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PATENT APPLICATION

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S I N G A P O R E

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ENTITLED

"HYDRAULIC CEMENT SET-ACCELERATING ADMIXTURES
INCORPORATING GLYCOLS"

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**HYDRAULIC CEMENT SET-ACCELERATING ADMIXTURES
INCORPORATING GLYCOLS**

5 This invention relates to improvements in
set-accelerating admixtures for hydraulic cement
compositions such as mortars, grouts and concretes.
More particularly the invention relates to novel
set-accelerating admixtures and methods for
set-acceleration employing the addition of certain low
10 molecular weight glycols, e.g., glycerol and ethylene
glycol.

Set accelerators are used when it is necessary to
work with hydraulic cement compositions at freezing or
15 near-freezing temperatures. The rate of hydration of
Portland cement, for example, is very dependent on
temperature, such that, at lower temperatures, Portland
cement compositions will often harden at a rate slower
than desired unless the hardening process is
20 accelerated. In addition to accelerating the set, it is
desirable to also attain an increase in the rate of
early strength development at normal or low
temperatures. This reduces curing and protection
periods necessary to achieve specified strengths in
25 concrete. Some techniques for accelerating the set are:
increasing the proportion of cement in the mix, heating
the mix, and using chemical admixtures that act on the
components of the mix to increase the rate at which the
cement paste sets.

30 Several chemical set accelerators are well-known.
They include alkali hydroxides, silicates,
fluorosilicates, calcium formate, sodium chloride,



calcium chloride, and calcium nitrate and calcium nitrite.

5 Calcium chloride is widely used because it is easy and inexpensive to produce and its effects on hydraulic cement are predictable and well-documented. However, like sodium chloride, it has the disadvantage of corroding steel. Thus, it can cause the corrosion of steel reinforcing bars in concrete. Other drawbacks of calcium chloride use include reduced compressive
10 strength at later ages, reduced response to air entrainment, and blotching of hardened concrete surfaces (Concrete Admixtures, Dodson: Van Nostrand Reinhold, 1990).

15 It is thus an object of this invention to provide new set-accelerating admixtures which reduce the set time of hydraulic cement compositions at lower temperatures, without inducing or promoting corrosion of steel reinforcement. Further objects of the invention are to provide methods for preparing such cement compositions
20 and to provide methods for reducing the set time of hydraulic cement compositions.

This invention is directed toward new hydraulic cement set-accelerating admixture compositions, to
25 cement compositions containing such admixtures, and to methods for preparing said cement compositions. The admixture compositions comprise a set accelerator component and a C_2 to C_6 glycol component present in an amount effective to increase the set acceleration
30 properties of the set-accelerator component. The invention further relates to a method of making a hydraulic cement composition comprising adding to a cement composition comprising a hydraulic cement binder, a set-accelerating component, and a C_2 to C_6 glycol
35 component in an amount effective to increase



the set-acceleration properties of the set-accelerator component, and to a cement composition comprising a hydraulic cement binder, a set-accelerating component, and a C₂ to C₆ glycol component present in an amount effective to increase the set acceleration properties of the set-accelerator component.

It has been found that admixtures comprising a set-accelerating compound and certain low molecular weight glycols are surprisingly effective in reducing the set time of hydraulic cement compositions. Such admixtures are also found to be quite effective at lower working temperatures, i.e., below about 50°F. It appears that these low molecular weight glycols increase the set-acceleration properties of a set-accelerating compound. Additionally, admixtures of this invention may be formulated in such a way as to produce a composition that will inhibit corrosion in steel reinforcing bars commonly imbedded in cement compositions.

The term "glycol" as used herein is intended to mean two to six carbon, i.e., "C₂ to C₆", aliphatic di- and trihydric alcohols. Glycols suitable for use in the invention are those such as ethylene glycol, propylene glycol, and glycerol. Other compounds meeting the above definition will be apparent to those skilled in the art. Until now these compounds have not been known to have any set-accelerating qualities, i.e., they have been used primarily as grinding aids and set retarders. For this reason these compounds were not seen as having any value as part of a set-accelerating admixture. As such it was surprising to the inventors that a glycol as described herein could be used with a set-accelerating compound to significantly increase the set acceleration of a cement composition over that obtained by the addition of the set accelerator alone to



the cement composition. Thus this invention utilizes the glycol component to give the set acceleration of the cement composition containing the set accelerator a desired "boost."

5 The term "cement composition" as used herein refers to pastes, mortars and concrete compositions comprising a hydraulic cement binder. The above terms are terms of art. Pastes are mixtures composed of a hydraulic cement binder, for example, Portland cement, either alone or in
10 combination with fly ash, silica fume or blast furnace slag, and water; mortars are pastes additionally including fine aggregate, and concretes are mortars additionally including coarse aggregate. Such compositions may additionally include other admixtures
15 such as defoaming agents, air-entraining or detraining agents, set retarders, water reducing agents, superplasticizers, and other components known to those in the art for altering properties of the composition. The cement compositions of this invention are formed by
20 mixing required amounts of certain materials, e.g., a hydraulic cement, water, and fine or coarse aggregate, as may be applicable for the particular cement composition being formed.

 The set-accelerating component may be any compound
25 which, when added to a cement composition (as described above), reduces the amount of time required for the cement composition to harden. For example, an alkali or alkaline earth metal salt which is a salt of an organic or inorganic acid may be employed. Although the
30 following list is not meant to be limiting, examples of these compounds are alkali or alkaline earth metal nitrate, nitrite, and formate; alkali or alkaline earth metal salts of Group VI halogen and pseudohalogen acids, such as alkali or alkaline earth metal chloride,
35 bromide, iodide, thiocyanate, thiosulfate and



perchlorate; and alkali or alkaline earth metal aluminates, silicates, and hydroxides, e.g., sodium hydroxide. Calcium salts are particularly advantageous, especially calcium nitrate, calcium chloride, and calcium formate, and calcium nitrite.

It is also feasible to use a mixture of alkali or alkaline earth metal salts, for example, a mixture of calcium nitrate and calcium nitrite. Any ratio of the salts used may be employed; in a preferred calcium nitrate/calcium nitrite mixture, a range of weight ratios of from about 1:3 to 3:1 may be used. The inventors have found that such an admixture, using a calcium nitrate/calcium nitrite mixture as the set-accelerator component, is beneficial in inhibiting corrosion in steel reinforcing bars commonly imbedded in cement compositions.

If the set-accelerating component and glycol component are added to the cement composition separately, the glycol may be added, generally, in percent solids on solids ("% s/s"), in the range of about 0.05% s/s to 1.0% s/s (based on the weight of hydraulic cement binder in the cement composition), with a preferred range of about 0.1% s/s to 0.75% s/s, such concentrations being generally those which provide the desired boost in acceleration. The set-accelerating component may be added in the usual amounts necessary for set-acceleration, but generally in a range of from about 0.05% s/s to about 4.0% s/s. (Note that through the use of a glycol component of the invention, it is also possible to reduce the amount of set-accelerator component normally required for a certain level of set acceleration, because of the better set-acceleration provided by the combination of the glycol and the set-accelerator.)



However, the inventors find it is preferable to combine the glycol component and the set-accelerating component in desired amounts before addition to a cement composition, so only one composition need be metered out and added to the cement composition. This is a simpler and more precise method than adding each component separately and reduces the opportunity for error in dispensing the correct formulation. If the set-accelerating component and glycol component are to be mixed before addition to a cement composition, the glycol component and the set-accelerating component may be combined in any proportion effective to give the desired results. Generally, the amount of the glycol in the mixture may range from about 0.5 to 40 weight % (based on the combined weight of glycol component and accelerator component), and preferably from about 2 to 30 weight %.

An admixture of the invention should be mixed into a hydraulic cement composition in an amount effective to allow the acceleration desired. The specific amount of the admixture can be readily determined and will depend on the cement composition, the ratio of components of the composition, and the degree of acceleration desired. The admixture is generally added to a cement composition in an amount which, as noted above, provides a glycol concentration of from about 0.05% s/s to 1.0% s/s, preferably from about 0.1% s/s to 0.75% s/s, such concentrations being generally those which provide the desired boost in acceleration.

The admixtures of this invention can be added to cement compositions in any conventional manner familiar to those in the art. The admixture should be substantially uniformly mixed with the cement composition.

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The following examples are given for illustrative purposes only. Unless otherwise indicated, all parts and proportions are by weight.

Example 1

5 An admixture was prepared consisting of calcium nitrate and calcium nitrite, in a 2:1 ratio, in water. The total % solids of the admixture was 42.6%.

Example 2

10 An admixture of the invention was prepared consisting of calcium nitrate, calcium nitrite, and glycerol, in a 2:1:1 ratio (by weight), in water. The total % solids of the admixture was 45%.

Example 3

15 The admixtures prepared in Examples 1 and 2 were each added individually to mortars prepared using a Type I-II Portland cement, sand, and a water to cement ratio of 0.45. A blank mortar, containing no admixture, was also prepared. Each mortar was prepared by combining 4500g of sand, 900g of H₂O, and 2000g of cement in a Hobart mixer until homogeneous. A sufficient amount of the admixture solutions of Examples 1 and 2 was added to provide an admixture solids concentration of 0.5% s/s, and 2.0% s/s, based on the weight of hydraulic cement in the admixture. Set times were measured in accordance with ASTM C403. The test was performed at 55°F.

25 Table 1 presents the data, which demonstrate, at different addition rates, the utility of adding a glycol component of the invention (glycerol), to improve the performance of a set-accelerating compound, in this case
30 a mixture of calcium nitrate and calcium nitrite.



Example 4

5 An admixture of the invention was prepared consisting of calcium nitrate, calcium nitrite and glycerol, in a proportion of 60:16:24 (by weight), in water. The total % solids of the admixture was 45%.

Example 5

10 The admixture prepared in Example 4 was added to mortars prepared using three different Type I-II Portland cements ("Cements 1, 2, and 3"), sand, and a water to cement ratio of 0.45. Blank mortars, containing no admixture, were also prepared with each cement. Each mortar was prepared by combining 4500g of sand, 900g of H₂O, and 2000g of cement in a Hobart mixer until homogeneous. A sufficient amount of the admixture
15 solution of Example 4 was added to provide an admixture solids concentration of 2.5% s/s, based on the weight of hydraulic cement in the admixture. Set times were measured in accordance with ASTM C403. The test was performed at 40°F.

20 Table 2 presents the results, which show the set time performance with the three cement types. The data demonstrate the cold-temperature performance of a set accelerating cement admixture of the invention.

25 The preceding description of the invention has been intended to illustrate rather than limit the invention. The inventors intend that various modifications or changes be made within the scope of the appended claims without departing from the spirit of the invention.



Table 1

<u>Admixture of Example #</u>	<u>Initial Set Time (hr)</u>	<u>Change In Initial Set Time (hr)</u>
blank	11.08	-
1 (at 0.5% s/s)	8.94	2.14
2 (at 0.5% s/s)	7.97	3.11
1 (at 2.0% s/s)	5.05	6.03
2 (at 2.0% s/s)	3.74	7.34

Table 2

<u>Admix. of Example #</u>	<u>Initial Set Time (hr)</u>			
	<u>Cement 1</u>	<u>Cement 2</u>	<u>Cement 3</u>	<u>Avg.</u>
blank	9.50	11.40	10.18	10.36
4	7.57	8.57	8.33	8.16

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CLAIMS

1. An admixture for reducing the set time of a cement composition which contains a hydraulic cement binder, the admixture comprising
 - 5 (a) a set-accelerator component; and
 - (b) a C₂ to C₆ glycol component, present in an amount effective to increase the set acceleration properties of the set-accelerator component.
- 10 2. An admixture according to claim 1 wherein the amount of glycol component in the admixture is from 0.05 to 40 weight %, based on the combined weight of glycol component and accelerator component in the admixture.
- 15 3. An admixture according to claim 1 wherein the amount of glycol component in the admixture is from 2.0 to 30 weight %, based on the combined weight of glycol component and accelerator component in the admixture.
- 20 4. An admixture according to any one of claims 1 to 3 wherein the set-accelerating component is an alkali or alkaline earth metal salt of an organic or inorganic acid, or a mixture thereof.
5. An admixture according to claim 4 wherein the set-accelerating component is calcium nitrate, calcium nitrite, or a mixture thereof.
- 25 6. A cement composition comprising a hydraulic cement binder and
 - (a) a set-accelerator component; and



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- (b) a C_2 to C_6 glycol component in an amount effective to increase the set acceleration properties of the set-accelerator component.

7. A composition according to claim 6 wherein the amount of glycol component is from 0.05% s/s to 1.0% s/s, based on the amount of hydraulic cement binder in the composition.

8. A composition according to claim 6 wherein the amount of glycol component is from 0.1% s/s to 0.75% s/s, based on the weight of hydraulic cement binder in the composition.

9. A composition according to claim 6, 7 or 8 wherein the set-accelerator and/or the glycol are as defined in any one of claims 2 to 5.

10. A method for making a cement composition according to any one of claims 6 to 9 which contains a hydraulic cement binder, said method comprising adding to said cement composition

(a) a set-accelerator component; and

(b) a C_2 to C_6 glycol component, in an amount effective to increase the set acceleration properties of the set-accelerator component.

11. A method according to claim 10 wherein the set-accelerating component and glycol are as defined in any one of claims 2 to 5.

12. A corrosion-inhibiting, set-accelerating admixture for reducing the set time of a cement composition





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which contains a hydraulic cement binder, said admixture comprising

- 5 (a) a set-accelerator component comprising a mixture of alkaline earth metal nitrate and alkaline earth metal nitrite; and
- (b) a C₂ to C₆ glycol component, present in an amount effective to increase the set acceleration properties of the set-accelerator component.

10 13. An admixture according to claim 12 wherein the glycol component is glycerol and the set-accelerating component is a mixture of calcium nitrate and calcium nitrite.

14. A product comprising
- 15 (a) a set-accelerator component comprising a mixture of alkaline earth metal nitrate and alkaline earth metal nitrite; and
- (b) a C₂ to C₆ glycol component, present in an amount effective to increase the set
- 20 acceleration properties of the set-accelerator component;

for simultaneous, separate or sequential use in reducing the set time of a cement composition which contains a hydraulic cement binder.



ABSTRACT

5 New set-accelerating admixtures for hydraulic cement compositions are disclosed. These admixtures incorporate known set accelerators and certain low molecular weight glycols, e.g., glycerol and ethylene glycol, are found to be surprisingly effective in decreasing the initial set time of hydraulic cements, mortars, and concretes, and are advantageous as reduced-temperature set-accelerators.

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HYDRAULIC CEMENT SET ACCELERATING ADMIXTURES INCORPORATING GLYCOS

This invention relates to improvements in set-accelerating admixtures for hydraulic cement compositions such as mortars, grouts and concretes. More particularly the invention relates to novel set-accelerating admixtures and methods for set-acceleration employing the addition of certain low molecular weight glycols, e.g., glycerol and ethylene glycol, to use of glycols to increase the set acceleration properties of a set-accelerator.

The invention so relates >

Set accelerators are used when it is necessary to work with hydraulic cement compositions at freezing or near-freezing temperatures. The rate of hydration of Portland cement, for example, is very dependent on temperature, such that, at lower temperatures, Portland cement compositions will often harden at a rate slower than desired unless the hardening process is accelerated. In addition to accelerating the set, it is desirable to also attain an increase in the rate of early strength development at normal or low temperatures. This reduces curing and protection periods necessary to achieve specified strengths in concrete. Some techniques for accelerating the set are: increasing the proportion of cement in the mix, heating the mix, and using chemical admixtures that act on the components of the mix to increase the rate at which the cement paste sets.

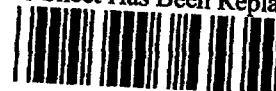
Several chemical set accelerators are well-known. They include alkali hydroxides, silicates, fluorosilicates, calcium formate, sodium chloride,

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calcium chloride, and calcium nitrate and calcium nitrite.

Calcium chloride is widely used because it is easy and inexpensive to produce and its effects on hydraulic cement are predictable and well-documented. However, like
5 sodium chloride, it has the disadvantage of corroding steel. Thus, it can cause the corrosion of steel reinforcing bars in concrete. Other drawbacks of calcium chloride use include reduced compressive strength at later ages, reduced response to air entrainment, and blotching of
10 hardened concrete surfaces (Concrete Admixtures, Dodson: Van Nostrand Reinhold, 1990).

DE-A-3,636,659, WO-A-89/0827 and FR-A-2,227,240 disclose cementitious compositions which may comprise set-acceleration and glycol additives.

15 It is thus an object of this invention to provide new set-accelerating admixtures which reduce the set time of hydraulic cement compositions at lower temperatures, without inducing or promoting corrosion of steel reinforcement. Further objects of the invention are to
20 provide methods for preparing such cement compositions and to provide methods for reducing the set time of hydraulic cement compositions.

The present invention provides a corrosion-inhibiting, set-acceleration admixture for reducing the set
25 time of a cement composition which contains a hydraulic cement binder, the admixture comprising

- (a) a set-accelerator component comprising a mixture of alkaline earth metal nitrate and alkaline earth metal nitrite; and
- 30 (b) a C₂ to C₆ glycol component, present in an amount effective to increase the set acceleration properties of the set-accelerator component.

The invention further provides a cement composition
35 comprising a hydraulic cement binder and

- (a) a set-accelerator component comprising a mixture of alkaline earth metal nitrate and

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alkaline earth metal nitrite; and

- (b) a C₂ to C₆ glycol component in an amount effective to increase the set acceleration properties of the set-accelerator component;

5 and wherein (a) and (b) are present in amounts effective to inhibit corrosion.

The invention also provides a method for making a cement composition of the invention which contains a hydraulic cement binder, said method comprising adding to
10 said cement composition

- (a) a set-accelerator component comprising a mixture of alkaline earth metal nitrate and alkaline earth metal nitrite, and

15 (b) a C₂ to C₆ glycol component, in an amount effective to increase the set acceleration properties of the set-accelerator component; and wherein (a) and (b) are added in amounts effective to inhibit corrosion.

The invention yet further provides a product
20 comprising

- (a) a set-accelerator component comprising a mixture of alkaline earth metal nitrate and alkaline earth metal nitrite; and

25 (b) a C₂ to C₆ glycol component, present in an amount effective to increase the set acceleration properties of the set-accelerator component;

30 for simultaneous, separate or sequential use as a corrosion-inhibiting, set-accelerating admixture in reducing the set time of a cement composition which contains a hydraulic cement binder.

The invention still further provides use of a C₂ to C₆ glycol component to increase the set acceleration properties of a set-accelerator component ^{< , >} in an admixture
35 for reducing the set time of a cement composition which contains a hydraulic cement binder

< comprising a mixture of alkaline earth metal nitrate and alkaline earth metal nitrite > This is the replacement sheet

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~~the set-acceleration properties of the set-accelerator component, and to a cement composition comprising a hydraulic cement binder, a set-accelerating component, and a C₂ to C₆ glycol component present in an amount effective to increase the set acceleration properties of the set-accelerator component.~~

It has been found that admixtures comprising a set-accelerating compound and certain low molecular weight glycols are surprisingly effective in reducing the set time of hydraulic cement compositions. Such admixtures are also found to be quite effective at lower working temperatures, i.e., below about ^{10°C}(50°F). It appears that these low molecular weight glycols increase the set-acceleration properties of a set-accelerating compound. Additionally, admixtures of this invention may be formulated in such a way as to produce a composition that will inhibit corrosion in steel reinforcing bars commonly imbedded in cement compositions.

The term "glycol" as used herein is intended to mean two to six carbon, i.e., "C₂ to C₆", aliphatic di- and trihydric alcohols. Glycols suitable for use in the invention are those such as ethylene glycol, propylene glycol, and glycerol. Other compounds meeting the above definition will be apparent to those skilled in the art. Until now these compounds have not been known to have any set-accelerating qualities, i.e., they have been used primarily as grinding aids and set retarders. For this reason these compounds were not seen as having any value as part of a set-accelerating admixture. As such it was surprising to the inventors that a glycol as described herein could be used with a set-accelerating compound to significantly increase the set acceleration of a cement composition over that obtained by the addition of the set accelerator alone to

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the cement composition. Thus this invention utilizes the glycol component to give the set acceleration of the cement composition containing the set accelerator a desired "boost."

5 The term "cement composition" as used herein refers to pastes, mortars and concrete compositions comprising a hydraulic cement binder. The above terms are terms of art. Pastes are mixtures composed of a hydraulic cement
10 binder, for example, Portland cement, either alone or in combination with fly ash, silica fume or blast furnace slag, and water; mortars are pastes additionally including fine aggregate, and concretes are mortars additionally including coarse aggregate. Such compositions may additionally include other admixtures
15 such as defoaming agents, air-entraining or detraining agents, set retarders, water reducing agents, superplasticizers, and other components known to those in the art for altering properties of the composition. The cement compositions of this invention are formed by
20 mixing required amounts of certain materials, e.g., a hydraulic cement, water, and fine or coarse aggregate, as may be applicable for the particular cement composition being formed. used according to the invention

25 The set-accelerating component used according to the invention may be any compound which, when added to a cement composition (as described above), reduces the amount of time required for the cement composition to harden. For example, an alkali or alkaline earth metal salt which is a salt of an organic or inorganic acid may be employed. Although the
30 following list is not meant to be limiting, examples of these compounds are alkali or alkaline earth metal nitrate, nitrite, and formate; alkali or alkaline earth metal salts of Group VI halogen and pseudohalogen acids, such as alkali or alkaline earth metal chloride,
35 bromide, iodide, thiocyanate, thiosulfate and



perchlorate; and alkali or alkaline earth metal aluminates, silicates, and hydroxides, e.g., sodium hydroxide. Calcium salts are particularly advantageous, especially calcium nitrate, calcium chloride, and calcium formate, and calcium nitrite.

It is also feasible to use a mixture of alkali or alkaline earth metal salts, for example, a mixture of calcium nitrate and calcium nitrite. Any ratio of the salts used may be employed; in a preferred calcium nitrate/calcium nitrite mixture, a range of weight ratios of from about 1:3 to 3:1 may be used. ^{The} ~~of the invention~~ inventors have found that such an admixture ~~using a~~ calcium nitrate/calcium nitrite mixture as the set-accelerator component, is beneficial in inhibiting corrosion in steel reinforcing bars commonly imbedded in cement compositions.

If the set-accelerating component and glycol component are added to the cement composition separately, the glycol may be added, generally, in percent solids on solids ("% s/s"), in the range of about 0.05% s/s to 1.0% s/s (based on the weight of hydraulic cement binder in the cement composition), with a preferred range of about 0.1% s/s to 0.75% s/s, such concentrations being generally those which provide the desired boost in acceleration. The set-accelerating component may be added in the usual amounts necessary for set-acceleration, but generally in a range of from about 0.05% s/s to about 4.0% s/s. (Note that through ^{according to the invention} the use ~~of a glycol component~~ ~~of the invention~~ it is also possible to reduce the amount of set-accelerator component normally required for a certain level of set acceleration, because of the better set-acceleration provided by the combination of the glycol and the set-accelerator.)



However, the inventors find it is preferable to combine the glycol component and the set-accelerating component in desired amounts before addition to a cement composition, so only one composition need be metered out and added to the cement composition. This is a simpler and more precise method than adding each component separately and reduces the opportunity for error in dispensing the correct formulation. If the set-accelerating component and glycol component are to be mixed before addition to a cement composition, the glycol component and the set-accelerating component may be combined in any proportion effective to give the desired results. Generally, the amount of the glycol in the mixture may range from about 0.5 to 40 weight % (based on the combined weight of glycol component and accelerator component), and preferably from about 2 to 30 weight %.

An admixture ^{used in} ~~of~~ the invention should be mixed into a hydraulic cement composition in an amount effective to allow the acceleration desired. The specific amount of the admixture can be readily determined and will depend on the cement composition, the ratio of components of the composition, and the degree of acceleration desired. The admixture is generally added to a cement composition in an amount which, as noted above, provides a glycol concentration of from about 0.05% s/s to 1.0% s/s, preferably from about 0.1% s/s to 0.75% s/s, such concentrations being generally those which provide the desired boost in acceleration.

The admixtures ^{used in} ~~of~~ this invention can be added to cement compositions in any conventional manner familiar to those in the art. The admixture should be substantially uniformly mixed with the cement composition.



The following examples are given for illustrative purposes only. Unless otherwise indicated, all parts and proportions are by weight.

Example 1 (Comparative)

5 An admixture was prepared consisting of calcium nitrate and calcium nitrite, in a 2:1 ratio, in water. The total % solids of the admixture was 42.6%.

Example 2

10 An admixture of the invention was prepared consisting of calcium nitrate, calcium nitrite, and glycerol, in a 2:1:1 ratio (by weight), in water. The total % solids of the admixture was 45%.

Example 3

15 The admixtures prepared in Examples 1 and 2 were each added individually to mortars prepared using a Type I-II Portland cement, sand, and a water to cement ratio of 0.45. A blank mortar, containing no admixture, was also prepared. Each mortar was prepared by combining 4500g of sand, 900g of H₂O, and 2000g of cement in a Hobart mixer until homogeneous. A sufficient amount of the admixture solutions of Examples 1 and 2 was added to provide an admixture solids concentration of 0.5% s/s, and 2.0% s/s, based on the weight of hydraulic cement in the admixture. Set times were measured in accordance with ASTM C403. The test was performed at ^{12.8°C} 55°F.

25 Table 1 presents the data, which demonstrate, at different addition rates, the utility of adding a glycol component of the invention (glycerol), to improve the performance of a set-accelerating compound, in this case
30 a mixture of calcium nitrate and calcium nitrite.



Example 4

An admixture of the invention was prepared consisting of calcium nitrate, calcium nitrite and glycerol, in a proportion of 60:16:24 (by weight), in water. The total
5 % solids of the admixture was 45%.

Example 5

The admixture prepared in Example 4 was added to mortars prepared using three different Type I-II Portland cements ("Cements 1, 2, and 3"), sand, and a
10 water to cement ratio of 0.45. Blank mortars, containing no admixture, were also prepared with each cement. Each mortar was prepared by combining 4500g of sand, 900g of H₂O, and 2000g of cement in a Hobart mixer until homogeneous. A sufficient amount of the admixture
15 solution of Example 4 was added to provide an admixture solids concentration of 2.5% s/s, based on the weight of hydraulic cement in the admixture. Set times were measured in accordance with ASTM C403. The test was performed ^{4.4}at 40°F.

20 Table 2 presents the results, which show the set time performance with the three cement types. The data demonstrate the cold-temperature performance of a set accelerating cement admixture of the invention.

25 The preceding description of the invention has been intended to illustrate rather than limit the invention. The inventors intend that various modifications or changes be made within the scope of the appended claims without departing from the spirit of the invention.

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Table 1

<u>Admixture of Example #</u>	<u>Initial Set Time (hr)</u>	<u>Change In Initial Set Time (hr)</u>
blank	11.08	-
1 (at 0.5% s/s)	8.94	2.14
2 (at 0.5% s/s)	7.97	3.11
1 (at 2.0% s/s)	5.05	6.03
2 (at 2.0% s/s)	3.74	7.34

Table 2

<u>Admix. of Example #</u>	<u>Initial Set Time (hr)</u>			
	<u>Cement 1</u>	<u>Cement 2</u>	<u>Cement 3</u>	<u>Avg.</u>
blank	9.50	11.40	10.18	10.36
4	7.57	8.57	8.33	8.16

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Date: 31 MAY 1997



CLAIMS

1. A corrosion-inhibiting, set-accelerating admixture for reducing the set time of a cement composition which contains a hydraulic cement binder, the admixture

5 comprising

(a) a set-accelerator component comprising a mixture of alkaline earth metal nitrate and alkaline earth metal nitrite; and

10 (b) a C₂ to C₆ glycol component, present in an amount effective to increase the set acceleration properties of the set-accelerator component.

2. An admixture according to claim 1 wherein the amount of glycol component in the admixture is from 0.05 to 15 40 weight %, based on the combined weight of glycol component and accelerator component in the admixture.

3. An admixture according to claim 2 wherein the amount of glycol component in the admixture is from 2.0 to 30 weight % based on the combined weight of glycol 20 component and accelerator component in the admixture.

4. An admixture according to claim 1, 2 or 3 wherein the set-accelerating component comprises a mixture of calcium nitrate and calcium nitrite.

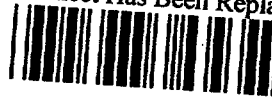
5. An admixture according to claim 4 which 25 comprises calcium nitrate and calcium nitrite in a weight ratio from 1:3 to 3:1.

6. An admixture according to any one of the preceding claims wherein the glycol component comprises an

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ethylene glycol.

7. An admixture according to any one of claims 1 to 5 wherein the glycol component comprises a propylene glycol.

5 8. An admixture according to any one of claims 1 to 5 wherein the glycol components comprises a glycerol.

9. A cement composition comprising a hydraulic cement binder and

(a) a set-accelerator component comprising a
10 mixture of alkaline earth metal nitrate and alkaline earth metal nitrite; and

(b) a C₂ to C₆ glycol component in an amount effective to increase the set acceleration properties of the set-accelerator component;
15 and wherein (a) and (b) are present in amounts effective to inhibit corrosion.

10 10. A composition according to claim 9 wherein the amount of glycol component is from 0.05% s/s to 1.0% s/s, based on the amount of hydraulic cement binder in the
20 composition.

11. A composition according to claim 10 wherein the amount of glycol component is from 0.1% s/s to 0.75% s/s, based on the weight of hydraulic cement binder in the composition.

25 12. A composition according to claim 9, 10 or 11 wherein the set-accelerator and/or the glycol are as defined in any one of claims 2 to 8.

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13. A method for making a cement composition according to any one of claims 9 to 12 which contains a hydraulic cement binder, said method comprising adding to said cement composition

- 5 (a) a set-accelerator component comprising a mixture of alkaline earth metal nitrate and alkaline earth metal nitrite, and
- (b) a C_2 to C_6 glycol component, in an amount effective to increase the set acceleration
- 10 properties of the set-accelerator component; and wherein (a) and (b) are added in amounts effective to inhibit corrosion.

14. A method according to claim 13 wherein the set-accelerating component and glycol are as defined in any one

15 of claims 2 to 8.

15. A product comprising

- (a) a set-accelerator component comprising a mixture of alkaline earth metal nitrate and alkaline earth metal nitrite; and
- 20 (b) a C_2 to C_6 glycol component, present in an amount effective to increase the set acceleration properties of the set-accelerator component;

for simultaneous, separate or sequential use as a

25 corrosion-inhibiting, set-accelerating admixture in reducing the set time of a cement composition which contains a hydraulic cement binder.

16. Use of a C_2 to C_6 glycol component to increase



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the set acceleration properties of a set-accelerator
component ^{< >} in an admixture for reducing the set time of a
cement composition which contains a hydraulic cement binder

17. Use according to claim 16 wherein the amount of
5 glycol component in the admixture is from 0.05 to 40
weight %, based on the combined weight of glycol component
and the accelerator component in the admixture.

18. Use according to claim 17 wherein the amount of
glycol component in the admixture is from 2.0 to 30
10 weight %, based on the combined weight of glycol component
and accelerator component in the admixture.

19. Use according to any one of claims 16 to 18
wherein the set-accelerating component is an alkali or
alkaline earth metal salt of an organic or inorganic acid,
15 or a mixture thereof.

20. Use according to claim 19 wherein the set-
accelerating component is calcium nitrate, calcium nitrite,
or a mixture thereof.

21. Use according to any one of claims 16 to 20
20 wherein the amount of glycol component is from 0.05% s/s to
1.0% s/s, based on the amount of hydraulic cement binder.

22. Use according to claim 21 wherein the amount
of glycol component is from 0.1% s/s to 0.75% s/s, based on
the weight of hydraulic cement binder.

< comprising a mixture of alkaline earth metal
nitrate and alkaline earth metal nitrite >



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REPLACEMENT SHEETS		SG
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☒ Abstract :	paged 19 to paged 20	
DATE OF RECEIPT		- 6 MAR 1998

REPLACEMENT SHEET

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HYDRAULIC CEMENT SET-ACCELERATING ADMIXTURES INCORPORATING GLYCOLS

This invention relates to improvements in set-accelerating admixtures for hydraulic cement compositions such as mortars, grouts and concretes. More particularly the invention relates to novel set-accelerating admixtures and methods for set-acceleration employing the addition of certain low molecular weight glycols, eg., glycerol and ethylene glycol, the invention also relates to use of glycols to increase the set acceleration properties of a set-accelerator.

Set accelerators are used when it is necessary to work with hydraulic cement compositions at freezing or near-freezing temperatures. The rate of hydration of Portland cement, for example, is very dependent on temperature, such that, at lower temperatures, Portland cement compositions will often harden at a rate slower than desired unless the hardening process is accelerated. In addition to accelerating the set, it is desirable to also attain an increase in the rate of early strength development at normal or low temperatures. This reduces curing and protection periods necessary to achieve specified strengths in concrete. Some techniques for accelerating the set are: increasing the proportion of cement in the mix, heating the mix, and using chemical admixtures that act on the components of the mix to increase the rate at which the cement paste sets.

Several chemical set accelerators are well-known. They include alkali hydroxides, silicates, fluorosilicates, calcium formate, sodium chloride,

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calcium chloride, and calcium nitrate and calcium nitrite.

Calcium chloride is widely used because it is easy and inexpensive to produce and its effects on hydraulic cement are predictable and well-documented. However, like
5 sodium chloride, it has the disadvantage of corroding steel. Thus, it can cause the corrosion of steel reinforcing bars in concrete. Other drawbacks of calcium chloride use include reduced compressive strength at later ages, reduced response to air entrainment, and blotching of
10 hardened concrete surfaces (Concrete Admixtures, Dodson: Van Nostrand Reinhold, 1990).

DE-A-3,636,659, WO-A-89/0827 and FR-A-2,227,240 disclose cementitious compositions which may comprise set-acceleration and glycol additives.

15 It is thus an object of this invention to provide new set-accelerating admixtures which reduce the set time of hydraulic cement compositions at lower temperatures, without inducing or promoting corrosion of steel reinforcement. Further objects of the invention are to
20 provide methods for preparing such cement compositions and to provide methods for reducing the set time of hydraulic cement compositions.

The present invention provides a corrosion-inhibiting, set-acceleration admixture for reducing the set
25 time of a cement composition which contains a hydraulic cement binder, the admixture comprising

- (a) a set-accelerator component comprising a mixture of alkaline earth metal nitrate and alkaline earth metal nitrite; and
- 30 (b) a C₂ to C₆ glycol component, present in an amount effective to increase the set acceleration properties of the set-accelerator component.

The invention further provides a cement composition
35 comprising a hydraulic cement binder and

- (a) a set-accelerator component comprising a mixture of alkaline earth metal nitrate and

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alkaline earth metal nitrite; and

- (b) a C₂ to C₆ glycol component in an amount effective to increase the set acceleration properties of the set-accelerator component;

5 and wherein (a) and (b) are present in amounts effective to inhibit corrosion.

The invention also provides a method for making a cement composition of the invention which contains a hydraulic cement binder, said method comprising adding to
0 said cement composition

- (a) a set-accelerator component comprising a mixture of alkaline earth metal nitrate and alkaline earth metal nitrite, and

5 (b) a C₂ to C₆ glycol component, in an amount effective to increase the set acceleration properties of the set-accelerator component; and wherein (a) and (b) are added in amounts effective to inhibit corrosion.

The invention yet further provides a product
0 comprising

- (a) a set-accelerator component comprising a mixture of alkaline earth metal nitrate and alkaline earth metal nitrite; and

5 (b) a C₂ to C₆ glycol component, present in an amount effective to increase the set acceleration properties of the set-accelerator component;

for simultaneous, separate or sequential use as a corrosion-inhibiting, set-accelerating admixture in
). reducing the set time of a cement composition which contains a hydraulic cement binder.

The invention still further provides use of a C_2 to C_6 glycol component to increase the set acceleration properties of a set-accelerator component comprising a mixture of alkaline earth metal nitrate and alkaline earth metal nitrite in an admixture for reducing the set time of a cement composition which contains a hydraulic cement binder.

It has been found that admixtures comprising a set-accelerating compound and certain low molecular weight glycols are surprisingly effective in reducing the set time of hydraulic cement compositions. Such admixtures are also found to be quite effective at lower working temperatures, i.e., below about 10°C (50°F). It appears that these low molecular weight glycols increase the set-acceleration properties of a set-accelerating compound. Additionally, admixtures of this invention may be formulated in such a way as to produce a composition that will inhibit corrosion in steel reinforcing bars commonly imbedded in cement compositions.

The term "glycol" as used herein is intended to mean two to six carbon, i.e., " C_2 to C_6 ", aliphatic di- and trihydric alcohols. Glycols suitable for use in the invention are those such as ethylene glycol, propylene glycol, and glycerol. Other compounds meeting the above definition will be apparent to those skilled in the art. Until now these compounds have not been known to have any set-accelerating qualities, i.e., they have been used primarily as grinding aids and set retarders. For this reason these compounds were not seen as having any value as part of a set-accelerating admixture. As such it was surprising to the inventors that a glycol as described herein could be used with a set-accelerating compound to significantly increase the set acceleration of a cement composition over that obtained by the addition of the set accelerator alone to

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the cement composition. Thus this invention utilizes the glycol component to give the set acceleration of the cement composition containing the set accelerator a desired "boost."

The term "cement composition" as used herein refers to pastes, mortars and concrete compositions comprising a hydraulic cement binder. The above terms are terms of art. Pastes are mixtures composed of a hydraulic cement binder, for example, Portland cement, either alone or in combination with fly ash, silica fume or blast furnace slag, and water; mortars are pastes additionally including fine aggregate, and concretes are mortars additionally including coarse aggregate. Such compositions may additionally include other admixtures such as defoaming agents, air-entraining or detraining agents, set retarders, water reducing agents, superplasticizers, and other components known to those in the art for altering properties of the composition. The cement compositions of this invention are formed by mixing required amounts of certain materials, e.g., a hydraulic cement, water, and fine or coarse aggregate, as may be applicable for the particular cement composition being formed.

The set-accelerating component used according to the invention may be any compound which, when added to a cement composition (as described above), reduces the amount of time required for the cement composition to harden. For example, an alkali or alkaline earth metal salt which is a salt of an organic or inorganic acid may be employed. Although the following list is not meant to be limiting, examples of these compounds are alkali or alkaline earth metal nitrate, nitrite, and formate; alkali or alkaline earth metal salts of Group VI halogen and pseudohalogen acids, such as alkali or alkaline earth metal chloride, bromide, iodide, thiocyanate, thiosulfate and

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perchlorate; and alkali or alkaline earth metal aluminates, silicates, and hydroxides, e.g., sodium hydroxide. Calcium salts are particularly advantageous, especially calcium nitrate, calcium chloride, and calcium formate, and calcium nitrite.

It is also feasible to use a mixture of alkali or alkaline earth metal salts, for example, a mixture of calcium nitrate and calcium nitrite. Any ratio of the salts used may be employed; in a preferred calcium nitrate/calcium nitrite mixture, a range of weight ratios of from about 1:3 to 3:1 may be used. The inventors have found that such an admixture of the invention using a calcium nitrate/calcium nitrite mixture as the set-accelerator component, is beneficial in inhibiting corrosion in steel reinforcing bars commonly imbedded in cement compositions.

If the set-accelerating component and glycol component are added to the cement composition separately, the glycol may be added, generally, in percent solids on solids ("s/s"), in the range of about 0.05% s/s to 1.0% s/s (based on the weight of hydraulic cement binder in the cement composition), with a preferred range of about 0.1% s/s to 0.75% s/s, such concentrations being generally those which provide the desired boost in acceleration. The set-accelerating component may be added in the usual amounts necessary for set-acceleration, but generally in a range of from about 0.05% s/s to about 4.0% s/s. (Note that through the use according to the invention of a glycol component, it is also possible to reduce the amount of set-accelerator component normally required for a certain level of set acceleration, because of the better set-acceleration provided by the combination of the glycol and the set accelerator.)

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However, the inventors find it is preferable to combine the glycol component and the set-accelerating component in desired amounts before addition to a cement composition, so only one composition need be metered out and added to the cement composition. This is a simpler and more precise method than adding each component separately and reduces the opportunity for error in dispensing the correct formulation. If the set-accelerating component and glycol component are to be mixed before addition to a cement composition, the glycol component and the set-accelerating component may be combined in any proportion effective to give the desired results. Generally, the amount of the glycol in the mixture may range from about 0.5 to 40 weight % (based on the combined weight of glycol component and accelerator component), and preferably from about 2 to 30 weight %.

An admixture used in the invention should be mixed into a hydraulic cement composition in an amount effective to allow the acceleration desired. The specific amount of the admixture can be readily determined and will depend on the cement composition, the ratio of components of the composition, and the degree of acceleration desired. The admixture is generally added to a cement composition in an amount which, as noted above, provides a glycol concentration of from about 0.05% s/s to 1.0% s/s, preferably from about 0.1% s/s to 0.75% s/s, such concentrations being generally those which provide the desired boost in acceleration.

The admixtures used in this invention can be added to cement compositions in any conventional manner familiar to those in the art. The admixture should be substantially uniformly mixed with the cement composition.

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The following examples are given for illustrative purposes only. Unless otherwise indicated, all parts and proportions are by weight.

Example 1 (Comparative)

An admixture was prepared consisting of calcium nitrate and calcium nitrite, in a 2:1 ratio, in water. The total % solids of the admixture was 42.6%.

Example 2

An admixture of the invention was prepared consisting of calcium nitrate, calcium nitrite, and glycerol, in a 2:1:1 ratio (by weight), in water. The total % solids of the admixture was 45%.

Example 3

The admixtures prepared in Examples 1 and 2 were each added individually to mortars prepared using a Type I-II Portland cement, sand, and a water to cement ratio of 0.45. A blank mortar, containing no admixture, was also prepared. Each mortar was prepared by combining 4500g of sand, 900g of H₂O, and 2000g of cement in a Hobart mixer until homogeneous. A sufficient amount of the admixture solutions of Examples 1 and 2 was added to provide an admixture solids concentration of 0.5% s/s, and 2.0% s/s, based on the weight of hydraulic cement in the admixture. Set times were measured in accordance with ASTM C403. The test was performed at 12.8°C (55°F).

Table 1 presents the data, which demonstrate, at different addition rates, the utility of adding a glycol component of the invention (glycerol), to improve the performance of a set-accelerating compound, in this case a mixture of calcium nitrate and calcium nitrite.

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Example 4

An admixture of the invention was prepared consisting of calcium nitrate, calcium nitrite and glycerol, in a proportion of 60:16:24 (by weight), in water. The total % solids of the admixture was 45%.

Example 5

The admixture prepared in Example 4 was added to mortars prepared using three different Type I-II Portland cements ("Cements 1, 2, and 3"), sand, and a water to cement ratio of 0.45. Blank mortars, containing no admixture, were also prepared with each cement. Each mortar was prepared by combining 4500g of sand, 900g of H₂O, and 2000g of cement in a Hobart mixer until homogeneous. A sufficient amount of the admixture solution of Example 4 was added to provide an admixture solids concentration of 2.5% s/s, based on the weight of hydraulic cement in the admixture. Set times were measured in accordance with ASTM C403. The test was performed at 44°C (40°F).

Table 2 presents the results, which show the set time performance with the three cement types. The data demonstrate the cold-temperature performance of a set accelerating cement admixture of the invention.

The preceding description of the invention has been intended to illustrate rather than limit the invention. The inventors intend that various modifications or changes be made within the scope of the appended claims without departing from the spirit of the invention.

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Table 1

<u>Admixture of Example #</u>	<u>Initial Set Time (hr)</u>	<u>Change In Initial Set Time (hr)</u>
blank	11.08	-
1 (at 0.5% s/s)	8.94	2.14
2 (at 0.5% s/s)	7.97	3.11
1 (at 2.0% s/s)	5.05	6.03
2 (at 2.0% s/s)	3.74	7.34

Table 2

<u>Admix. of Example #</u>	<u>Initial Set Time (hr)</u>			
	<u>Cement 1</u>	<u>Cement 2</u>	<u>Cement 3</u>	<u>Avg.</u>
blank	9.50	11.40	10.18	10.36
4	7.57	8.57	8.33	8.16

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CLAIMS

1. A corrosion-inhibiting, set-accelerating admixture for reducing the set time of a cement composition which contains a hydraulic cement binder, the admixture comprising
 - (a) a set-accelerator component comprising a mixture of alkaline earth metal nitrate and alkaline earth metal nitrite; and
 - (b) a C₂ to C₆ glycol component, present in an amount effective to increase the set acceleration properties of the set-accelerator component.
2. An admixture according to claim 1 wherein the amount of glycol component in the admixture is from 0.05 to 40 weight %, based on the combined weight of glycol component and accelerator component in the admixture.
3. An admixture according to claim 2 wherein the amount of glycol component in the admixture is from 2.0 to 30 weight % based on the combined weight of glycol component and accelerator component in the admixture.
4. An admixture according to claim 1, 2 or 3 wherein the set-accelerating component comprises a mixture of calcium nitrate and calcium nitrite.
5. An admixture according to claim 4 which comprises calcium nitrate and calcium nitrite in a weight ratio from 1:3 to 3:1.
6. An admixture according to any one of the preceding claims wherein the glycol component comprises an



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ethylene glycol.

7. An admixture according to any one of claims 1 to 5 wherein the glycol component comprises a propylene glycol.

8. An admixture according to any one of claims 1 to 5 wherein the glycol components comprises a glycerol.

9. A cement composition comprising a hydraulic cement binder and

(a) a set-accelerator component comprising a mixture of alkaline earth metal nitrate and alkaline earth metal nitrite; and

(b) a C₂ to C₆ glycol component in an amount effective to increase the set acceleration properties of the set-accelerator component; and wherein (a) and (b) are present in amounts effective to inhibit corrosion.

10. A composition according to claim 9 wherein the amount of glycol component is from 0.05% s/s to 1.0% s/s, based on the amount of hydraulic cement binder in the composition.

11. A composition according to claim 10 wherein the amount of glycol component is from 0.1% s/s to 0.75% s/s, based on the weight of hydraulic cement binder in the composition.

12. A composition according to claim 9, 10 or 11 wherein the set-accelerator and/or the glycol are as defined in any one of claims 2 to 8.



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13. A method for making a cement composition according to any one of claims 9 to 12 which contains a hydraulic cement binder, said method comprising adding to said cement composition

- (a) a set-accelerator component comprising a mixture of alkaline earth metal nitrate and alkaline earth metal nitrite, and
- (b) a C_2 to C_6 glycol component, in an amount effective to increase the set acceleration properties of the set-accelerator component; and wherein (a) and (b) are added in amounts effective to inhibit corrosion.

14. A method according to claim 13 wherein the set-accelerating component and glycol are as defined in any one of claims 2 to 8.

15. A product comprising

- (a) a set-accelerator component comprising a mixture of alkaline earth metal nitrate and alkaline earth metal nitrite; and
- (b) a C_2 to C_6 glycol component, present in an amount effective to increase the set acceleration properties of the set-accelerator component;

for simultaneous, separate or sequential use as a corrosion-inhibiting, set-accelerating admixture in reducing the set time of a cement composition which contains a hydraulic cement binder.

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the set acceleration properties of a set-accelerator component comprising a mixture of alkaline earth metal nitrate and alkaline earth metal nitrite in an admixture for reducing the set time of a cement composition which contains a hydraulic cement binder.

17. Use according to claim 16 wherein the amount of glycol component in the admixture is from 0.05 to 40 weight %, based on the combined weight of glycol component and the accelerator component in the admixture.

18. Use according to claim 17 wherein the amount of glycol component in the admixture is from 2.0 to 30 weight %, based on the combined weight of glycol component and accelerator component in the admixture.

19. Use according to any one of claims 16 to 18 wherein the set-accelerating component is an alkali or alkaline earth metal salt of an organic or inorganic acid, or a mixture thereof.

20. Use according to claim 19 wherein the set-accelerating component is calcium nitrate, calcium nitrite, or a mixture thereof.

21. Use according to any one of claims 16 to 20 wherein the amount of glycol component is from 0.05% s/s to 1.0% s/s, based on the amount of hydraulic cement binder.

22. Use according to claim 21 wherein the amount of glycol component is from 0.1% s/s to 0.75% s/s, based on the weight of hydraulic cement binder.



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Hydraulic Cement Set-Accelerating Admixtures Incorporating Glycols**ABSTRACT**

New set-accelerating admixtures for hydraulic cement compositions are disclosed. These admixtures incorporate known set accelerators and certain low molecular weight glycols, e.g., glycerol and ethylene glycol, are found to be surprisingly effective in decreasing the initial set time of hydraulic cements, mortars, and concretes, and are advantageous as reduced-temperature set-accelerators.