types of cement are listed in DIN-EN
197-1.

Cement production is accompanied by the release of a significant amount of carbon dioxide
15 caused by the energy consumption in the rotary kiln while producing the clinker and also
caused by the calcining of limestone. For example, during 1 ton of cement production, 1 ton
of carbon dioxide can be released. Thereby, in prior art, the release of carbon dioxide is tried
to be reduced via the reduction of clinker production. Carbon dioxide emission in cement
production could be reduced if the quantity of clinker is reduced by about 35%. Instead of
20 clinker, mineral additives are added to the cement. However, the low amount of clinker and
higher number of mineral additives cause to a reduction in the required specifications of
cement and concrete such as strength, hardness and time of setting.

The use of additives is known in the prior art in order to minimize the energy utilization by
accelerating of grinding or milling process. Such additives can be plasticizers, retarders,
25 accelerators and/or stabilizers and they are generally used in order to increase the efficiency
of the grinding step of the cement production by lowering the energy used. For example, U.S.
Patent No. 2,673,810 discloses that potassium nitrate is an effective retarder. Organic amines
such as trialkanolamines are examples of accelerators used in the grinding of the clinker as
disclosed in "Cement and Concrete Research", Ramachandran, (1973). In addition,
30 polycarboxylates are also used as grinding aid during the production of cement.

These additives may lead to a change of the specifications of the cement while improving the energy utilization. However, there is still a need in the art for novel methods and compositions to provide stronger, cost-effective and ecological concretes while reducing the carbon dioxide emissions.

5 SUMMARY OF THE INVENTION

It is therefore a primary aspect of the present invention to provide a method for manufacturing high performance cement by introducing together or separately an additive composition and an aqueous composition of polycarboxylate polymer into the grinding of cement clinker.

10 In another aspect, the present invention provides a grinding aid composition for use in the production of high-performance cement wherein the composition comprises a first additive comprising at least one organic amine and at least one amino alcohol and a second additive comprising at least one alkanolamine and at least one glycol.

15 In a further aspect, the present invention provides a grinding aid composition for use in the production of high-performance cement, wherein the composition is an aqueous composition comprising at least one polycarboxylate polymer and at least one surfactant.

In another aspect, the present invention provides a method for manufacturing high performance cement comprising the following steps;

- a) providing a first additive by mixing at least one organic amine and at least one amino alcohol,
- 20 b) providing a second additive by mixing at least one alkanolamine and at least one glycol,
- c) mixing first additive with second additive in order to obtain an additive composition,
- d) providing an aqueous composition of polycarboxylate polymer comprising at least one surfactant, and
- e) introducing together or separately said additive composition and said aqueous composition
- 25 of polycarboxylate polymer into the grinding of cement clinker.

In another aspect, the present invention provides a high-performance cement obtained by the method according to the present invention, wherein the cement comprises 5 to 45% of mineral additives or preferably 10 to 35% of mineral additives by weight of the cement.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a novel aqueous composition for use as grinding aid in the production of high-performance cement, wherein the composition comprises at least one polycarboxylate polymer and at least one surfactant.

- 5 According to the present invention, the surfactant may be a non-ionic surfactant such as modified fatty alcohol or non-ionic fatty acid ester. The surfactant may also include 1 to 10% glycol.

As used herein, "polycarboxylate polymer" means the polymer having carboxy groups. Said polycarboxylate polymer can be obtained by means of polymer-like reaction.

10

Polycarboxylate polymers according to the present invention may be polycarboxylate ether or polycarboxylate ester polymer.

- 15 It has been found that the polycarboxylate polymers with the addition of surfactant enhances the grinding efficiency and the strength of the cement. The dispersibility of cement clinker during grinding is improved by the addition of polycarboxylate polymer composition according to the present invention. In addition, this composition used as a grinding aid results in a reduced energy consumption.

- 20 According to the present invention, said aqueous composition of polycarboxylate polymer is obtained by diluting the polycarboxylate polymer with non-ionized water and with a surfactant by mixing during 30 to 40 minutes. The dilution is preferably performed at 30°C.

- 25 The present invention also provides a novel method for producing a high-performance cement comprising the following steps;

- a) providing a first additive by mixing at least one organic amine and at least one amino alcohol,
- b) providing a second additive by mixing at least one alkanolamine and at least one glycol,
- c) mixing first additive with second additive in order to obtain an additive composition,
- 30 d) providing an aqueous composition of polycarboxylate polymer according to any one of the claims 1 to 5, and

e) introducing together or separately said additive composition and said aqueous composition of polycarboxylate polymer into the grinding of cement.

It has been found that the novel method according to the present invention provides an
5 increase in the substitution amount of minerals and additives to the clinker.

Second additive is prepared by mixing at least one alkanolamine and at least one glycol in reactor. The temperature of said mixing step of alkanolamine with glycol is preferably between 30° C to 50°C and most preferably 40°C. The mixing time of alkanolamine with
10 glycol is preferably 1 hour in order to obtain a homogenous mixture.

According to the present invention, first additive and/or second additive may further comprise a non-ionic surfactant. The surfactant is between 0,1% to 0.5 and preferably 0,2% to 0,3% by weight of the grinding aid composition.

Amino alcohol according to the present invention is selected from the group consisting of 1-
15 (N,N-Bis(2-hydroxyethyl)amino)propan-2-ol (Diethanolisopropanolamine, also known as DEIPA), ethanolamine, diethanolamine, triethanolamine, N-butyldiethanolamine, M-methyldiethanolamine, diaminomethanal (urea), N-ethyldiethanolamine, diisopropanolamine, methyl diisopropanolamine, tetrahydroxypropylethylenediamin, trimethylaminoethylethanolamine and combinations thereof. Preferred amino alcohol is
20 diethanolisopropanolamine (DEIPA). Amino alcohol is in an amount of 30 to 50% by weight of the first additive.

Organic amine according to the present invention is selected from the group consisting of 2-ethyldiisopropylamine (DIPEA/EDIPA), diethylamine, triethylamine, dimethylamine pyridine, ethyldiisopropylamine, procaine, dibenzylamine, N-methylmorpholine,
25 dihydroabietylamine, 1-phenamine, methyl-piperidine and combinations thereof. Preferred organic amine is 2-ethyldiisopropylamine (DIPEA). Organic amine is in an amount of 50 to 70% by weight of the first additive.

Alkanolamine according to the present invention is selected from the group consisting of 2,2,2-nitrilotriethanol (triethanolamine), 1,1,1-nitrilopropan-2-ol (triisopropanolamine),
30 diethanolamine, diethoxylated isopropylamine and combinations thereof. Preferred

alkanolamine is triethanolamine. Alkanolamine is in an amount of 70 to 90% by weight of second additive.

Glycol according to the present invention is selected from the group consisting of 2-(hydroxyethoxy)ethan-2-ol (diethylene glycol), ethylene glycol, propylene glycol, glycerol
5 (propan-1,2,3-triole), polyethylene glycol, monopropylene glycol and combinations thereof. Preferred glycol is glycerol and/or diethylene glycol. Glycol is in an amount of 10 to 30% by weight of second additive.

According to the present invention, first additive may further comprise diaminomethanal (urea). The amount of urea used in the production method is between 5% to 25% by weight
10 on the weight of the first additive and preferably between 10% to 20% by weight.

The step of mixing first and second additive is occurred at 30 to 65°C and preferably 40 to 60°C.

According to the present invention, the ratio of first additive to second additive is between 1:0.5 and 4:1.

15 It has been surprisingly found that the method according to the present invention enables the mill to grind the clinker to a smaller size with less energy and within a short time. The reduction in amount of energy necessary allows the carbon dioxide emissions from the production of cement clinker to be greatly reduced by substitution of mineral(s). The method and polycarboxylate polymer composition that has a density of 1.0 -1.10 g/cm³ and a pH of
20 between 7 to 9, also provide the cement having an increased 1-day, 2-day, 7-day and 28-day compressive strength.

The method may further comprises adding other additives during or before grinding such as retarders, anti-corrosion agents, dryers, fluidizer, anti-foaming, anti-freezing agents and water reducing agents.

25 Said polycarboxylate polymer composition and said mixture of first and second additive in the production method of high-performance cement can be defined as grinding aid and cement chemical admixture compositions. These admixture compositions are suitable for use on conventional grinding mills such as ball mills or roller mills. Thus, grinding of cement clinker is performed in those grinding mills.

Accordingly, in another embodiment, the present invention provides the use of the aqueous composition of polycarboxylate polymer and the mixture of first additive and second additive according to the present invention in the production of cement, as grinding aids. Said compositions increase the normal setting time and the normal compressive strength of a cement and a concrete mixture. The strength is enhanced both in the near-term, first day, and in the long-term, after 28 days.

According to the present invention, the tests can be performed with respect to the standard tests in the prior art such as EN 197-1, EN 197-2 or ASTM C150/150 M-18. More specifically, EN 196-7, EN 196-2, EN 196-3, EN 196-6, EN 196-1 or ASTM C595/C595M, ASTM C109/C109M, ASTM C150.

Cements may further comprise mineral additives selected from the group consisting of siliceous fly ash, calcareous fly ash, blast-furnace slag, limestone (as calcium carbonate), silicon dioxide (as silica sand), natural pozzolan, industrial pozzolan and burnt shale. The kind and percentage of cement's composition determine the type of cement. Accordingly, 27 types of cement in total are specified. Basic cement types are portland cement (CEM I), portland composite cement (CEM II), blast furnace cement (CEM III), pozzolanic cement (CEM IV), hydraulic cement, slag cement or composite cement (CEM V). According to the present invention, cement is preferably portland cement and others.

Clays and limestone are raw materials to produce the clinker which is the hydraulic compound mainly used in the production of cement. Clinker comprises calcium silicates which can be tricalcium silicate, dicalcium silicate, tricalcium aluminate and aluminoferrite.

In one embodiment of the present invention, cements may further comprise nano-sized minerals such as micro and nano particles of silica, aluminum and ferrite oxides.

It is possible to add nano-sized minerals or additives in the high-performance cement obtained by the process according to the present invention. As explained before, the process performed with the addition of additive composition according to the present invention provides a well-grinded cement and allows the cement to be mixed with the nano-sized minerals.

Clinker process according to the present invention is the conventional process utilizing a rotary kiln. Cement raw materials such as calcareous material is firstly grinded into fine powder. Then, they are introduced in the kiln in which said raw materials are mixed to

produce a uniform composition and are heated at 1000°C - 1500°C and preferably 1350°C - 1450°C. Finally, the mixture which can be named as clinker is cooled in the cooler.

Accordingly, cement production method comprises the step of grinding a clinker in the presence of said aqueous composition of polycarboxylate polymer and the mixture of first
5 additive and second additive according to the present invention. Thus, the clinker amount can be reduced in the cements, being this a reduction of specific energy consumption and CO₂ emission is provided.

The amount of grinding aid in the cement is between 100 and 3000 g/ton and preferably between 500 and 2500 g/ton by weight of the cement.

10 The clinker is introduced into a grinding apparatus and grinding is affected until the desired fineness of cement is obtained. Degrees of fineness of the cement comprising the grinding aid of the present invention are between 2000 to 10000 g/cm², preferably between 3000 to 6000 g/cm² and more preferably between 3500 to 4500 g/cm².

The addition of the polycarboxylate polymer composition and/or first and second additive
15 mixture may be performed by spraying onto the clinker. The spraying is performed by a conventional dosing pump.

According to the present invention, the polycarboxylate polymer composition and the mixture of first and second additive can be added separately onto the clinker. In addition, first additive and second additive can be added separately without mixing to the clinker in order to perform
20 the grinding step.

In the grinding of cement production process, gypsum may be added with the clinker. Gypsum is sulfate mineral comprising calcium sulfate dihydrate. Gypsum is added in the grinding process in order to regulate the setting time.

These grinding aid compositions in the cement production method is between 0.1% and 5%
25 and preferably 0.3% to 2.5% by weight of the cement.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

The invention now will be described in particularity with the following illustrative examples; however, the scope of the present invention is not intended to be, and shall not be, limited to the exemplified embodiments below.

EXAMPLES

5 Example 1

Mixture of first additive and second additive

Ingredient	Amount (gr)
Diaminomethanal	10
Diethanolisopropanolamine	12.5
2-ethyldiisopropylamine	12.5
Triethanolamine	5
Glycerol	4
Diethylene glycol	5
Modified fatty alcohol	1
Water	50

Production Method of the Grinding Aid

- mixing urea with water at 40°C,
- 10 - adding diethanolisopropanolamine, 2-ethyldiisopropylamine and surfactant to the mixture of urea, thus obtaining first additive,
- mixing water, triethanolamine, diethylene glycol and glycerol in order to obtain second additive,
- reacting first additive formulation with second additive formulation at 50°,
- 15 - adding the mixture of first and second additive polycarboxylate ester.

Aqueous composition of polycarboxylate polymer

Ingredient	Amount (gr)
Surfactant	50
Polycarboxylate ether polymer (PCE)	500
Water	500

Production method of the aqueous composition of polycarboxylate polymer
- providing polycarboxylate polymer which is synthesized by etherification reaction of carboxylated acrylic acid monomer,

- 5 - diluting polycarboxylate polymer with non-ionized water and non-ionic surfactant in mixer during 40 minutes and at 30°C. (pH is neutral at 7)

Cement examples produced by using mixture of first and second additive and composition of polycarboxylate polymer:

10 Said mixture and composition are introduced together during the grinding of cement.

Cement Example 1

Ingredients (CEM II/A-S 42.5R)	Amount (Percentages)
Clinker (K)	%80
Blast furnace slag (S)	%13
Limestone (L)	%7
Mineral	%5

15 Cement Example 2

Ingredients (CEM II/A-V 42.5R-SR)	Amount (Percentages)
Clinker (K)	%65
Fly ash (V)	%27
Limestone (L)	%8
Mineral	%5

Cement Example 3

Ingredients (CEM I 42.5R)	Amount (Percentages)
Clinker (K)	%95
Mineral	%5

Cement examples 1-3 were compared with same cements produced without using the grinding
20 aid compositions of the present invention and the results in the table below illustrate the effect

of grinding the clinker with the grinding aid compositions according to the present invention.

The tests are performed by using the standard ASTM C150.

	CEM I 42.5R		CEM II/A-S 42.5R		CEM IV/A-V 42.5R-SR	
	%91K+%5 L+%4 M		%78K+%12S+%5L+%4M		%67K+%24V+%5L+%4M	
MPa	R- CEMI	ECO CEM I	R-CEM II	ECO CEM II	R-CEM IV	ECO CEM IV
1st day	20,1	35,7	18,9	25,8	16,3	28,0
2nd day	32,3	43,5	29,6	38,8	27,0	44,5
7th day	44,5	50,4	39,8	45,0	36,5	53,8
28th day	52,3	61,0	51,0	55,1	50,4	65,8
Fineness (g/cm ²)	3699	3681	4194	4356	4210	4304

CLAIMS

1. An aqueous composition for use as grinding aid composition in the production of high-performance cement, comprising at least one polycarboxylate polymer and at least one surfactant.
2. An aqueous composition according to claim 1, wherein the polycarboxylate polymer is polycarboxylate ether or polycarboxylate ester polymer.
3. An aqueous composition according to claim 1 or 2, wherein the molecular weight of polycarboxylate polymer is between 2000 and 50000.
4. An aqueous composition according to any one of claims 1 to 3, wherein the surfactant is non-ionic.
5. An aqueous composition according to any one of claims 1 to 4, wherein the surfactant in an amount of between 0,1% and 0,3% by weight of the composition.
6. An aqueous composition according to any one of claims 1 to 5, obtained by diluting the polycarboxylate polymer with non-ionized water and with a surfactant by mixing during 30 to 40 minutes.
7. Use of the aqueous composition according to any one of claims 1 to 6 in the production of high-performance cement.
8. A method for manufacturing high performance cement comprising the steps of;
 - a) providing a first additive by mixing at least one organic amine and at least one amino alcohol,
 - b) providing a second additive by mixing at least one alkanolamine and at least one glycol,
 - c) mixing first additive with second additive in order to obtain an additive composition,
 - d) providing an aqueous composition of polycarboxylate polymer according to any one of the claims 1 to 5, and

e) introducing together or separately said additive composition and said aqueous composition of polycarboxylate polymer into the grinding of cement.

5 **9.** A method according to claim 8, wherein first additive and second additive further comprise at least one surfactant.

10. A method according to claim 9, wherein the surfactant is non-ionic.

10 **11.** A method according to any one of claims 8 to 10, wherein first additive is provided by mixing at least one organic amine, at least one amino alcohol and sodium gluconate.

15 **12.** A method according to any one of claims 8 to 11, wherein organic amine is selected from the group consisting of 2-ethyldiisopropylamine, diethylamine, triethylamine, dimethylamine pyridine, ethyldiisopropylamine, procaine, dibenzylamine, N-methylmorpholine, dihydroabietylamine, 1-phenamine, methyl-piperidine and combinations thereof.

13. A method according to claim 12, wherein organic amine is 2- ethyldiisopropylamine.

20 **14.** A method according to any one of claims 8 to 13, wherein organic amine is in an amount of between 35% and 50% by weight of the first additive.

25 **15.** A method according to any one of claims 8 to 14, wherein amino alcohol is selected from the group consisting of 1-(N,N-Bis(2-hydroxyethyl)amino)propan-2-ol (Diethanolisopropanolamine, also known as DEIPA), ethanolamine, diethanolamine, triethanolamine, diaminomethanal (urea), N-butyldiethanolamine, M-methyldiethanolamine, N-ethyldiethanolamine, diisopropanolamine, methyl diisopropanolamine, tetrahydroxypropylethylenediamin, trimethylamino ethylethanolamine and combinations thereof.

30

16. A method according to claim 15, wherein amino alcohol is 1-(N,N-Bis(2-hydroxyethyl)amino)propan-2-ol (DEIPA).

17. A method according to any one of claims 8 to 16, wherein glycol is selected from the group consisting of 2-(hydroxyethoxy)ethan-2-ol (diethylene glycol), ethylene glycol, propylene glycol, glycerol (propan-1,2,3-triole), polyethylene glycol, monopropylene glycol and combinations thereof.

5

18. A method according to claim 17, wherein glycol is glycerol and/or diethylene glycol.

19. A method according to any one of claims 8 to 18, wherein the steps c) is occurred at 30 to 65°C.

10

20. A method according to claim 19, wherein the reaction steps c) is occurred at 40 to 60°C.

15

21. A method according to any one of claims 8 to 20, wherein the ratio of first additive to second additive is between 1:0.5 and 4:1.

20

22. A high-performance cement obtained by the method according to any one of claims 8 to 20, wherein the cement comprises 5 to 45% of mineral additives by weight of cement.

23. A high-performance cement according to claim 21, comprising 10 to 35% of mineral additives by weight of cement.

25

24. A high-performance cement according to claims 21 or 22, wherein mineral additives are selected from the group consisting of siliceous fly ash, calcareous fly ash, blast-furnace slag, limestone (calcium carbonate), silicon dioxide (silica sand), natural pozzolan, industrial pozzolan and burnt shale.

30

AMENDED CLAIMS**received by the International Bureau on 12 March 2021 (12.03.2021)**

1. An aqueous grinding aid composition for use in the production of high-performance cement, comprising at least one polycarboxylate polymer and at least one surfactant.
- 5 2. An aqueous grinding aid composition according to claim 1, wherein the polycarboxylate polymer is polycarboxylate ether or polycarboxylate ester polymer.
3. An aqueous grinding aid composition according to claim 1 or 2, wherein the molecular weight of polycarboxylate polymer is between 2000 and 50000.
- 10 4. An aqueous grinding aid composition according to any one of claims 1 to 3, wherein the surfactant is non-ionic.
5. An aqueous grinding aid composition according to any one of claims 1 to 4, wherein
15 the surfactant in an amount of between 0,1% and 0,3% by weight of the composition.
6. An aqueous grinding aid composition according to any one of claims 1 to 5, obtained by diluting the polycarboxylate polymer with non-ionized water and with a surfactant by mixing during 30 to 40 minutes.
- 20 7. Use of the aqueous grinding aid composition according to any one of claims 1 to 6 in the production of high-performance cement.
8. A method for manufacturing high performance cement comprising the steps of;
25 a) providing a first additive by mixing at least one organic amine and at least one amino alcohol,
b) providing a second additive by mixing at least one alkanolamine and at least one glycol,
c) mixing first additive with second additive in order to obtain an additive
30 composition,
d) providing an aqueous composition of polycarboxylate polymer according to any one of the claims 1 to 5, and

e) introducing together or separately said additive composition and said aqueous composition of polycarboxylate polymer into the grinding of cement.

9. A method according to claim 8, wherein first additive and second additive further
5 comprise at least one surfactant.

10. A method according to claim 9, wherein the surfactant is non-ionic.

11. A method according to any one of claims 8 to 10, wherein first additive is provided by
10 mixing at least one organic amine, at least one amino alcohol and sodium gluconate.

12. A method according to any one of claims 8 to 11, wherein organic amine is selected
from the group consisting of 2-ethyldiisopropylamine, diethylamine, triethylamine,
dimethylamine pyridine, ethyldiisopropylamine, procaine, dibenzylamine, N-
15 methylmorpholine, dihydroabietylamine, 1-phenamine, methyl-piperidine and
combinations thereof.

13. A method according to claim 12, wherein organic amine is 2- ethyldiisopropylamine.

14. A method according to any one of claims 8 to 13, wherein organic amine is in an
20 amount of between 35% and 50% by weight of the first additive.

15. A method according to any one of claims 8 to 14, wherein amino alcohol is selected
from the group consisting of 1-(N,N-Bis(2-hydroxyethyl)amino)propan-2-ol
25 (Diethanolisopropanolamine, also known as DEIPA), ethanolamine, diethanolamine,
triethanolamine, diaminomethanal (urea), N-butyldiethanolamine, M-
methyldiethanolamine, N-ethyldiethanolamine, diisopropanolamine, methyl
diisopropanolamine, tetrahydroxypropylethylenediamin, trimethylamino
ethylethanolamine and combinations thereof.

16. A method according to claim 15, wherein amino alcohol is 1-(N,N-Bis(2-
30 hydroxyethyl)amino)propan-2-ol (DEIPA).

17. A method according to any one of claims 8 to 16, wherein glycol is selected from the group consisting of 2-(hydroxyethoxy)ethan-2-ol (diethylene glycol), ethylene glycol, propylene glycol, glycerol (propan-1,2,3-triole), polyethylene glycol, monopropylene glycol and combinations thereof.

5

18. A method according to claim 17, wherein glycol is glycerol and/or diethylene glycol.

19. A method according to any one of claims 8 to 18, wherein the steps c) is occurred at 30 to 65°C.

10

20. A method according to claim 19, wherein the reaction steps c) is occurred at 40 to 60°C.

15

21. A method according to any one of claims 8 to 20, wherein the ratio of first additive to second additive is between 1:0.5 and 4:1.

22. A high-performance cement obtained by the method according to any one of claims 8 to 20, wherein the cement comprises 5 to 45% of mineral additives by weight of cement.

20

23. A high-performance cement according to claim 21, comprising 10 to 35% of mineral additives by weight of cement.

25

24. A high-performance cement according to claims 21 or 22, wherein mineral additives are selected from the group consisting of siliceous fly ash, calcareous fly ash, blast-furnace slag, limestone (calcium carbonate), silicon dioxide (silica sand), natural pozzolan, industrial pozzolan and burnt shale.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/TR2019/050945

A. CLASSIFICATION OF SUBJECT MATTER

C04B 24/00 (2006.01)i; C04B 28/28 (2006.01)i

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)

C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Turkpatent Database

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI Data, EPO Abstract and Fulltext Databases

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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