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QUICK SETTING CONCRETE COMPOSITIONS FOR USE AS LINING CONSTRUCTION
CONCRETE

The invention relates to compositions and methods of manufacturing and applying quick setting concrete. The concrete is capable of retaining fluidity for a long period of time and then rapidly setting.

The quick setting compositions of this invention are particularly applicable in lining construction.

Lining construction is a process whereby concrete is applied to a surface (e.g. of a tunnel or underground cavern). There are two major types of lining construction processes, as follows:

1. Shotcreting.

This can be carried out using a dry mix concrete (the dry mix system) or a wet mix concrete (the wet mix system).

a) The dry mix system.

The dry mix system is one in which dry mixed concrete is pneumatically conveyed through a delivery hose and is applied by projecting it out from the nozzle under pressure; water and a quick setting agent being added, upstream of the nozzle just prior to passage through the nozzle. With this system it is difficult to control the quantity of water added and therefore to control the water-cement ratio (hereinafter referred to as the W/C ratio). Further a lot of dust is generated and this is a drawback. Alternatively the quick setting agent can be added at the point of mixing instead of vicinal to the nozzle.

b) The wet mix system

The wet mix system is a system in which the concrete is mixed in the presence of water and is pneumatically conveyed through a delivery hose to a nozzle and is then projected out of the nozzle; a quick setting agent being added upstream of the nozzle just prior to passage through the nozzle. There are also examples of this system where the concrete can be pumped, rather than pneumatically conveyed, to a point midway between the point of mixing and the nozzle in the delivery hose followed by pneumatic conveying between this midpoint and nozzle. The system allows good control of W/C ratio and generates little dust.

2. Press-on method

This is also known as pressure bonding. The concrete is mixed, and then pumped (not pneumatically conveyed) to a nozzle through a hose, with the quick setting agent being added upstream of the nozzle just prior to passage through the nozzle. The concrete is then poured into a form at an excavated surface. The concrete is very fluid (about 18 cms in terms of slump) after pouring into the form until immediately before hardening, that is to say for several minutes after adding of a quick setting agent. This long setting time can be a disadvantage because, in order to increase efficiency, one wants to be able to remove the sheaths of the form as quickly as possible for the next job and before one can do this, the concrete has to harden to least a compressive strength of 1 kg/cm^2 in 3 to 5 minutes.

According to the invention, there is provided a cementitious composition for use e.g., in lining construction comprising;

- a) cement and preferably aggregate (hereinafter referred to as component a)
- b) an admixture containing a polycarboxylate copolymer (the admixture hereinafter being referred to as component b); and
- c) a quick setting agent or accelerator (herein after referred to

as component c),

the copolymer of component (b) being selected from

d) a water-soluble copolymer of an olefin and an α , β unsaturated dicarboxylic acid.

e) a water-soluble copolymer of an ester of a polyethylene glycol monoaryl ether with maleic acid and monomers capable of copolymerization therewith;

f) a water-soluble copolymer of isobutylene, styrene and maleic acid;

g) a water-soluble copolymer of isobutylene, acrylic acid ester and maleic acid;

h) a water-soluble copolymer of isobutylene, styrene, acrylic acid ester and maleic acid; and

i) a water-soluble salt of a copolymer derived from a polyalkylene glycol monomethacrylic acid or polyalkylene glycol monoacrylic acid ester and acrylic acid or methacrylic acid, optionally together with a monomer capable of being copolymerised therewith.

Further according to the invention, there is provided a process for the production and application of a cementitious composition comprising;

w) mixing components a) and b) together, preferably in the presence of water;

x) transferring the mixture to a nozzle for expelling the mixture;

y) introducing component c) upstream of the nozzle prior to passing the mixture through the nozzle; and

z) expelling the mixture through the nozzle, to apply the mixture to a surface to be coated.

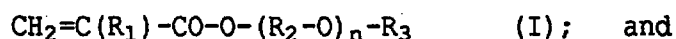
Preferably component a) is concrete. This concrete may have a high proportion of fine aggregate (e.g. sand) in the total quantity of aggregate. Preferably in component a) the cement used is portland cement and the aggregate that is preferably present is fine aggregate, preferably sand having an average particle size of less than 5mm. The aggregate when present may also include coarse aggregate, having a particle size on average of about 15 mm. Preferably the amount of aggregate is 50 to 400% by weight.

Examples of a monomer capable of being copolymerised are esters of C₁₋₂₀ aliphatic alcohols and methacrylic acid or acrylic acid; methacrylic amides or acrylic amides, maleic acid or fumaric acid or mono- or di- esters thereof with C₁₋₂₀ aliphatic alcohols, C₂₋₄ alkylene glycols or poly C₂₋₄ polyalkylene glycols; C₂₋₆ alkenyl acetates (e.g. vinyl acetate and propenyl acetate); aromatic vinyl compound (e.g. styrene, p-methyl styrene, styrene sulphonate) or vinyl halides (e.g. vinyl chloride).

Preferably the copolymer is derived from a poly C₂₋₄ alkylene glycol monomethacrylic acid or poly C₂₋₄ alkylene glycol monoacrylic acid ester and acrylic acid or methacrylic acid, neutralised with alkali.

More preferably the copolymer is derived from

j) a monomer of formula I



k) a monomer of formula II



in which

each R_1 independently is hydrogen or methyl;

R_2 is C_{2-4} alkylene;

R_3 is hydrogen or C_{1-6} alkyl;

n is an integer of from 1 to 100 inclusive; and

X is a monovalent or $1/2$ equivalent of a divalent metal, ammonium or an amine group.

Preferably the copolymer of component b) has a molecular weight of 23,000 to 27,000.

The dosages of component b) used are preferably at least 0.01%, more preferably from 0.01% to 0.5% based on the weight of cement, most preferably in a range of 0.03 to 0.2%. What is known as the "super-fast accelerating effect" becomes larger as dosage is increased, but when dosages in excess of the upper limit of 0.5% are used, a ceiling in effectiveness is reached and thus further addition becomes uneconomical.

"Accelerator" (component c) is as defined p. 106-7, 548 of Concrete Admixtures Handbook by V.S. Ramachandran 1984 Noyes Publications, the contents of which are incorporated herein by reference.

"Quick-setting agent" (component c) is defined in JIS A 0203, "Concrete Terminology," as "a chemical admixture to be used to accelerate the hydration reaction of cement and to markedly shorten time of setting of cement." Typical examples include:

1) inorganic salts (solid or liquid) comprising alkali aluminates and alkali carbonates, or mixtures thereof,

m) cement minerals, and

n) natural minerals (e.g. aluminates, water glass and calcium sulfo-aluminate).

Inorganic salt quick-setting agents include quick-setting agents comprising an aluminate and/or a carbonate. Natural mineral quick-setting agents include calcinated alunite to which carbonates and/or aluminates have been added. Cement mineral quick-setting agents include cementitious materials comprising calcium aluminates such as $\text{CaO} \cdot \text{Al}_2\text{O}_3$, $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$, $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$, $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaF}_2$, and $3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaF}_2$, amorphous forms of these minerals, and may also additionally include amounts of gypsum and/or inorganic salt base quick-setting agents.

Calcinated Alunite is obtained by burning alunite at a very high temperature below its melting point. Alunite (or Alum Stone) is a hydrated basic aluminium and potassium sulphate mineral which has served as a source of potash and of alumina. Alunite is $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ having a hardness of 3.5 to 4 on the Moh's scale.

The amount or dosage of component c) used can be expressed in terms of percentages by weight of the weight of cement in the cementitious composition. These are

i) approximately 2 to 8% (solid or liquid product) in case of inorganic salt quick setting agents,

ii) approximately 5 to 10% in case of cement mineral quick setting agents, and

iii) approximately 4 to 10% in case of natural mineral quick setting agents.

As quick-setting agents are expensive compared with cement, sand and gravel (the principal materials used in concrete, which is the preferred cementitious composition) and the dosage of quick-setting agent required to obtain optimum super-fast accelerating effect is larger than for chemical admixtures in general, it is an important factor in determining the cost of a lining concrete. Accordingly, it is desirable for the required super-fast accelerating effect to be achieved with as small a dosage as possible.

Further, with a wet-mix shotcreting process, the super-fast accelerating effect is smaller than compared with a dry-mix shotcreting process. One of the causes of this is that cement particles are in contact with water well before they come in contact with quick-setting agent and so a thin film of initial hydration product is formed on the surface of the cement particles, and these obstruct contact between cement particles and quick-setting agent. Another cause is that the W/C ratio is higher in case of a wet-mix shotcreting process than for a dry mix shotcreting process. A dry-mix shotcreting process has a W/C ratio of about 0.45:1, whereas for a wet shotcreting process it is 0.55:1 or higher. The quicksetting effect is acutely influenced by the W/C ratio with the super-fast accelerating effect diminishing the higher the W/C ratio. In case of a wet-mix process shotcreting system, the consistency of concrete must be made fairly fluid so that it can be transferred smoothly through the delivery hose to the nozzle and therefore, it is unavoidable for W/C ratio to be high. Similarly, the consistency of concrete must also be fluid for a press-on construction method or pressure bonding method in order to allow good pourability when the concrete is poured into forms. In both cases, the quick-setting property is impaired by having a high W/C ratio.

The use of the component b) in concrete to be mixed before the addition of a quick setting agent has succeeded in increasing the super-fast accelerating effect of quick-setting agent in concrete without impairing the fluidity of the concrete that is to be used as lining concrete, where the concrete mixed prior to the later addition

of the quick-setting agent, that is then applied to the excavated surface of a tunnel or underground cavern.

By using a method accordingly to the invention in a wet-mix shotcreting process, both markedly improving the super-fast accelerating property of shotcrete while retaining fluidity of concrete is obtained, and thereby, it is possible for the dosage of quick-setting agent to obtain identical super-fast accelerating effect to be reduced over conventional wet mix shotcreting processes. Further, since the super-fast accelerating property is improved, there is a reduction in rebound of material (rate of material falling off when shotcreted on to a surface) in the shotcreting method which is a very positive economic bonus. Further, in producing concrete linings by the press-on or pressure bonding methods, it is possible to increase working efficiency by shortening the time required for setting after addition of quick-setting agent whilst maintaining fluidity of the concrete. This is of great importance.

The invention will now be illustrated by the following Examples.

Example 1 and 2

The concrete of the Examples is made up in the proportions given in Table to form a lining concrete.

(1) Concrete Ingredients:

(a) Cement:

A blend of "Onoda", "Mitsubishi" and "Sumitomo" (trade marks) brand ordinary portland cements in equal amounts.

(b) Coarse Aggregate:

Ohme graywacke crushed stone (specific gravity 2.64, absorption 0.67%, F.M. = 6.35, maximum size 15 mm)

(c) Fine Aggregate:

A blend of Oi River System pit sand and Chiba pit sand in equal amounts.

(d) Admixture:

a) Polycarboxylic Acid Admixture

Calcium salt of the copolymer of poly C₂₋₄ alkylene glycol monomethacrylic acid ester and methacrylic acid (referred to as "A": manufactured by Nisso Master Builders Co., Ltd.)

b) Lignosulfonate Admixture

Proprietary name: "Pozzolith" (trade mark) No. 8 (referred to as "B": manufactured by Nisso Master Builders Co., Ltd.)

c) Oxycarboxylate Admixture

Sodium gluconate (referred to as "C")

- d) Sulfonated-Naphthalene Formaldehyde-Condensate Admixture
Proprietary name: "Mighty" 150 (referred to as "D":
manufactured by Kao Soap Co., Ltd.)

- e) Sulfonated-Melamine Formaldehyde Condensate Admixture
Proprietary name: NL-4000 (referred to as "E": manufactured
by Nisso Master Builders Co., Ltd.)

- f) Inorganic Salt Powder Quick-Setting Agent
Proprietary name: QP-500 (referred to as "F": manufactured
by Nisso Master Builders Co., Ltd.)

- g) Cement Mineral Quick-Setting Agent
Proprietary name: QP-55 (referred to as "G": manufactured
by Nisso Master Builders Co., Ltd.)

The dosages of admixtures are the standard dosages respectively recommended by the manufacturers and are expressed in terms of percentage by weight of cement.

Table 1 Mix Proportions of Concrete

Test No.	Example No.	Admixture		Quick-setting		Amount of (kg/m ³)			
		Type	Dosage	Type	Dosage	Cement	Water	Fine Aggregate	Coarse Aggregate
1	Example 1	A	0.12	F	3	360	176	1058	705
2	I	-	-	F	3	360	200	1047	698
3	II	B	0.50	F	3	360	176	1058	705
4	III	C	0.20	F	3	360	176	1058	705
5	IV	D	0.45	F	3	360	176	1058	705
6	V	E	0.50	F	3	360	176	1058	705
7	Example 2	A	0.12	G	6	360	176	1058	705
8	VI	-	-	G	6	360	200	1047	698
9	VII	B	0.50	G	6	360	176	1058	705
10	VIII	C	0.20	G	6	360	176	1058	705
11	IX	D	0.45	G	6	360	176	1058	705
12	X	E	0.50	G	6	360	176	1058	705

In the above Table 1, Examples 1 and 2 illustrate the invention and Examples I to X are comparative.

After mixing the cement, water, fine aggregate and coarse aggregate together and admixture A to E if appropriate, the resultant mortar, obtained by separating the mortar portion and coarse aggregate using a 5-mm screen, is left standing for 30 minutes. The quick-setting agent is added and hand-mixed for 20 seconds. The initial time of setting (time required for penetration resistance to reach 35 kg/cm² according to the method of "test for time of setting of concrete" is measured for each mortar. The time of setting is considered here as the time (minutes and seconds) from addition of quick-setting agent.

Test results

The test results when quick-setting agent F is used, are as given in Table 2, and the test results when quick-setting agent G is used, are as given in Table 3.

Table 2

Time of setting Measurement Results (Quick-setting Agent F)

Test No.	Example No.	Time of Setting Initial (min-sec)
1	1	13 min 40 sec
2	I	more than 20 min
3	II	more than 20 min
4	III	more than 20 min
5	IV	more than 20 min
6	V	17 min 20 sec

Table 3

Time of Setting Measurement Results (Quick-Setting Agent G)

Test No.	Example No.	Time of Setting Initial (min-sec)
7	2	less than 1 min
8	VI	3 min 30 sec
9	VII	4 min 20 sec
10	VIII	more than 20 min
11	IX	4 min
12	X	3 min 10 sec

Where the quick setting agent used is F, the mortar made in the absence of any admixture A to E or with any of the other comparative

admixtures B to E, does not reach the initial set within 17 minutes, but by using the polycarboxylate admixture (A), initial set is reached in 13 minutes and 40 seconds.

Where the quick-setting agent used is G, and the polycarboxylate admixture (A), the initial set is reached within 1 minute, whereas none of the other comparative tests show an initial set under 3 minutes. This illustrates that time of setting is greatly shortened using Admixture A rather than Admixtures B to E with the same quick-setting agent

The extent to which the fluidity of concrete (prior to addition of quick-setting) is maintained, is shown.

The materials used in the tests and the mix proportions of concrete are the same as those given in Table 1 for Example 1 and comparative Examples I, IV and V. Further, the admixtures used in these tests are the polycarboxylate admixture (A), the sulfonated-naphthalene formaldehyde condensate admixture (D) and the sulfonated-melamine formaldehyde condensate admixture (E).

After mixing the cement, water, aggregate and admixtures with a tilting mixer, all of the concrete is discharged and slump is measured. The concrete is returned to the mixer, and whilst continuing to rotate the mixer at low speed (2 rpm) for the required length of time. The slumps are measured after 30 minutes and 60 minutes.

Test Results

The test results are given in Table 4.

Table 4
Concrete Slump Loss Test Results

Test No.	Example No. (Table 1)	Admixture		Slump (cm)		
		Type	Dosage	Imme- diate	After 30 min	After 60 min
13	I	A	0.12	13.5	10.0	8.5
14	I	-	-	14.0	9.0	7.5
15	IV	D	0.45	13.5	8.0	6.0
16	V	E	0.50	14.0	6.5	5.0

It can be seen from Table 4 that the slump of the concrete using the polycarboxylate admixture A is not reduced compared with others even after a long period of time has elapsed. In the comparative Example using the admixture E, it can be seen that the time of setting is comparatively fast, but the time-dependent change in slump is great (reaching less than 5 cm after 60 minutes).

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CLAIMS

1. A cementitious composition comprising

a) cement (hereinafter referred to as component a);

b) an admixture containing a polycarboxylate copolymer (the admixture hereinafter referred to as component b); and

c) a quick setting agent or accelerator (hereinafter referred to as component c),

the copolymer of component b) being selected from

d) a water-soluble copolymer of an olefin and an α , β unsaturated dicarboxylic acid;

e) a water-soluble copolymer of an ester of a polyethylene glycol monoaryl ether with maleic acid and monomer capable of copolymerization therewith;

f) a water-soluble copolymer of isobutylene, styrene and maleic acid;

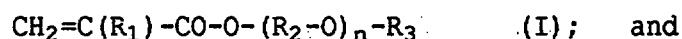
g) a water-soluble copolymer of isobutylene, acrylic acid ester and maleic acid;

h) a water-soluble copolymer of isobutylene, styrene, acrylic acid ester and maleic acid; and

i) a water-soluble salt of a copolymer derived from a polyalkylene glycol monomethacrylic acid or polyalkylene glycol monoacrylic acid ester and acrylic acid or methacrylic acid, optionally together with a monomer capable of being copolymerised therewith.



2. A cementitious composition according to claim 1 in which component a) is concrete.
3. A composition according to any one of the preceding claims in which component b) comprises the copolymer derived from a poly C₂₋₄alkylene glycol monomethacrylic acid ester or poly C₂₋₄alkylene glycol monoacrylic acid ester and acrylic acid or methacrylic acid, neutralized with alkali.
4. A composition according to claim 1 or claim 2 in which component b) comprises a copolymer derived from
 - j) a monomer of formula I



- k) a monomer of formula II



in which

each R₁ independently is hydrogen or methyl;

R₂ is C₂₋₄ alkylene;

R₃ is hydrogen or C₁₋₆ alkyl;

n is an integer of from 1 to 100 inclusive; and

X is a monovalent or 1/2 equivalent of a divalent metal, ammonium or an amine group.

5. A composition according to any one of the preceding claims in which the copolymer of component b) has a molecular weight of 23,000 to 27,000.



-18-

6. A composition according to any one of the preceding claims in which the amount of component b) used is at least 0.01% based on the weight of cement.
 7. A composition according to claim 6 in which the amount of component b) used is 0.01 to 0.5%.
 8. A composition according to any one of the preceding claims in which component c) is selected from
 - l) inorganic salts (solid or liquid) comprising alkali aluminates and alkali carbonates, or mixtures thereof,
 - m) cement minerals, and
 - n) natural minerals.
 9. A composition according to any one of the preceding claims in which the amount of component c) used is 2 to 10% based on dry weight of cement.
 10. A process for the production and application of a cementitious composition according to any one of the preceding claims comprising
 - w) mixing components a) and b) together;
 - x) transferring the mixture to a nozzle for expelling the mixture;
 - y) introducing component c) upstream of the nozzle prior to passing the mixture through the nozzle; and
 - z) expelling the mixture through the nozzle, to apply the mixture to a surface to be coated.
 11. A cementitious composition substantially as herein described with reference to Examples 1 and 2.
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