Abstract:
The present invention provides methods and compositions for the delay in the onset of corrosion or for the reduction of the corrosion rate of steel reinforcements embedded in a concrete structure after the onset of corrosion. Applications include the treatment of already hardened concrete structures or the addition of the admixture to the fresh reinforced concrete. The inventive new compositions are essentially based on one or more amino-and/or hydroxyalkylamino compounds(s), which are partially or completely neutralized with one or more organophosphonic acids along with surfactants or an additive facilitating penetration, wicking, and surface wetting.
CORROSION INHIBITION OF REINFORCING STEEL EMBEDDED IN
A CONCRETE STRUCTURE BY MEANS OF SURFACE APPLICATION
OR BY ADDITION OF THE CORROSION-INHIBITING
COMPOSITION TO THE FRESH REINFORCED CONCRETE

The present invention is related to the inhibition of corrosion of reinforcing steel embedded in a concrete structure. In particular, this invention provides compositions for the delay in the onset of corrosion or for the reduction of the corrosion rate of corroding steel reinforcements embedded in a hardened concrete structure as well as for the protective corrosion inhibition of steel reinforcements embedded in fresh concrete.

BACKGROUND OF THE INVENTION

Durability limitations of steel reinforced concrete are well documented. Corrosive environments (e.g. the presence of chlorides, bromides or combinations thereof), carbonation of concrete structures, poor workmanship and other factors can quickly cause corrosion of the reinforcing steel. Chloride ions in concrete can originate from the ingress of de-icing salts, seawater or airborne salts, diffusing to the reinforcement through the pore network of concrete, as well as from contaminated aggregates or from contaminated mixing water (cast in chlorides).

Carbon dioxide as well as other atmospheric borne acidic corrosive react with the free alkali contained in concrete. Over a period of time the initial alkaline pH value of the outermost concrete layer decreases, resulting in a net loss of the natural protection of the steel embedded in reinforced concrete.

Normally, reinforcing steel embedded in concrete is protected because the concrete cover acts as a gas diffusion barrier and the high pH value of the pore fluid assures a passive state of the reinforcing steel. Both the presence of chloride ions at concentrations above a minimum threshold levels and carbonation can put reinforcing steel into an active state and result in corrosion rates that markedly
decrease the expected service lives of reinforced concrete structures. The oxidation products are expansive in the concrete structure and can cause spalling and breakdown of the concrete structure, hastening corrosion. 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-inhibiting compositions for the rehabilitative repassivation of corroded reinforcing steel embedded in hardened concrete as well as for the precautionary, protective corrosion inhibition of non-corroded reinforcing steel embedded in hardened concrete structures exposed to corrosive environments. Said corrosion-inhibiting compositions contain corrosion inhibitors with alkaline buffer capacities as well as affinity for the iron in steel reinforcements and may optionally contain water repellent agents and optionally some other inhibitors agent. Said composition when applied to the surface of the concrete structure causes a reduction of the corrosion rate of corroding reinforcing steel embedded in a hardened concrete structure as well as delaying the onset of corrosion of non-corroded reinforcing steel embedded in a hardened concrete structure respectively. Said composition can be also added to a fresh concrete mixture, effectively delaying the onset of steel reinforcement corrosion.

Corrosion inhibitors are compounds or compositions that, when added in small concentrations to a corrosive environment, decrease the corrosion rate. The use of corrosion inhibitors is widespread and well established. For example, protection systems based on corrosion inhibitors are used to limit the corrosion of process equipment such as cooling systems, pipelines, or central heating systems. Various types of corrosion inhibitors designed for different applications are available in the marketplace. Corrosion inhibitors may be classified into the following groups: anodic oxidizing passivators (e.g. chromates, nitrites), anodic non-oxidizing passivators (e.g. molybdates), cathodic corrosion inhibitors (e.g. oxygen scavengers such as sulfites or cathodic poisons such as arsenates),
film-forming inhibitors of the adsorption type (e.g. amines, alkanolamines). The film-forming corrosion inhibitors, which are typically organic compounds, represent the largest group of corrosion inhibitors and may exhibit anodic, cathodic or mixed behavior.

Sprayable anticorrosion inhibitors are known. Use of phosphonic acid salts as the neutralizing acid is not known. The mixtures of the invention constitute a new composition of matter for the industry and provide effective reductions in corrosion properties versus a control.

**SUMMARY OF THE INVENTION**

Hence, it is an object of the invention to provide novel compositions as defined in claim 1 suitable for the reduction of the corrosion rate of already corroding steel reinforcements embedded in a hardened concrete structure as well as for the protective corrosion inhibition of non-corroded steel reinforcements embedded in a hardened concrete structure. Said compositions mixed in a fresh concrete are able to delay the onset of corrosion of reinforcing steel.

It is also an object of the invention the use of novel compositions comprising amino and/or hydroxyalkylamino compound(s) neutralized with a novel acid with a strong affinity for steel substrates for a final process that reduces the corrosion rate of already corroding steel reinforcements embedded in a hardened concrete structure as well as for the protective corrosion inhibition of non-corroded steel reinforcements embedded in a concrete structure exposed to aggressive environments.

These aims are achieved according to the invention in particular through the elements of the independent claims. Further, preferred embodiments follow moreover from the dependent claims and from the description.

Thus, the aqueous corrosion-inhibiting compositions according to the invention comprise the following components:

A) one or more amino- and/or hydroxyalkylamino compound(s), partially
or completely neutralized with one or more acid(s) selected from the group consisting of any alkyl, aryl, alkyl aryl, phosphonic acid soluble in water in an amount sufficient to inhibit corrosion of said steel reinforcement after topical application to cured concrete surface.

5  B) one or more surfactant(s) providing an enhanced wetting and penetration capability by altering the surface tension when it is applied in one or more coats to the surface of a hardened reinforced concrete structure, which has undergone or is susceptible to corrosion of the reinforcing steel. Said hardened concrete, particularly the outermost layer(s) of said hardened concrete in dose vicinity of the outermost parts of the reinforcement, may be carbonated to any degree or not carbonated and/or may contain chloride ions.

10  C) one or more water repellant organic agent and additives such as silanes, siloxanes, alkali siliconates, fluorinated hydrocarbons, fluorinated acrylic polymers, and/or other organic film forming polymers of low surface tension.

15  D) one or more corrosion inhibitor agent selected from the group of alkali metal and alkaline earth metal nitrates and/or nitrites.

The disclosed corrosion-inhibiting compound or composition features the ability to delay the onset of corrosion or to reduce the corrosion rates of corroded steel reinforcement embedded in concrete, due to their corrosion-inhibiting action as well as buffering the concrete surrounding the reinforcing steel due to their alkalinities and the affinity of the phosphonic acid to bond to the mild reinforcement steel.

The careful selection of the amino- and/or hydroxyalkylamino compounds as well as of the inorganic acid and/or carboxylic acid compounds allows the formulation of corrosion-inhibiting impregnations. When applied on the surface of a carbonated hardened reinforced concrete structure, said corrosion-inhibiting compositions are capable of raising the pH value of the concrete's pore fluid in the vicinity of the reinforcing steel to a level, where the corrosion rate is markedly
Amines and alkanolamines and salts thereof have the unique feature to move a considerable distance through hardened reinforced concrete because of their physico-chemical properties. They interact with the reinforcing steel embedded in the concrete resulting in a protection of the reinforcing steel.

According to the invention, it has been found that when certain amino- and/or hydroxyalkylamino compounds are combined with some phosphonic acids and/or derivatives, as well as one or more surfactants, said composition not only provides a corrosion-inhibition of non-corroded reinforcing steel embedded in concrete, but the corrosion rate of already corroded reinforcing steel embedded in a concrete structure can be reduced significantly.

The most preferred amino- and/or hydroxyalkylamino compounds are selected from the group comprising:

- Diethylene triamine
- Triethylene tetramine
- 3'-N, N-Dimethylaminopropyl amine (DMAPA)
- 3-N,N-Dihydroxyethylaminopropyl amine (DHMPA)
- 3-(Methylamino)propylamine
- 3-(Diethylamino)propylamine
- Cyclohexaneamine
- N-Methylcyclohexylamine
- N-Ethylcyclohexylamine
- 2-[(2-Aminoethyl)amino] ethanol
- 1-Amino-2-propanol
- 1-(Methylamino)-2-propanol
- 1-(Dimethylamino)-2-propanol
- 1-(Ethylamino)-2-propanol
- 1-(Cyclohexylamino)-2-propanol
3-Amino-1-propanol
2-Aminoethanol
2-(Methylamino)ethanol
2-(Dimethylamino)ethanol
2-(Ethylamino)ethanol
2-(Diethylamino)ethanol
2-(Butylamino)ethanol
2-[(1,1-Dimethylethyl)amino]ethanol
2-(Cyclohexylamino)ethanol
2,2'-Iminobisethanol
2,2'-(Methylimino)bisethanol
2,2'-[(1,1-Dimethylethyl)imino]bisethanol
3-Amino-1-propanol
2-Aminoethanol
2-(Methylamino)ethanol
2-(Dimethylamino)ethanol
2-(Ethylamino)ethanol
2-(Diethylamino)ethanol
2-(Butylamino)ethanol
2-[(1,1-Dimethylethyl)amino]ethanol
2-(Cyclohexylamino)ethanol
1,1'-Iminobis-2-propanol
2,2'-Iminobisethanol
2,2'-(Methylimino)bisethanol
1,1'-(Methylimino)bis-2-propanol
2,2'-(Butylimino)bisethanol
2,2'-[(1,1-Dimethylethyl)imino]bisethanol
1, 1', 1"-Nitrilotris-2-propanol 2,2',2"-Nitrilotrisethanol

Said phosphonic acid(s) and/or derivatives according to the invention is (are) selected from: alkyl, aryl, alkyl aryl substituted phosphonic acids with or without heteroatom substitution. The most preferred acid(s) and/or the derivatives thereof and/or the carboxylic acid(s) and/or the derivatives thereof of component a) are selected from the group comprising:

Methyl phosphonic acid and/or its anhydride or polyanhydride
Ethyl phosphonic acid and/or its anhydride or polyanhydride
2-Hydroxyethyl phosphonic acid and/or its anhydride or polyanhydride
Phenyl phosphonic acid and/or its anhydride or polyanhydride
Benzyl phosphonic acid and its anhydride or polyanhydride
2-Hydroxyphenyl phosphonic acid and/or its anhydride or polyanhydride
3-Hydroxyphenyl phosphonic acid and/or its anhydride or polyanhydride
4-Hydroxyphenyl phosphonic acid and/or its anhydride or polyanhydride or mixtures thereof.

Suitable amounts of component A) are from 1.0% to 80.0%, preferably from 2% to 50%, by weight, based on the weight of said aqueous corrosion-inhibiting composition.

Said surfactants of component B) are preferably selected from the group comprising:

- substituted propargylic alcohols and diols, N-(Cg-C22-acyl)sarcosine, preferably N-lauroylsarcosine, and/or N-cocoylsarcosine, and/or N-oleylsarcosine, N-(Cg-C22-Acyl)-beta-alanine, preferably N-lauroyl-beta-alanine, and/or N-cocoyl-beta-alanine, and/or N-oleyl-beta-alanine, Cg-C22-fatty acid monoethanolamide, Cg-C22-fatty acid diethanolamide, l-(C6-Ci 2-alkyl)-2-pyrrolidinone, preferably l-octyl-2-pyrrolidinone and/or l-dodecyl-2-pyrrolidinone fluoro-surfactants and alkanolammonium or sodium salt thereof.

Examples of said surfactants include Tetramethyl-5-decyne-4,7-diol (Surfynol 104 - Air products), N-Oleylsarcosine sodium salt, l-Octyl-2-pyrrolidinone.

Said alkanolammonium salts of the corresponding surfactant(s) are based on alkanolamines selected from 2-aminoethanol, 2-(methylamino)ethanol, 2-(butylamino)-ethanol, 2,2'- iminobisethanol, 2,2',2"-nitrilotrisethanol.

Suitable amounts of said surfactants of component B) according to the invention are 0.01% to 10.0%, preferably 0.1% to 5.0%, by weight, based on the weight of said aqueous corrosion inhibiting composition.

The compositions according to the invention may also comprise further components such as biocidal agents, stabilizers etc., as desired.

Subsequent to the disclosed surface-applied treatment, corrosion-inhibiting compounds penetrate into the concrete and adsorb chemically on the surface of both, corroding and non-corroding reinforcing steel. The rates and degree of penetration
of said corrosion-inhibiting compounds are sufficient to cause a reduction of the corrosion rate of corroded reinforcing steel as well as to protect non-corroded reinforcing steel over extended periods of time.

In a preferred embodiment of the invention, the corrosion-inhibiting solution or emulsion or microemulsion is applied on the concrete surface in several coats by brush, by paint roller or by a spraying device in a total amount of 50-2000 g/m², preferably 100-1000 g/m². The addition to fresh water is done together with the concrete mixing water and in a total amount of 0.01 to 10% referred to the cement content, preferably 0.1 to 3%.

A further aspect of the invention is the use of said novel compositions for the rehabilitative reduction of the corrosion rate of corroded steel reinforcements embedded in a hardened, reinforced concrete structure as well as for the precautionary, protective corrosion inhibition of non-corroded steel reinforcements embedded in a hardened, reinforced concrete structure by impregnation of said hardened reinforced concrete structure, or to delay the onset of corrosion of non-corroded reinforcement steel, adding it to the fresh concrete used to prepare a concrete element.

The following example shows that such compositions are able to reduce the corrosion rate of corroding reinforcing steel to a negligible value (repassivation effect) as well as to protect non-corroded steel from corrosion. All component percentages are by weight unless otherwise indicated.

**EXAMPLES**

**EXAMPLE 1**

In this example the effect of the corrosion-inhibiting composition in Table 1 according to the invention on reinforcing steel will be set forth.
This example reports the influence of the corrosion-inhibiting composition from Table 1 according to ASTM G109. The testing was conducted according to the following parameters:

**Concrete Mix Design:**

- Cement: 310 kg/m³ (Lafarge — Type I/1 1):
- Fine Aggregate: 800 kg/m³/(ASTM C 33);
- Coarse Aggregate: 1040 kg/m³ (ASTM C 33) - SSD;
- Vinsol Resin-based air entrainer: 0.14 kg/m³
- Water: 155 kg/m³

**Water/Cement Ratio: 0.50**

**Concrete Mix Information:**

- Slump: S2
- Air Content: 6.2%
- Compressive Strength @ 28 days — 31.1 MPa

**ASTM G 109 - Specimen Information:**

- Number: Three specimens each per test

Test A: corrosion test results according to ASTM G 109 of reference samples

Test specimens: non-treated reference concrete 1
**Specimen A1**

<table>
<thead>
<tr>
<th>Duration</th>
<th>Test Date</th>
<th>Current (µA)</th>
<th>Total Corrosion (coulombs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 month</td>
<td>04/15/13</td>
<td>86</td>
<td>104.1</td>
</tr>
<tr>
<td>2 months</td>
<td>05/15/13</td>
<td>95</td>
<td>338.5</td>
</tr>
<tr>
<td>3 months</td>
<td>06/15/13</td>
<td>133</td>
<td>641.0</td>
</tr>
</tbody>
</table>

**Specimen A2**

<table>
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<tr>
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<th>Test Date</th>
<th>Current (µA)</th>
<th>Total Corrosion (coulombs)</th>
</tr>
</thead>
<tbody>
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<td>79</td>
<td>95.6</td>
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<tr>
<td>2 months</td>
<td>05/15/13</td>
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</tr>
<tr>
<td>3 months</td>
<td>06/15/13</td>
<td>138</td>
<td>637.1</td>
</tr>
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</table>

**Specimen A3**

<table>
<thead>
<tr>
<th>Duration</th>
<th>Test Date</th>
<th>Current (µA)</th>
<th>Total Corrosion (coulombs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 month</td>
<td>04/15/13</td>
<td>69</td>
<td>83.5</td>
</tr>
<tr>
<td>2 months</td>
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<td>286.8</td>
</tr>
<tr>
<td>3 months</td>
<td>06/15/13</td>
<td>128</td>
<td>572.4</td>
</tr>
</tbody>
</table>

**AVERAGE**

Total Corrosion (TC) @ 1 month — 94.4 C
Total Corrosion (TC) @ 2 months — 316.7 C
Total Corrosion (TC) @ 3 months — 616.9 C

**Test B**: corrosion test results according to ASTM G 109 of treated samples.

Test specimens: hardened concrete_1 samples (28dd) treated by applying corrosion inhibitor as described in Table 1 at rate of 200 g/m²

**Specimen B1**

<table>
<thead>
<tr>
<th>Duration</th>
<th>Test Date</th>
<th>Current (µA)</th>
<th>Total Corrosion (coulombs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 month</td>
<td>04/15/13</td>
<td>33</td>
<td>39.9</td>
</tr>
<tr>
<td>2 months</td>
<td>05/15/13</td>
<td>50</td>
<td>147.4</td>
</tr>
<tr>
<td>3 months</td>
<td>06/15/13</td>
<td>128</td>
<td>380.7</td>
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</table>
Specimen B2

<table>
<thead>
<tr>
<th>Duration</th>
<th>Test Date</th>
<th>Current (µA)</th>
<th>Total Corrosion (coulombs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 month</td>
<td>04/15/13</td>
<td>35</td>
<td>42.4</td>
</tr>
<tr>
<td>2 months</td>
<td>05/15/13</td>
<td>44</td>
<td>144.7</td>
</tr>
<tr>
<td>3 months</td>
<td>06/15/13</td>
<td>108</td>
<td>344.5</td>
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</table>

Specimen B3

<table>
<thead>
<tr>
<th>Duration</th>
<th>Test Date</th>
<th>Current (µA)</th>
<th>Total Corrosion (coulombs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 month</td>
<td>04/15/13</td>
<td>30</td>
<td>36.3</td>
</tr>
<tr>
<td>2 months</td>
<td>05/15/13</td>
<td>65</td>
<td>159.3</td>
</tr>
<tr>
<td>3 months</td>
<td>06/15/13</td>
<td>113</td>
<td>392.4</td>
</tr>
</tbody>
</table>

**AVERAGE**

- Total Corrosion (TC) @ 1 month — 39.5 C
- Total Corrosion (TC) @ 2 months — 150.5 C
- Total Corrosion (TC) @ 3 months — 372.5 C

**EXAMPLE 2**

Table 1

**Corrosion Inhibitor Composition #1**

<table>
<thead>
<tr>
<th></th>
<th>Percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Di water</td>
<td>86.52</td>
</tr>
<tr>
<td>Surfynol 104 dpm</td>
<td>0.02</td>
</tr>
<tr>
<td>Butyl cellosolve</td>
<td>1.92</td>
</tr>
<tr>
<td>Phenyl phosphonic acid</td>
<td>5.77</td>
</tr>
<tr>
<td>Triethylene tetra amine (teta)</td>
<td>5.77</td>
</tr>
</tbody>
</table>

Totals: 100.00

This example reports the influence of the corrosion-inhibiting composition from Table 1 according to ASTM G109. The testing was conducted according to the following parameters:

- **Concrete 2_Mix Design:**
  - Cement: 310 kg/m³ (Lafarge — Type 1/1)
  - Fine Aggregate: 800 kg/m³/(ASTM C 33)
Coarse Aggregate: 1040 kg/m$^3$ (ASTM C 33) - SSD;
Vinsol Resin-based air entrainer: 0.14 kg/m$^3$

**Corrosion inhibitor composition #1: 5 kg/m$^3$**
Water: 155 kg/m$^3$
Water/Cement Ratio: 0.50

Concrete Mix Information:
Slump: S2
Air Content: 5.4%
Compressive Strength @ 28 days — 29.7 MPa

ASTM G 109 - Specimen Information:
Number: Three specimens each per test

**Test C**: corrosion test results according to ASTM G 109 of treated samples.
Test specimens: fresh concrete_2 samples (treated by adding corrosion inhibitor as described in Table 2 at dosage of 5kg/m$^3$) cured for 28dd before testing

<table>
<thead>
<tr>
<th>Specimen CI</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Duration</strong></td>
</tr>
<tr>
<td>1 month</td>
</tr>
<tr>
<td>2 months</td>
</tr>
<tr>
<td>3 months</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Specimen C2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Duration</strong></td>
</tr>
<tr>
<td>1 month</td>
</tr>
<tr>
<td>2 months</td>
</tr>
<tr>
<td>3 months</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Specimen C3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Duration</strong></td>
</tr>
<tr>
<td>1 month</td>
</tr>
<tr>
<td>2 months</td>
</tr>
<tr>
<td>3 months</td>
</tr>
</tbody>
</table>
AVERAGE

Total Corrosion (TC) @ 1 month — 28.3 C
Total Corrosion (TC) @ 2 months — 118.6 C
Total Corrosion (TC) @ 3 months — 255.2 C

Table 2

Corrosion Inhibitor Composition #2

<table>
<thead>
<tr>
<th></th>
<th>Percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Di water</td>
<td>8.52</td>
</tr>
<tr>
<td>Surfynol 104 dpm</td>
<td>0.02</td>
</tr>
<tr>
<td>Butyl cellosolve</td>
<td>1.92</td>
</tr>
<tr>
<td>Phenyl phosphonic acid</td>
<td>5.77</td>
</tr>
<tr>
<td>2,2’-iminobisethanol</td>
<td>5.77</td>
</tr>
</tbody>
</table>

Totals 100.00

Table 3

Corrosion Inhibitor Composition #3

<table>
<thead>
<tr>
<th></th>
<th>Percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Di water</td>
<td>86.52</td>
</tr>
<tr>
<td>Surfynol 104 dpm</td>
<td>0.02</td>
</tr>
<tr>
<td>Butyl cellosolve</td>
<td>1.92</td>
</tr>
<tr>
<td>Phenyl phosphonic acid</td>
<td>5.77</td>
</tr>
<tr>
<td>Triethylene tetra amine (teta)</td>
<td>2.53</td>
</tr>
<tr>
<td>2,2’-iminobisethanol</td>
<td>3.24</td>
</tr>
</tbody>
</table>

Totals 100.00
EXAMPLE 3

Table 4

Corrosion Inhibitor Composition #4

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent by weight</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrosion inhibitor composition from Table 1</td>
<td>20.10</td>
<td>Base corrosion inhibitor</td>
</tr>
<tr>
<td>Polidene37-0065 (Scott Bader)</td>
<td>2.01</td>
<td>Film forming polymer</td>
</tr>
<tr>
<td>Silres BS 16 (Wacker)</td>
<td>1.00</td>
<td>Methyl silicone salt</td>
</tr>
</tbody>
</table>

This example reports the influence of the corrosion-inhibiting composition from Table 4 according to ASTM G109. The testing was conducted according to the following parameters:

Concrete 3_Mix Design:
- Cement: 310 kg/m³ (Lafarge — Type 1/1 1):
  - Fine Aggregate: 800 kg/m³ /(ASTM C 33);
  - Coarse Aggregate: 1040 kg/m³ (ASTM C 33) - SSD;
  - Vinsol Resin-based air entrainer: 0.14 kg/m³
  - Water: 155 kg/m³
- Water/Cement Ratio: 0.50

Concrete Mix Information:
- Slump: S2
- Air Content: 5.1%
  - Compressive Strength @ 28 days — 33,1 MPa

ASTM G 109 - Specimen Information:
- Number: Three specimens each per test

Test D: corrosion test results according to ASTM G 109 of treated samples. Test specimens: hardened concrete_3 samples (28dd) treated by applying
corrosion inhibitor as described in Table 5 at rate of 200 g/m²

**Specimen D1**

<table>
<thead>
<tr>
<th>Duration</th>
<th>Test Date</th>
<th>Current (µA)</th>
<th>Total Corrosion (coulombs)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>04/15/13</td>
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<td>21.8</td>
</tr>
<tr>
<td>2 months</td>
<td>05/15/13</td>
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<td>75.8</td>
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<tr>
<td>3 months</td>
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<td>225.9</td>
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</tbody>
</table>

**Specimen D2**

<table>
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<th>Test Date</th>
<th>Current (µA)</th>
<th>Total Corrosion (coulombs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 month</td>
<td>04/15/13</td>
<td>21</td>
<td>25.4</td>
</tr>
<tr>
<td>2 months</td>
<td>05/15/13</td>
<td>42</td>
<td>120.5</td>
</tr>
<tr>
<td>3 months</td>
<td>06/15/13</td>
<td>79</td>
<td>303.3</td>
</tr>
</tbody>
</table>

**Specimen D3**

<table>
<thead>
<tr>
<th>Duration</th>
<th>Test Date</th>
<th>Current (µA)</th>
<th>Total Corrosion (coulombs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 month</td>
<td>04/15/13</td>
<td>21</td>
<td>25.4</td>
</tr>
<tr>
<td>2 months</td>
<td>05/15/13</td>
<td>37</td>
<td>88.6</td>
</tr>
<tr>
<td>3 months</td>
<td>06/15/13</td>
<td>81</td>
<td>267.7</td>
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**AVERAGE**

Total Corrosion (TC) @ 1 month — 24.2 C
Total Corrosion (TC) @ 2 months — 95.0 C
Total Corrosion (TC) @ 3 months — 265.6 C
**CLAIMS**

1. A corrosion-inhibiting composition comprising a solution and/or an emulsion and/or a micro-emulsion of:

   A) one or more amino- and/or hydroxyalkylamino compound(s), partially or completely neutralized with one or more acid(s) selected from the group consisting of any alkyl, aryl, alkyl aryl substituted phosphonic acid soluble in water, whereby said phosphonic acid(s) may optionally contain one or more hydroxyl groups, all in an amount sufficient to inhibit corrosion of said steel reinforcement, and

   B) one or more surfactant(s) and/or co-solvents providing an enhanced wetting and penetration capability by altering the surface tension.

2. A composition according to claim 1 with additionally one or both of:

   - component C characterized in that it is one or more water repellant organic agent selected from the group of silanes, siloxanes, fluorinated hydrocarbons, fluorinated acrylic polymers, and/or other organic film-forming polymers of low surface tension;
   - component D characterized in that it is one or more corrosion inhibitor agent selected from the group of alkali metal and alkaline earth metal nitrates and/or nitrites.

3. A composition according to claim 1 or 2, wherein the amount of the component A) represents from about 1.0% to 60.0% by weight based on the weight of said aqueous solution or emulsion or microemulsion.

4. A Composition according to any one of claims 1-3, wherein the amount of the component B) represents from about 0.01% to 10.0% by weight based on the weight of said aqueous solution or emulsion or microemulsion.

5. A composition according to any one of claims 1-4, wherein the amount of the component C) represents from about 5% to 50.0% by weight based on the weight of
said aqueous solution or emulsion or microemulsion.

6. A composition according to any one of claims 1-5, wherein the amount of the component D) represents from about 5\% to 50.0\% by weight based on the weight of said aqueous solution or emulsion or microemulsion.

5 7. A composition according to any one of claims 1-6, wherein the amino- and/or hydroxyalkylamino compound is selected from:

- Diethylene triamine (DETA)
- Triethylene tetramine
- 2-[(2-Aminoethyl)amino]ethanol;
- 1-Amino-2-propanol;
- 1-(Methylamino)-2-propanol;
- 1-(Dimethylamino)-2-propanol;
- 1-(Ethylamino)-2-propanol;
- 3-Amino-1-propanol;
- 2-Amino ethanol;
- 2-(Methylamino) ethanol;
- 2-(Dimethylamino) ethanol;
- 2-(Ethylamino) ethanol;
- 2-(Diethylamino) ethanol;
- 2-(Butylamino) ethanol;
- 2-[(1,1-Dimethylethyl)amino]ethanol;
- 1,1'-Iminobis-2-propanol;
- 2,2'-Iminobisethanol;
- 2,2'-(Methylamino) bisethanol;
- 1,1'-(Methylimino) bis-2-propanol;
- 2,2'(Butylimino)bisetanol;
- 1,1'1''-Nitrilotris-2-propanol;
- 2,2'2''-Nitrilotrisethanol;
or mixtures thereof.

8. A composition according to any one of claims 1-7, wherein the phosphonic acid(s) are:

- Methyl phosphonic acid and/or its anhydride or poly anhydride
- Ethyl phosphonic acid and/or its anhydride or polyanhydride
- 2-hydroxyethyl phosphonic acid and/or its anhydride or polyanhydride
- Phenyl phosphonic acid and/or its anhydride or poly anhydride
- Benzyl phosphonic acid and its anhydride or poly anhydride
- 2-hydroxyphenyl phosphonic acid and/or its anhydride or poly anhydride
- 3-hydroxyphenyl phosphonic acid and/or its anhydride or poly anhydride
- 4-hydroxyPhenyl phosphonic acid and/or its anhydride or poly anhydride or mixtures thereof.

9. A composition according to any one of claims 1-8, wherein the component B) is:

- N-(Cg-C22 -Acyl)-beta.-alanine, an alkanolammonium or sodium salt thereof;
- N-Cocoyl-beta-alanine, an alkanolammonium or sodium salt thereof,
- N-Oleyl-beta-alanine, an alkanolammonium or sodium salt thereof,
- Cg-C22 -Fatty acid monoethanolamide;
- Cg-C22 -Fatty acid diethanolamide;
- 1-(Cg-C\2-Alkyl)-2-pyrrolidinone;
- Alkylated Propargylic alcohols and diols or mixtures thereof.

10. A compositions according to claim 9, wherein the alkanolamine compound of said surface-active alkanolammonium salts is selected from:

- 2-Aminoethanol;
- 2(Methylamino)ethanol; 2-(Butylamino)ethanol; 2,2'-Iminobisethanol; or 2,2',2"-Nitrilotrisethanol; or mixtures thereof.

11. A composition to any one of claims 1-10, wherein the component C) is
selected from:

Silanes;
Alkylalkoxysilanes;
Oligomeric siloxanes;
Alkali siliconates;
Polyvinylidene fluoride or copolymers derived from vinylidene fluoride;
Polyvinylidine chloride or copolymers derived from C-2 to C-6 vinylidene chloride monomer;
Fluorinated acrylic latex polymers;
dispersion of hydrocarbon resins;
film forming acrylic latex dispersions.

12. The use of the compositions of claims 1-11 for the rehabilitative reduction of the corrosion rate of corroded steel reinforcements embedded in a hardened, reinforced concrete structure as well as for the precautionary, protective corrosion inhibition of non-corroded steel reinforcements embedded in a hardened, reinforced concrete structure by impregnation of said hardened reinforced concrete structure.

13. The use of the compositions of claims 1-11 for the delay of the onset of corrosion of non-corroded reinforcement in fresh concrete, or for the reduction of the corrosion rate of steel reinforcements embedded in a concrete structure.
A. CLASSIFICATION OF SUBJECT MATTER
- C23F11/10
- C04B41/00
- C04B41/46
- C04B41/50
- C04B41/62
- C23F11/14
- C23F11/167
- E04C5/01
- C23F11/08

ADD. According to International Patent Classification (IPC) and both national classification and IPC

B. FIELDS SEARCHED
- Minimum documentation searched (classification system followed by classification symbols)
  - C23F
  - C04B
  - E04C

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

Electronic database consulted during the international search (name of data base and, where practicable, search terms used)
- EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuity of Box C. See patent family annex.

- Special categories of cited documents:
  - "A" document defining the general state of the art which is not considered to be of particular relevance
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- "A" document member of the same patent family

Date of the actual completion of the international search: 2 February 2015

Date of mailing of the international search report: 09/02/2015

Name and mailing address of the ISA:
- European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk
- Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016

Authorized officer: Handrea-Haller, M
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