Cement Additive

This invention relates to a cement additive and more particularly, to a cement additive used to improve the fluidity and appearance of strength of cement slurry, cement paste, mortar and concrete.

Various cement additives comprising polycarboxylic acid type copolymers have been proposed for enhancing the fluidity and flowability of concrete. While this works well for ordinary concretes, it is not so effective when high strength and high durability are required, as such copolymers tend to entrain an excess of air and retard setting.

In relation to pre-formed concrete products, it is strongly desired to decrease the total time spent in a form and to prevent defects when the form is removed. For such products, good appearance is also highly desirable, when the form is removed after steam curing. Various polycarboxylate materials to achieve this have been proposed, but none have been entirely satisfactory, causing such problems as retarded setting and low fluidity.

It has now been found that a cement additive containing a polycarboxylic acid type copolymer and a polyalkylene glycol derivative having a specific molecular structure can alleviate and sometimes completely remove all the above-mentioned problems, by having a high dispersing ability for various concretes, improving and retaining the fluidity of concrete, and also making it possible to increase the strength of pre-formed concrete, such that form removal after steam curing can be carried out relatively early, giving a product with low aeration.

The invention therefore provides a cement additive containing a polycarboxylic acid type copolymer and/or the salts thereof and a polyalkylene glycol derivative, said polycarboxylic acid type copolymer contains at least one species of copolymer, the monomers of which copolymer comprise at least an unsaturated polyalkylene glycol type monomer (A) and an unsaturated mono- or dicarboxylic acid type monomer (B).

The invention also relates to a cement additive, wherein the polycarboxylic acid type copolymers are copolymers which additionally include as monomer components an

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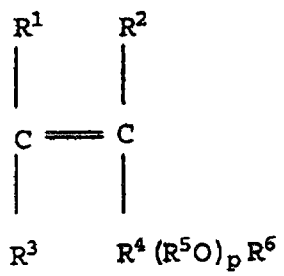
unsaturated polyalkylene glycol ester type monomer (C) and/or a monomer (D) polymerizable with the above-mentioned monomers (A) and (B), or with the monomers (A), (B) and (C).

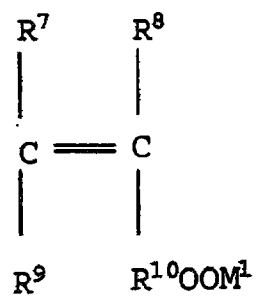
The invention further relates to the above-mentioned cement additive, wherein the monomer (A) is a compound according to the general formula (1):



(1)

wherein R^1, R^2 and R^3 are each independently hydrogen or methyl, provided that not all are methyl; R^4 is $-CH_2O-$, $-(CH_2)_2O-$, $-C(CH_3)_2O-$ or $-O-$; the total carbon number of R^1, R^2, R^3 and R^4 is 3; R^5O is one or more species of C_2-C_4 oxyalkylene groups, and in the case of two or more species may be block or random; R^6 is hydrogen or a C_1-C_{22} alkyl, phenyl or C_1-C_{18} alkylphenyl group; p is an integer from on average 1 to 100;

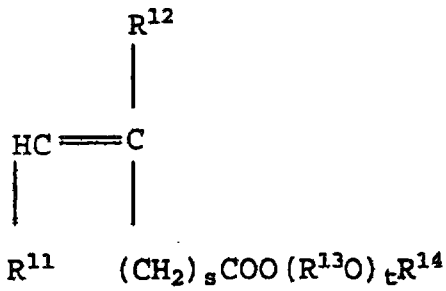
the monomer (B) is a compound according to the general formula (2):



(2)

wherein R^7 and R^8 are each independently hydrogen or methyl; R^9 is hydrogen, methyl or $-(CH_2)_qCOOM^2$; R^{10} is $-(CH2)_r-$; q and r are each independently an integer from 0 to 2; M^1 and M^2 are a monovalent metal, a divalent metal, ammonium or an organic amine;

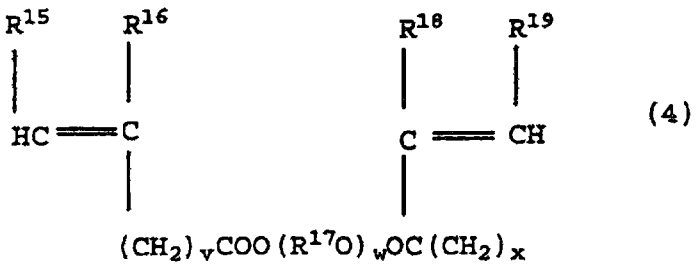
the monomer (C) is a compound according to the general formula (3):



(3)

wherein R^{11} and R^{12} are each independently hydrogen, methyl or $(CH_2)_uCOOM^3$, u is an integer from 0 to 2, M^3 is a monovalent metal, a divalent metal, ammonium or an organic amine; $R^{13}O$ is one or more species of C_1-C_4 oxyalkylene groups, and in the case of two or more species may be block or random; R^{14} is hydrogen or a C_1-C_{22} alkyl, phenyl or C_1-C_{22} alkylphenyl group; s is an integer from 0 to 2; t is an integer an average from 1 to 300; and

the monomer (D) is a compound according to the general formula (4):



(4)

wherein R^{15}, R^{16}, R^{18} and R^{19} are each independently hydrogen or methyl, provided that not all are methyl; $R^{17}O$ is one or more species of C_2-C_4 oxyalkylene groups, and in the case of two or more species may be block or random; w is an integer an average from 1 to 300; v and x are each independently an integer from 0 to 2.

The invention also relates to the abovementioned cement additive, wherein the composition ratios of the monomers (A) and (B) in the polycarboxylic acid-type copolymers are 30-100 mole % based on the total mole amount of the monomers, and the average molecular weight of said polycarboxylic acid-type copolymer is from 3,000-

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100,000 (all molecular weights (MW) referred to herein were measured by gel permeation chromatography with polyethylene glycol as standard).

The invention also relates to the abovementioned cement additive, wherein the average molecular weight of the polyalkylene glycol derivatives is from 1,000-100,000, in which the alkylene is one or more C_2-C_4 species, and the terminal groups of the polyalkylene glycol is hydrogen or a C_1-C_{18} alkyl or phenyl group.

Further, the invention relates to the abovementioned cement additive containing 100 weight parts of the polycarboxylic acid type copolymers and 5-50 weight parts of the polyalkylene glycol derivatives.

Also, the invention relates to the abovementioned cement additive, wherein the amount of the polycarboxylic acid type copolymers added to cement is 0.05-1.0 % by weight based on the weight of cement, and the amount of the polyalkylene glycol derivatives added to cement is 0.0025-0.5 % by weight based on the weight of cement.

Further, the invention relates to use of the abovementioned cement additive in high strength concrete.

The invention also relates to the use of the abovementioned cement additive in the formation of pre-formed concrete articles by steam curing.

The invention further provides a method of preparation of a high-strength concrete mix, comprising the incorporation in the mix of a cement additive as hereinabove described.

The invention further provides a method of preparation of a concrete mix adapted to be used for the manufacture of articles by steam curing, comprising the incorporation in the mix of a cement additive as hereinabove described.

In a cement additive according to the invention, the monomers (A) are typically compounds according to the abovementioned general formula (1), more specifically, the

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compounds in which 1-100 mole of an alkylene oxide is added to an unsaturated alcohol such as 3-methyl-2-buten-1-ol, 3-methyl-3-buten-1-ol, 2-methyl-3-buten-2-ol. One or more species of unsaturated alcohol may be used.

Examples of monomers (B) include compounds according to general formula (2), more specifically, for example, acrylic acid, methacrylic acid, crotonic acid, maleic acid, fumaric acid, itaconic acid and citraconic acid. One or more species of these may be used.

Monomers (C) are typically compounds according to general formula (3). Specific examples include unsaturated polyalkylene glycol monoester type monomers such as polyethylene glycol monoesters, polypropylene oxide monoesters, monoesters of polyethylene glycol/polypropylene oxide copolymers, derivatives in which a terminal hydrogen of these glycols is etherified, and the like, such as triethylene glycol monoacrylate, polyethylene glycol (MW 200) monoacrylate, polyethylene glycol (MW 400) monoacrylate, polyethylene glycol (MW 600) monoacrylate, polyethylene glycol (MW 1000) monoacrylate, polyethylene glycol (MW 2000) monoacrylate, polyethylene glycol (MW 4000) monoacrylate, polyethylene glycol (MW 6000) monoacrylate, triethylene glycol monomethacrylate, polyethylene glycol (MW 200) monomethacrylate, polyethylene glycol (MW 400) monomethacrylate, polyethylene glycol (MW 600) monomethacrylate, polyethylene glycol (MW 1000) monomethacrylate, polyethylene glycol (MW 2000) monomethacrylate, polyethylene glycol (MW 4000) monomethacrylate and polyethylene glycol (MW 6000) monomethacrylate, and one or more species of these may be used.

The monomers (D) are typically compounds according to general formula (4), specific examples including unsaturated polyalkylene glycol diester type monomers and/or styrene, styrenesulfonic acid and/or the salts thereof, acrylic acid alkyl esters (alkyl of C_{22} maximum), methacrylic acid alkyl ester (alkyl of C_{22} maximum), maleic anhydride, maleic acid monoesters (alkyl of C_{22} maximum), and/or alkylene glycol of C_3 maximum and 1-300 alkylene glycol units, maleic acid diester (alkyl of C_{22} maximum and /or alkylene glycol of C_3 maximum and 1-300 alkylene glycol units, vinyl acetate, acrylamide and acrylamide methylpropansulfonic acid and/or the salts thereof.

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Specific examples include styrene, styrenesulfonic acid and/or the salts thereof, acrylic acid methyl ester, acrylic acid ethyl ester, acrylic acid butyl ester, methacrylic acid methyl ester, methacrylic acid ethyl ester, methacrylic acid butyl ester, maleic anhydride, maleic acid methyl monoester, maleic acid ethyl monoester, maleic acid methyl diester, maleic acid ethyl diester, vinyl acetate, acrylamide, acrylamide methylpropansulfonic acid and/or the salts thereof, methallyl sulfonic acid and/or the salts thereof. One or more species of these may be used.

Specific non-limiting examples of polycarboxylic acid type copolymers are those described in JP, A, H5-306152, JP, A, H6-211949, JP, A, H9-286647 and JP, A, H10-236858.

The composition ratio of the monomers (A) and (B) in the polycarboxylic acid type copolymers in the invention to total amount of the monomers is preferably 30-100 mole %, and the average molecular weight is preferably 3,000-100,000.

In the polyalkylene glycol derivatives of the invention, the average molecular weight is 1,000-150,000, preferably 1,000-100,000, more preferably 4,000-50,000, the alkylene is one or more C_2-C_4 species, and it may be block or random in the case of 2 or more species, the terminal groups of polyalkylene glycol are hydrogen, C_{18} maximum alkyl or phenyl groups.

In a cement additive of the invention, the preferred proportions are 100 weight parts of polycarboxylic acid type copolymers and 5-50 weight parts of polyalkylene glycol derivatives.

A cement additive of the invention is preferably used in such a quantity that polycarboxylic acid type copolymers are present in the proportion 0,05-1.0 % by weight based on cement weight and polyalkylene glycol derivatives are present in the proportion 0.0025-0.5 % by weight based on cement weight. However, the amount of the cement additive according to the invention to be used can be appropriately determined according to a cement composition used, it basically being the amount which is necessary to attain the desired strength development and improved time to form removal after steam curing,

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and it is possible that suitable proportions outside these limits may be found.

A cement additive according to the invention may be used for stiff consistency concrete, plastic concrete, high fluidity concrete, high strength concrete, cement paste as generally used, mortar, grout, concrete and the like, although the beneficial effects of the invention are most noticeable in high strength concrete in which the water/cement ratio is low.

A cement additive according to the invention may be mixed, if desired, with other additives to expand its versatility. Typical examples of other additives are conventional water-reducing agents (lignosulfonate, oxycarboxylate, polyalkylsulfonate, polycarboxylate), air content-regulating agents, drying shrinkage reducing agents, accelerators, retarders, foaming agents, anti-foaming agents, anti-rust agents, set acceleration agents, high early-strengthening agents, efflorescence-inhibiting agents, bleeding inhibitors, pumping aids, and water-soluble polymers.

A cement additive according to the invention exhibits a high dispersing ability of a degree never obtained by use only of polycarboxylic acid-type copolymers to various concretes such as ordinary concrete, high strength concrete and steam curing concrete. Without restricting the scope of the invention in any way, it is believed that this is the result of a synergistic effect of the polycarboxylic acid type copolymers and the polyalkylene glycol derivatives. It both enhances the fluidity of concrete and maintains this fluidity, thereby making it possible to increase the strength development and decrease the time for form removal after steam curing. The latter is particularly valuable in that it permits economies such as the reduction of time spent in a form used and the reduction of defects in concrete products manufactured in a concrete factory.

The invention is now further illustrated by the following non-limiting examples wherein are used the cement additives containing polycarboxylic acid type copolymers and polyalkylene glycol derivatives according to the invention.

Examples

The compositions of the polycarboxylic acid type copolymers in the cement

additives used in the examples and in the comparative examples are shown in Table 1. Said polycarboxylic acid type copolymers can be obtained by known polymerization methods described in, for example, JP, A, H5-306152, JP, A, H6-211949, JP, A, H9-286647 and JP, A, H10-236858. The polyalkylene glycol derivatives in the cement additives used in the examples and in the comparative examples are also shown in Table 2.

In order to illustrate the effect of these cement additives, the concrete compositions (shown in Table 3) are designed to have slump of 18.5±1 cm and air content 4.5%. The total quantity of materials in each case is 80 litres, and all the materials are added to a 100 litre pan-type forced mixing mixer, and mixed for 120 sec. to give the concrete compositions. The concrete compositions thus obtained are measured for slump , air content, setting time and compressive strength. Further, the compressive strength in the case of accelerating the appearance of strength by steam curing was measured.

1) Slump: measured according to JIS A 1101,

2) Air content: measured according to JIS A 1128,

3) Setting time: measured according to JIS A 6204 Supplement 1,

4) Compressive strength

Ordinary curing: measured according to JIS A 1108,

Steam curing: the sample is pre-cured at 20°C for 2 hr, then warmed to 65°C in 2 hrs 30 min, kept at 65°C for 4 hrs. After allowing to cool to 20°C over 4 hrs, the testing is carried out according to JIS A 1108.

(Materials used)

Mixing water: tap water,

Cement: ordinary portland cement (density 3.16 g/cm^3),

Fine aggregate: Oi River pit sand (specific gravity 2.59, FM=2.74),

Coarse aggregate: Oume crushed stone (specific gravity 2.65, MS[median size?]=20mm).

The results of the above measurement are shown in Table 4. In the Table, the examples 1-13 and the comparative examples 1-4 are for the results obtained from the ordinary cement, and the examples 14, 15 and the comparative examples 5, 6 are those

obtained from the high strength concrete.

The examples 1-7 show the cases in which the type of the polycarboxylic acid type copolymers is changed, and the examples 1 and 8-13 are the cases in which the type of the polyalkylene glycol derivatives is changed.

The comparative examples 1 and 5 show the cases in which a polyalkylene glycol derivative is not used, and the comparative examples 2-4 and 6 are the cases in which compounds other than the polycarboxylic acid type copolymers in the invention are used.

As is evident from the comparison between the comparative example 1 and the examples 1-13, and from the comparison between the comparative example 5 and the examples 14 and 15, the ordinary concrete and the high strength concrete, in which the cement additives together with the polyalkylene glycol derivatives of the invention are used, both show a tendency to accelerate setting, whereby the slump values are large (fluidity) and their slump lowering over 60 min is small (high flowability), demonstrating a preferable compressive strength both for ordinary curing and steam curing.

The comparative examples 2-4 and 6 are those in which compounds other than the polycarboxylic acid type copolymers in the invention are used, though in these examples the development of compressive strength is not sufficient, because there is demonstrated a retardation of setting.

Table 1

Type of Polycarboxylic Acid-type copolymer	Type of monomer and composition ratio										Average Molecular Weight
	Monomer (A)		Monomer (B)			Monomer (C)			Monomer (D)		
	Mole ratio (%)	Type	AG No.	Mole ratio (%)	Type	Mole ratio (%)	Type	AG No.	Mole ratio (%)	Type	
PCA-1	1.5	Polyethylene glycol mono-vinyl ether	50	1	Maleic acid	-	-	-	-	-	20000
PCA-2	1.5	2-Methyl 2-propen-1-ol alkylene oxide adduct	50	1	Maleic acid	-	-	-	-	-	30000
PCA-3	1.5	Polyethylene glycol mono-vinyl ether	50	1	Maleic acid	0.2	Polyethylene glycol maleic acid ester	75	-	-	35000
PCA-4	1.5	Polyethylene glycol polypropylene glycol allyl ether	50	1	Maleic acid	0.3	Polyethylene glycol maleic acid ester	25	0.1	Maleic anhydride	24000
PCA-5	1.5	Polyethylene glycol allyl ether	12	1	Maleic acid	-	-	-	0.2	Styrene	32000
PCA-6	1.5	2-Methyl 2-propen-1-ol alkylene oxide adduct	25	1	Acrylic acid	-	-	-	0.2	Acrylamide methylpropan sulfonic acid	27000
PCA-7	1.5	2-Methyl 2-propen-1-ol alkylene oxide adduct	75	1	Acrylic acid	-	-	-	0.2	Polyethylene glycol dimethacrylic acid ester	75000
P-1	1	2-Methyl 2-propen-1-ol alkylene oxide adduct	50	1	Maleic acid	2	Polyethylene glycol maleic acid ester	25	-	-	30000
P-2	1	Polyalkylene glycol monovinyl ether	50	1	Maleic acid	2	Polyethylene glycol methacrylic acid ester	25	-	-	28000
P-3	-	-	-	1	Acrylic acid	2	Polyethylene glycol methacrylic acid ester	100	-	-	28000

Table 2

Sample mark	Component name of polyalkylene glycol	Average molecular weight
PAG-1	Polyethylene glycol	4000
PAG-2	Polyethylene glycol	6000
PAG-3	Polyethylene glycol	10000
PAG-4	Polyethylene glycol	20000
PAG-5	Polyethylene glycol	50000
PAG-6	Polyethylene glycol-polypropylene glycol block polymer	4000
PAG-7	Polyethylene glycol oleic acid ester	5000

Table 3 (Blend)

Type of Concrete	W/C (%)	s/a (%)	Unit amount (Kg/m^3)			
			W	C	S	G
Ordinary Concrete	50	46	160	320	823	993
High-strength concrete	35.6	44	160	450	741	968

Table 4 (Concrete test)

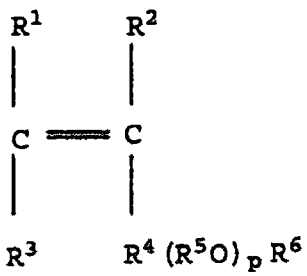
	Type of blend	No.	Polycarboxylic acid type copolymer		PAG		Slump (cm)		Air content (%)		Setting time (min)		Compressive strength (N/mm^2)	
			Type	Amount added (wt%)	Type	Amount added (wt%)	Just after	60 min later	Just after	60 min later	Start	End	Standard curing age 3 days	steam curing age 7 hrs
Example	Ordinary Concrete	1	PCA-1	0.2	PAG-4	0.03	19.0	15.0	4.5	4.5	355	450	25.0	27.6
		2	PCA-2	0.2	PAG-4	0.03	18.5	16.0	4.4	4.4	350	450	25.4	27.9
		3	PCA-3	0.2	PAG-4	0.03	18.0	15.5	4.6	4.5	355	450	25.2	27.6
		4	PCA-4	0.2	PAG-4	0.03	18.5	19.0	4.4	4.5	355	460	24.5	27.1
		5	PCA-5	0.2	PAG-4	0.03	18.0	15.0	4.4	4.3	355	450	25.6	28.3
		6	PCA-6	0.2	PAG-4	0.03	18.0	15.0	4.6	4.5	355	450	25.2	27.4
		7	PCA-7	0.2	PAG-4	0.03	18.5	18.5	4.3	4.4	355	450	24.1	29.2
		8	PCA-1	0.2	PAG-1	0.05	18.0	15.0	4.2	4.3	355	450	25.2	28.4
		9	PCA-1	0.2	PAG-2	0.05	18.0	15.0	4.4	4.5	355	450	25.6	28.3
		10	PCA-1	0.2	PAG-3	0.05	18.5	15.0	4.5	4.6	355	450	25.4	28.3
		11	PCA-1	0.2	PAG-5	0.05	18.0	15.0	4.5	4.3	355	450	25.3	28.3
		12	PCA-1	0.2	PAG-6	0.03	18.5	15.0	4.6	4.4	355	450	26.7	28.4
		13	PCA-1	0.2	PAG-7	0.03	18.5	15.0	4.6	4.5	355	450	26.7	27.1
	High Strength Concrete	14	PCA-1	0.2	PAG-4	0.03	19.0	15.0	4.5	4.5	300	395	36.4	39.1
		15	PCA-2	0.2	PAG-4	0.03	18.5	16.0	4.4	4.4	305	390	36.2	39.0
Comparative Example	Ordinary Concrete	1	PCA-1	0.3	-	-	17.5	6.0	4.4	4.0	380	485	20.4	23.4
		2	P-1	0.2	PAG-4	0.05	18.5	14.5	4.3	5.7	355	450	22.4	23.5
		3	P-2	0.2	PAG-4	0.05	19.0	13.5	4.5	5.9	355	455	22.6	23.8
		4	P-3	0.2	PAG-4	0.05	18.5	14.0	4.5	5.9	380	470	22.7	23.5
	High strength concrete	5	PCA-1	0.3	-	-	13.0	6.0	4.4	4.0	340	495	31.0	35.2
		6	P-3	0.3	PAG-4	0.05	18.5	14.0	4.5	5.9	350	445	31.5	36.0

Claims

1. A cement additive comprising a polycarboxylic acid type copolymer and/or a salt thereof and a polyalkylene glycol derivative, wherein said polycarboxylic acid type copolymer contains at least one species of copolymer derived from at least an unsaturated polyalkylene glycol ether type monomer (A) and an unsaturated mono- or dicarboxylic acid type monomer (B) as its monomer component.

2. A cement additive according to claim 1, wherein the polycarboxylic acid type copolymer is additionally derived from an unsaturated polyalkylene glycol ester type monomer (C) and/or a monomer (D), which is copolymerizable with the above monomers (A) and (B), or with the monomers (A), (B) and (C).

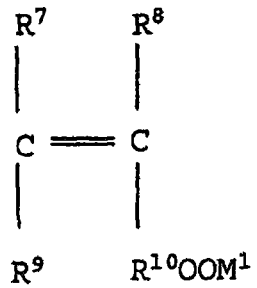
3. A cement additive according to claim 1 or 2, wherein the monomer (A) is a compound according to general formula (1):



(1)

wherein R^1, R^2 and R^3 are each independently hydrogen or methyl, provided that not all are methyl; R^4 is $-CH_2O-$, $-(CH_2)_2O-$, $-C(CH_3)_2O-$ or $-O-$; the total carbon number of R^1, R^2, R^3 and R^4 is 3; R^5O is one or more species of C_2-C_4 oxyalkylene groups, and, in the case of two or more species, may be block or random; R^6 is hydrogen or a C_1-C_{22} alkyl, phenyl or C_1-C_{18} alkylphenyl group; p is an integer from on average 1 to 100,

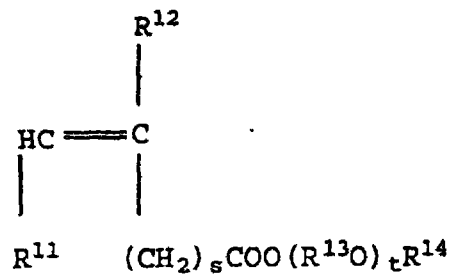
the monomer (B) is a compound according to general formula (2):



(2)

wherein R^7 and R^8 are each independently hydrogen or methyl; R^9 is hydrogen, methyl or -$(CH_2)_qCOOM^2$; R^{10} is -$(CH_2)_r$-; q and r are each independently an integer from 0 to 2; M^1 and M^2 are a monovalent metal, a divalent metal, ammonium or an organic amine;

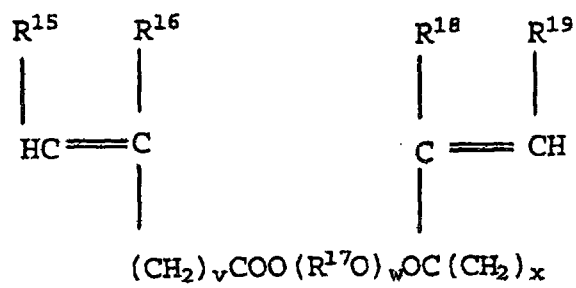
the monomer (C) is a compound according to general formula (3):



(3)

wherein R^{11} and R^{12} are each independently hydrogen, methyl or $(CH_2)_uCOOM^3$, u is an integer from 0 to 2, M^3 is a monovalent metal, a divalent metal, ammonium or an organic amine; $R^{13}O$ is one or more species of C_2-C_4 oxyalkylene groups, and, in the case of two or more species, may be block or random; R^{14} is a C_1-C_{22} hydrogen or an alkyl, phenyl or C_1-C_{22} alkylphenyl group; s is an integer from 0 to 2; t is an integer an average from 1 to 300; and

the monomer (D) is a compound according to the following general formula (4):



(4)

wherein R^{15}, R^{16}, R^{18} and R^{19} are each independently hydrogen or methyl, provided that not all are methyl; $R^{17}O$ is one or more species of C_2-C_4 oxyalkylene groups, and, in the case of two or more species, may be block or random; w is an integer an average from 1 to 300; v and x are each independently an integer from 0 to 2.

4. A cement additive according to any one of claims 1-3, wherein the composition ratios of the monomers (A) and (B) in the polycarboxylic acid type copolymer are 30-100 mole % based on the total mole amount of their monomers, and the average molecular weight of said polycarboxylic acid type copolymer is from 3,000 to 100,000.

5. A cement additive according to any one of claims 1-3, wherein the average molecular weight of the polyalkylene glycol derivative is from 1,000 to 100,000, and in which the alkylene is one or more C_2-C_4 species, and the terminal group of the polyalkylene glycol is hydrogen, a C_1-C_{18} alkyl group or a phenyl group.

6. A cement additive according to any one of claims 1-5, containing 100 weight parts of the polycarboxylic acid type copolymer and 5-50 weight parts of the polyalkylene glycol derivative in the mixing proportion.

7. A cement additive according to any one of claims 1-6, wherein the amount used in a cementitious composition is such that the amount of polycarboxylic acid type copolymer to cement is 0.05-1.0 % by weight based on the weight of cement, and the amount of the polyalkylene glycol derivative to cement is 0.0025-0.5 % by weight based on the weight of cement.

8. A high strength concrete mix, comprising a cement additive according to any one of claims 1-7.

9. A concrete mix for the production of articles by steam curing, comprising a cement additive according to any one of claims 1-7.

10. A method of preparation of a high-strength concrete mix, comprising the incorporation in the mix of a cement additive according to any one of claims 1-7.

11. A method of preparation of a high-strength concrete mix, comprising the incorporation in the mix of a cement additive according to any one of claims 1-7.