

## EUROPEAN QUALIFYING EXAMINATION 2004

### PAPER B CHEMISTRY

This paper comprises:

- \* Annex 1  
Patent Application 2004/B(Ch)/e/1-11
- \* Annex 2  
Communication 2004/B(Ch)/e/12-13
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**Annex 1 (Patent Application)**

Corrosion inhibitor for protecting steel reinforcement in concrete

The present invention is related to the inhibition of corrosion of reinforcing steel embedded in a concrete structure. In particular, this invention provides corrosion inhibitors for the protective corrosion inhibition of steel reinforcements embedded in a concrete structure when the structure is exposed to aggressive chloride-containing environments. The corrosion inhibitors are also useful for restoring a concrete structure by the reduction of the corrosion rate of already corroding steel reinforcements embedded in a concrete structure exposed to an aggressive chloride-containing environment.

Background of the invention

Durability limitations of steel reinforced concrete are well documented. Chloride-containing corrosive environments can quickly cause corrosion of the reinforcing steel. Chloride ions in concrete can originate from the ingress of de-icing salts or seawater diffusing to the reinforcement through the pore network of the concrete.

Normally, reinforcing steel embedded in concrete is protected because the concrete cover acts as a barrier and the high pH value of liquid in the pore-network of the concrete ensures that no significant corrosion occurs. The presence of chloride ions at concentrations above a given threshold level, however results in corrosion rates that markedly decrease the expected service lives of reinforced concrete structures. Thousands of bridges and other structures made of reinforced concrete need to be repaired worldwide as a consequence of corrosion of the steel reinforcement.

The present invention relates to corrosion inhibitors for the precautionary, protective corrosion inhibition of reinforcing steel exposed to chloride-containing corrosive environments as well as for application to restore corroded reinforcing steel embedded in hardened concrete.

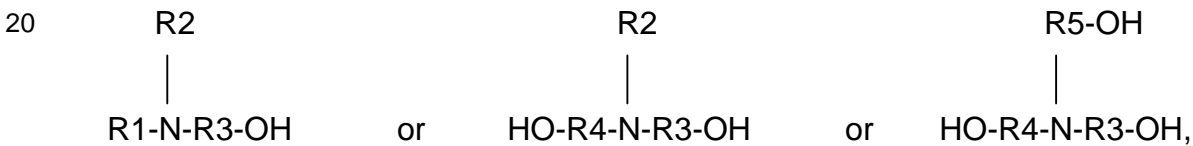
Corrosion inhibitors are compounds or compositions that, when used in small concentrations in a corrosive environment, decrease the corrosion rate. The use of corrosion inhibitors is widespread and well established. The most commonly used corrosion inhibitor for reinforcing steel in concrete is calcium nitrite. Cyclic amines such as dicyclohexylamine have also been used. These inhibitors are typically applied preventively and are mixed into the slurry from which the concrete is obtained.

The problem addressed by the present invention is to find improved corrosion inhibitors for reinforcing steel in concrete, which provide an effective protection against corrosion to reinforcing steel. In addition the inhibitors must be useful for the preventative treatment of reinforcing steel in new concrete structures and for the treatment of existing concrete structures during their repair to minimise further corrosion.

Summary of the invention

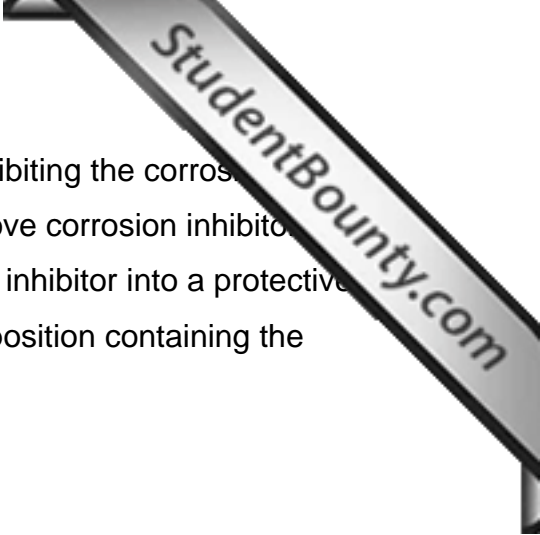
The corrosion inhibitor of the present invention consists of two components:

The first component is an alkanolamine of the formula:



in which R1 and R2 are, independently, hydrogen, C1-C6 alkyl or C4-C6 cycloalkyl, and wherein R3, R4, and R5 are, independently, C2-C6 alkylene or C4-C6 cycloalkylene.

The second component is an alkaline metal nitrite or an alkaline earth metal nitrite.

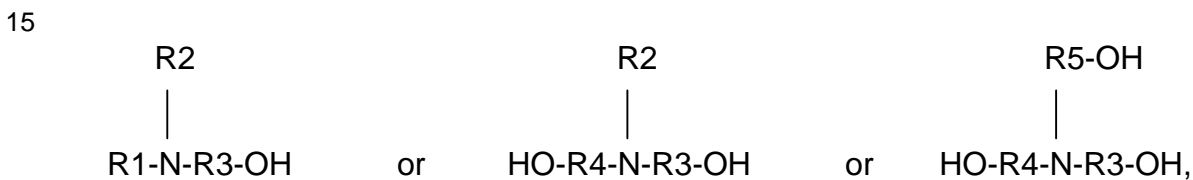


The present corrosion inhibitor can be used in methods for inhibiting the corrosion of steel reinforcements in concrete, which include adding the above corrosion inhibitor to the slurry from which the concrete is formed, incorporating the inhibitor into a protective polymer coating on the steel reinforcement or applying a composition containing the corrosion inhibitor to an existing concrete structure.

Detailed description of the invention

The present invention thus provides a corrosion inhibitor for inhibiting the corrosion of steel reinforcement members present in a concrete structure.

The alkanolamine and the nitrite are preferably used in a weight ratio varying between 5:1 and 1:5. The corrosion inhibitor of the present invention is a mixture of an alkanolamine of the formula:



(in which R1 and R2 are, independently, hydrogen, C1-C6 alkyl or C4-C6 cycloalkyl, and wherein R3, R4, and R5 are, independently, C2-C6 alkylene or C4-C6 cycloalkylene) with an alkaline metal nitrite or an alkaline earth metal nitrite.

Excellent results have been obtained when the alkanolamine is selected from 3-amino-1-propanol, 2-aminoethanol, 2-(dimethylamino)ethanol, 2-(ethylamino)ethanol, 2-(butylamino)ethanol, 2-[(1,1-dimethylethyl)amino]ethanol, 2-(cyclohexylamino)ethanol and triethanolamine. The nitrite is preferably selected from sodium and calcium nitrite.

The present corrosion inhibitors have been found to be highly effective when used in any of the standard methods for the preventative protection of reinforcing steel and are also useful for restoring concrete structures by reducing the corrosion rate of reinforcing steel in existing concrete structures.

Two standard methods are known which employ corrosion inhibitors for the protection of steel reinforcements from corrosion.

5 The first method comprises incorporating the corrosion inhibitor into the concrete slurry from which the structure is to be formed.

10 The amount of the corrosion inhibitor, which is incorporated into the concrete slurry, is normally within the range of from 0.01 to 1% by weight, based on the weight of the concrete slurry. The corrosion inhibitor when used in this method is dissolved in a minimum quantity of water and then mixed into the slurry.

15 The second standard preventative method for inhibiting the corrosion of steel reinforcements in concrete involves coating the steel reinforcements with a polymeric resin and then incorporating the coated steel into the concrete. The polymeric coating serves to restrict the access of the aggressive chloride ions to the metal. The corrosion rate of the metal can be further reduced if a corrosion inhibitor is also included in the coating.

20 The coating composition is preferably based on an alkyd resin. An alkyd resin is a synthetic resin made from a dicarboxylic acid and a diol or a triol. A particularly good protection against corrosion has been obtained when a composition containing 10-15 wt% alkyd resin, 10-20 wt% butyl glycol, and 4-9 wt% corrosion inhibitor of the present invention in deionised water is used. This composition preferably also contains up to 1 wt% of surfactant to improve its coating properties.

25 A further method in which the present corrosion inhibitor can be used is a method for the restoration of concrete structures. This method involves impregnating the surface of a hardened concrete structure with an aqueous composition containing the present corrosion inhibitor. It has surprisingly been found that the present corrosion inhibitor is able to penetrate into the concrete material to reach the steel reinforcements and reduce the corrosion rate of the steel reinforcements to an acceptable level.

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This method is economically very beneficial as compared to previous standards for the restoration of concrete structures. The standard restoration methods always involve the removal of the surface portion of the concrete structure so as to expose the steel reinforcement closest to the surface, which is always the most severely corroded.

5 The steel reinforcement is then cleaned or replaced and fresh concrete slurry is applied to replace the concrete removed. The present restoration method is very economical as compared to these standard methods as it requires no concrete to be removed.

The aqueous corrosion-inhibiting composition used in the restoration method is preferably applied on the concrete surface by brush, by paint roller or by a spraying device. The composition is typically used in a total amount of 200-2000 g/m<sup>2</sup>, preferably 300-1000 g/m<sup>2</sup>. This composition preferably contains as a further component an alkylalkoxysilane of the following formula:

10



in which R<sub>6</sub> is C<sub>6</sub> to C<sub>16</sub> alkyl and R<sub>7</sub> is C<sub>1</sub> to C<sub>3</sub> alkyl.

These alkylalkoxysilanes are commercially available and, as is well known in the art, produce a hydrophobic layer on the exterior of concrete structures. This hydrophobic layer when it contains the present corrosion inhibitor, has surprisingly been found to reduce the ingress of aggressive chloride ions into the concrete structure and improves the corrosion protection. The composition may also contain a surfactant, which when used in combination with the alkylalkoxysilane and the present corrosion inhibitor further improves the corrosion protection.

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A preferred composition for use in a restoration method comprises 10-20 wt% of the present corrosion inhibitor, 15-25 wt% of the alkylalkoxysilane, 1-5% of surfactant, remainder water.

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**Examples**

Example 1:

5 Preliminary tests were performed in a solution which simulates the liquid in a concrete structure. The solution used was a saturated calcium hydroxide solution containing a chloride concentration of 0.1 M. Some of the solutions tested contained the commercially available corrosion inhibitors dicyclohexylamine and calcium nitrite and others contained corrosion inhibitors of the present invention. All of the corrosion  
10 inhibitors were used at 1 g/l. The alkanolamine-nitrite inhibitors tested were always a 1:1 by weight mixture of the two components. Carefully weighed carbon steel rods with a surface area of 5 cm<sup>2</sup> were immersed in the solution. The rods were removed from the solution after 30 days, rinsed under running water, dried at 60 °C and reweighed. The corrosion rate was calculated from the weight loss data; the lower the value the more  
15 effective the inhibitor.

Inhibitor	Corrosion rate (micrometers/year)
None	11.7
Calcium nitrite	5.3
Dicyclohexylamine	3
Calcium nitrite + triethanolamine	0.5
Calcium nitrite + 2-aminoethanol	1
Calcium nitrite + 2-(cyclohexylamino)ethanol	1.5
Sodium nitrite + 2-aminoethanol	0.75

The present corrosion inhibitor is thus more effective than known corrosion inhibitors at reducing the corrosion rate of carbon steel in this solution.

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Example 2:

In this example the use of the corrosion inhibitors of the invention for the reduction of corrosion rates was investigated.

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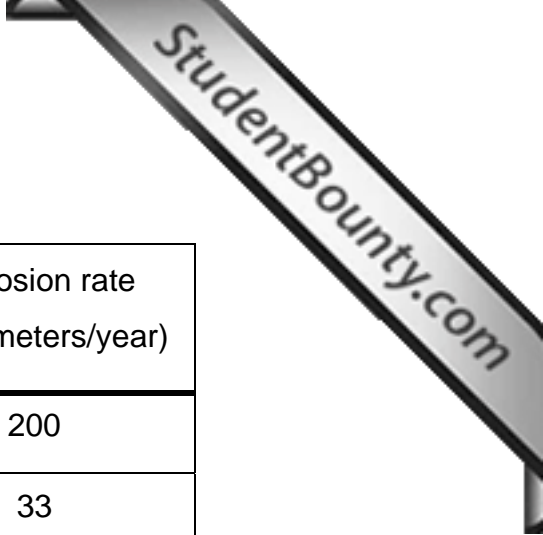
A concrete slurry consisting of cement (300 kg), sand (550 kg) and water (150 l) was prepared and divided into samples.

10 In one series of tests (Series A) the corrosion inhibitors listed below were added to samples of the slurry at a concentration of 0.2 % by weight of the slurry.

15 In a further series of tests (Series B) a carbon steel reinforcement rod was dipped for 30 seconds into an aqueous resin solution consisting of 12 wt% alkyd resin, 15 wt% butyl glycol, 7 wt% corrosion inhibitor (when used) balance water. The rod was subsequently removed from the solution and allowed to dry for 24 hours.

The alkanolamine-nitrite inhibitors tested were always a 1:1 by weight mixture of the two components.

20 In each experiment a sample of concrete slurry was cast around a carbon steel rod, and allowed to harden. The concrete sample was then immersed in an aqueous solution containing a chloride concentration of 0.5 M. Measurements of the ability of the candidate corrosion inhibitors to inhibit corrosion were made electrochemically using the method specified in ASTM standard G-5. The samples were monitored for 3 months and  
25 the average corrosion rate during this period was determined.



Series A

Inhibitor used in slurry	Corrosion rate (micrometers/year)
None	200
Calcium nitrite	33
Calcium nitrite + triethanolamine	10
Sodium nitrite + 2-aminoethanol	18

Series B

Coated steel reinforcements	Corrosion rate (micrometers/year)
Alkyd resin coating containing no corrosion inhibitor	20
Alkyd resin coating containing calcium nitrite and triethanolamine	1

Example 3:

In this example the use of the present corrosion inhibitors during the restoration of concrete structures was investigated.

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A series of identical carbon steel rods coated with hardened concrete were prepared using the method used in example 2. No corrosion inhibitors were added to the slurry and no protective coatings on the steel reinforcement were used. Each concrete sample was then immersed in an aqueous solution containing a chloride concentration of 0.5 M and allowed to corrode freely for 6 months. At the end of the 6 months the corrosion potential of the steel rods was determined electrochemically. The samples were then removed from the liquid, coated using a paint roller with 500 g/m<sup>2</sup> of one of the following compositions I-VII and the sample was re-immersed in the chloride solution. The corrosion potential was then monitored for each sample with respect to a standard calomel electrode: the higher (that is the less negative) the value of the corrosion potential, the lower the corrosion rate. A corrosion potential value less negative than -200 mV (for example -150 mV) with respect to the standard calomel electrode is indicative of a very good corrosion protection. A value of -700 mV is typical of a severe corrosion of a steel reinforcement with no corrosion protection.

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Composition I: Water 100 wt%.

Composition II: Calcium nitrite 5 wt%, triethanolamine 5 wt%, water 90 wt%.

Composition III: Sodium nitrite 5 wt%, 2-[(1,1-dimethylethyl)amino]ethanol 5 wt%, water 90 wt%.

Composition IV: Calcium nitrite 5 wt%, triethanolamine 5 wt%, Hydrosilox 20 wt%, water 70 wt%.

Composition V: Calcium nitrite 5 wt%, 2-[(1,1-dimethylethyl)amino]ethanol 5 wt%, Hydrosilox 20 wt%, water 70 wt%.

Composition VI: Calcium nitrite 5 wt%, triethanolamine 5 wt%, Hydrosilox 20 wt%, Proclean 2 wt%, water 68 wt%.

Composition VII: Calcium nitrite 5 wt%, 2-[(1,1-dimethylethyl)amino]ethanol 5 wt%, Proclean 2 wt%, Hydrosilox 20 wt%, water 68 wt%.

Proclean is a commercially available surfactant; Hydrosilox is a commercially available mixture of alkylalkoxysilanes consisting primarily of alkyltriethoxysilanes of the form  $\text{RSi}(\text{OC}_2\text{H}_5)_3$ ; where R is C8 to C10 alkyl.

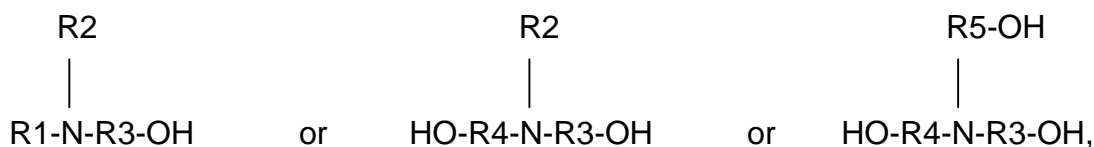
Composition No.	Corrosion potential (mV) pre-coating and after 1, 30 and 60 days.			
I	-700	-710	-705	-690
II	-710	-180	-210	-500
III	-715	-170	-200	-350
IV	-705	-190	-160	-210
V	-700	-150	-190	-220
VI	-700	-180	-150	-160
VII	-705	-170	-140	-130

These tests show that the present corrosion inhibitors are very effective for the restoration of concrete structures.

CLAIMS

1. A corrosion inhibitor for steel reinforcements in concrete comprising

an alkanolamine of the formula:



in which R1 and R2 are, independently, hydrogen, C1-C6 alkyl or C4-C6 cycloalkyl, and wherein R3, R4, and R5 are, independently, C2-C6 alkylene or C4-C6 cycloalkylene

and an alkaline metal nitrite or an alkaline earth metal nitrite.

2. A corrosion inhibitor in accordance with claim 1 where the alkanolamine is selected from 3-amino-1-propanol, 2-aminoethanol, 2-(dimethylamino)ethanol, 2-(ethylamino)ethanol, 2-(butylamino)ethanol, 2-[(1,1-dimethylethyl)amino]ethanol, 2-(cyclohexylamino)ethanol, and triethanolamine.
3. A corrosion inhibitor in accordance with claim 1, where the nitrite is selected from sodium and calcium nitrite.
4. A corrosion inhibitor in accordance with claim 1, where the weight ratio of alkanolamine to nitrite is 5:1 to 1:5.

## **Annex 2 (Communication)**

1. Document 1 (see 5<sup>th</sup> paragraph and claims) discloses the corrosion inhibitors defined in claims 1-4. The document also discloses their use in resin coatings used for the preventative coating of steel reinforcements to protect them against corrosion. The document also discloses the use of these coatings in a restoration treatment for a concrete structure with corroded reinforcements.
2. Document 2 (see claims and 3<sup>rd</sup> paragraph) also discloses the present corrosion inhibitors and their use in a concrete slurry.
3. Documents 1 and 2 are thus novelty destroying for the subject-matter of claims 1-4 (Articles 52(1), 54(1) and 54(2) EPC).
4. If the applicant wishes to maintain the application, new claims should be filed which take the above objections into account. Care should be taken to ensure that the new claims comply with the requirements of the EPC in respect of novelty, inventive step, clarity and if necessary unity (Articles 54, 56, 84 and 82 EPC). The applicant should also ensure that any amendments do not introduce subject-matter, which extends beyond the content of the application as originally filed (Article 123(2) EPC).
5. In the letter of reply, the difference between the new claims and the state of the art as well as its significance should be identified. In addition the invention should be presented in such a way that the technical problem being solved in view of the state of the art, the solution proposed to this problem, as well as the position of the applicant in respect of inventive step (Rule 27(1)(c) EPC and Guidelines C-IV, 9.5) can be clearly understood.
6. An independent claim must specify all the technical features necessary to define the invention (Guidelines C-III, 4.4). Thus each independent claim must contain all the technical features essential to the solution of the problem on which the invention is based.

7. In order to facilitate the examination as to whether the new claims contain matter which extends beyond the content of the application as filed, the applicant is requested to indicate precisely where in the application documents any amendments proposed find a basis (Article 123(2) EPC, Guidelines E-II, 1 and C-VI, 5.4).
  
8. It is suggested that the adaptation of the description to any new claims be postponed until the Examining Division indicates that a set of claims is allowable.

**Annex 3 (Document 1)**

Improvements in the corrosion protection of reinforced concrete structures

This invention relates to improvements in the prevention of corrosion in reinforced concrete structures such as buildings or bridges and to the restoration of such structures  
5 which have already corroded.

In the course of years concrete structures slowly deteriorate when exposed to chloride ions. This is largely due to the corrosion of the steel reinforcement, which in turn often destroys adhesion with the concrete so resulting in collapse of a structure.  
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It is the object of this invention to provide methods for the prevention of the corrosion of the steel reinforcements and for the restoration of corroded concrete structures.

According to the invention we provide a method for the prevention of the corrosion of steel reinforcements, which comprises coating the steel reinforcements prior to their  
15 incorporation into the concrete structure. We also provide a method for the restoration of concrete structures comprising the following steps: firstly, concrete is removed to expose the corroded reinforcement members, secondly, the reinforcement members are cleaned by sand blasting; if necessary, badly corroded bars are replaced, thirdly, the  
20 steel reinforcements are treated with the coating composition and finally concrete is reapplied.

The coating composition used in both of the above methods contains 10-15 wt% alkyd resin, 10-20 wt% butyl glycol, 4-9 wt% of a 1:1 by weight mixture of sodium or calcium  
25 nitrite and an alkanolamine; remainder deionised water. This composition preferably also contains up to 1 wt% of surfactant to improve its coating properties. Any alkanolamine may be used, but in view of their commercial availability and low cost one of the following compounds is preferred: 3-amino-1-propanol, 2-aminoethanol,  
2-(dimethylamino)ethanol, 2-(ethylamino)ethanol, 2-(butylamino)ethanol,  
30 2-[(1,1-dimethylethyl)amino]ethanol, 2-(cyclohexylamino)ethanol, or triethanolamine.



The coating is preferably applied preventatively to the steel reinforcements by dipping the rods in the coating solution for between 10 seconds and 1 minute.

5 When applying the methods of restoration, hand or power tools are used to remove old concrete, sand blast the reinforcement rods and so on, but the application of the coating and the reapplication of the fresh concrete is preferably performed by hand.

10 In practice it has been shown that structures protected against corrosion or restored in accordance with our processes have an enhanced life due to the special protection given by our coating composition.

CLAIMS

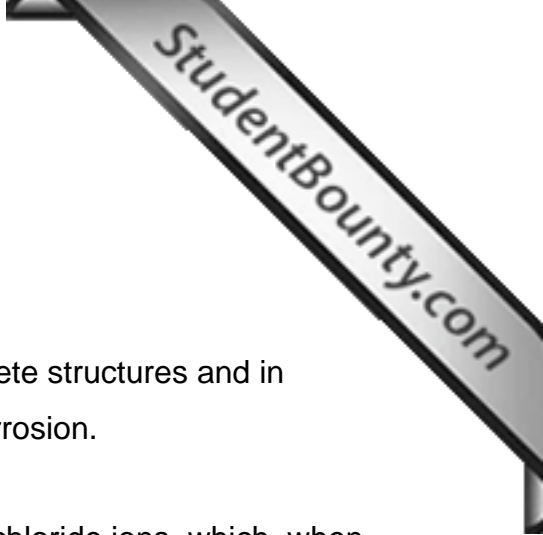
1. A method for protecting concrete structures against corrosion characterised that steel reinforcement rods used in the structure are coated with the following composition prior to their incorporation into the structure:

10-15 wt% alkyd resin;  
10-20 wt% butyl glycol;  
4-9 wt% of a 1:1 by weight mixture of sodium or calcium nitrite and an alkanolamine;  
0-1 wt% surfactant;  
and remainder deionised water.

2. A method for the restoration of concrete structures comprising the following steps: removing concrete to expose the corroded reinforcement members, cleaning the steel reinforcement members by sand blasting and if necessary replacing badly corroded bars, coating the steel reinforcements with the following coating composition:

10-15 wt% alkyd resin;  
10-20 wt% butyl glycol;  
4-9 wt% of a 1:1 by weight mixture of sodium or calcium nitrite and an alkanolamine;  
0-1 wt% surfactant;  
remainder deionised water;

and reapplying concrete over the coated steel reinforcement.



**Annex 4 (Document 2)**

Corrosion resistant concretes

The present invention concerns a method for protecting concrete structures and in particular the steel reinforcements in these structures from corrosion.

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Concrete is subject to substantial corrosion principally due to chloride ions, which, when present above a given threshold level, sooner or later destroy the structures. The restoration of damage due to corrosion of structures, such as bridges, is not only costly, but also proves that known anti-corrosive measures are not permanently satisfactory.

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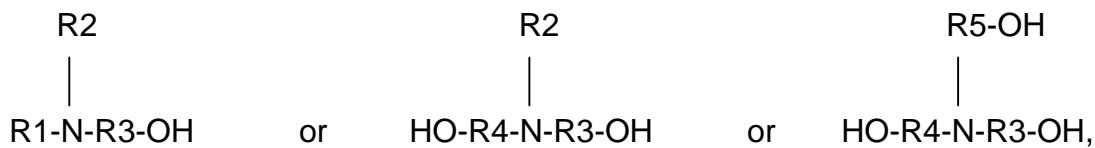
According to the present invention, there is provided a method of producing a corrosion-resistant concrete, wherein there is added to the concrete slurry prior to its hardening 0.01 to 1 % by weight of a composition consisting of sodium or calcium nitrite and an alkanolamine.

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The composition is preferably added in an aqueous saturated solution.

The composition used is preferably a mixture of an alkanolamine of the formula:

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in which R1 and R2 are, independently, hydrogen, C1-C6 alkyl or C4-C6 cycloalkyl, and wherein R3, R4, and R5 are, independently, C2-C6 alkylene or C4-C6 cycloalkylene, with sodium or calcium nitrite.

Excellent results have been obtained when the alkanolamine is selected from 3-aminopropanol, 1-propanol, 2-aminoethanol, 2-(dimethylamino)ethanol, 2-(ethylamino)ethanol, 2-(butylamino)ethanol, 2-[(1,1-dimethylethyl)amino]ethanol 2-(cyclohexylamino)ethanol, and triethanolamine.

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The alkanolamine and the nitrite are preferably used in a weight ratio varying between 5:1 and 1:5.

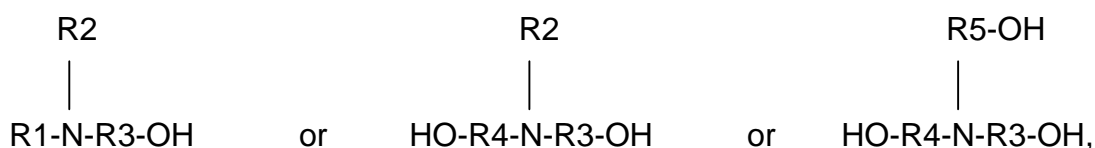
### Example

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A 1:1 by weight mixture of sodium nitrite and 2-aminoethanol in saturated, aqueous solution is added in a quantity of 0.2 % by weight to a concrete slurry. This slurry was poured over a mat of steel reinforcements and allowed to harden. An identical structure was then prepared using a concrete containing no nitrite or alkanolamine. The structures were sprayed with a saturated sodium chloride solution and then stored outside for 15 12 months. The concrete was subsequently removed and the steel reinforcements were inspected. The reinforcement made with the concrete containing the present corrosion inhibiting composition showed little corrosion whereas the steel reinforcement from the concrete without the composition was badly corroded.

CLAIMS

1. A method of producing a corrosion resistant concrete characterised in that there is added to the concrete slurry prior to its hardening 0.01 to 1 % by weight of a composition consisting of sodium or calcium nitrite and an alkanolamine.
2. A method in accordance with claim 1 in which the composition used is a mixture of an alkanolamine of the formula:



in which R1 and R2 are, independently, hydrogen, C1-C6 alkyl or C4-C6 cycloalkyl, and wherein R3, R4, and R5 are, independently, C2-C6 alkylene or C4-C6 cycloalkylene, with sodium or calcium nitrite.

3. A method in accordance with claim 2 in which the alkanolamine is selected from 3-amino-1-propanol, 2-aminoethanol, 2-(dimethylamino)ethanol, 2-(ethylamino)ethanol, 2-(butylamino)ethanol, 2-[(1,1-dimethylethyl)amino]ethanol, 2-(cyclohexylamino)ethanol, and triethanolamine.
4. A method in accordance with claim 1 in which the alkanolamine and the nitrite are used in a weight ratio varying between 5:1 and 1:5.