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Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 591 775 A1

(12)

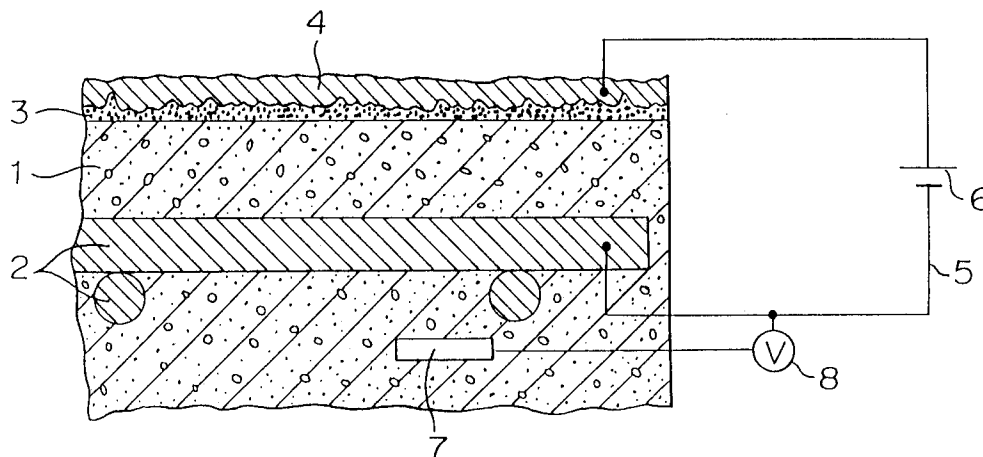
EUROPEAN PATENT APPLICATION(21) Application number: **93115369.6**(51) Int. Cl.⁵: **C23F 13/00, C23F 13/16**(22) Date of filing: **23.09.93**(30) Priority: **07.10.92 JP 268818/92**(43) Date of publication of application:
13.04.94 Bulletin 94/15(84) Designated Contracting States:
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(54) **Method for preventing corrosion of a reinforced concrete structure.**

(57) A method for preventing corrosion of a reinforced concrete structure having a reinforcing steel embedded therein, which comprises coating an aggregate-containing primer on the surface of the reinforced concrete structure, to form a primer layer having a rough surface, metal-spraying aluminum, an aluminum alloy or a zinc-aluminum pseudo alloy on the primer layer to form a metal spray coating layer, and applying a direct current voltage across the metal spray coating layer as an anode and the reinforcing steel as a cathode to conduct a corrosion preventive current.

FIGURE 1**EP 0 591 775 A1**

The present invention relates to a method for preventing corrosion of a reinforced concrete structure. Particularly, it relates to a method for preventing corrosion of a reinforced concrete structure, by means of an impressed current method whereby the reinforcing steel of the reinforced concrete structure can be protected effectively from corrosion for a long period of time.

Concrete structures usually have reinforcing steels embedded therein. Such reinforcing steels are likely to be corroded as a result of carbonation of concrete or by an influence of a salt content contained in the material for concrete or by an influence of chlorine ions or sulfuric acid ions contained in water penetrated into the concrete. Thus, the reinforcing steels of concrete structures had a drawback that the function as a reinforcing material was lost in a relatively short period of time. To prevent corrosion of reinforcing steels, it was common to employ (a) a method of coating a corrosion preventive paint on the surface of a concrete structure, (b) a method for electrolytic protection (cathodic protection) by means of a galvanic anode method, or (c) a method for electrolytic protection (cathodic protection) by means of an impressed current method.

However, (a) the method of coating a corrosion preventive paint on the surface of a concrete structure had a drawback that the coating film formed by the corrosion preventive paint did not have adequate physical strength, and it was susceptible to damages. As a consequence, corrosive factors tended to penetrate through the damaged portions, whereby the coating film was inferior in the corrosion prevention for a long period of time.

Whereas, (b) the method for electrolytic protection by means of a galvanic anode method is a method whereby the maintenance is easy, and when applied to e.g. a marine concrete structure immersed in the sea water, the electrical resistance of the concrete itself is low, so that the corrosion preventive current is easy to flow to provide excellent corrosion prevention. However, when it is applied to a land concrete structure in the atmosphere, the electrical resistance of the concrete itself is high, so that the corrosion preventive current is difficult to flow, whereby there is a drawback that no adequate corrosion prevention can be accomplished.

Whereas, (c) the method for electrolytic protection by means of an impressed current method is excellent in the corrosion prevention of the reinforcing steel for a long period of time, since the applied voltage can be freely adjusted even for a concrete structure in the atmosphere, and this method has been commonly employed.

For this impressed current method, (i) a conductive paint system (e.g. Japanese Unexamined Patent Publication No. 52090/1989) and (ii) a reticular anode system (e.g. WO 86/06759 and Japanese Unexamined Patent Publication No. 25975/1981) are known as typical systems. However, both systems have a drawback such that the practical application is difficult, or the workability is poor.

Namely, (i) the conductive paint system is a method wherein a kerf is formed on the surface of a concrete structure, then a platinum-plated titanium wire is laid in the kerf and an electrical conductive resin for its protection is filled in the kerf, to obtain a primary anode, and as a secondary anode, a carbon type or nickel type conductive paint is coated on the surface of the concrete structure. However, the application of this method is difficult particularly to a concrete structure having a complicated shape, and a number of steps are required to form the kerf on the concrete surface, whereby the workability is poor. Further, blistering or peeling of the coating film is likely to result as time passes, and the platinum-plated titanium wire has a drawback that it is expensive.

On the other hand, (ii) the reticular anode system is an anode system wherein the secondary anode in the above system (i) is omitted by arranging the primary anode connected directly to the power source, in a net form on the concrete surface to make the distribution of a current to the reinforcing steel uniform. Namely, this is a method wherein a titanium expanded mesh provided with a coating film of a platinum group metal oxide or a carbon type expanded mesh having the surface treated, is disposed on the concrete surface, and a mortar is coated thereon. However, the application of this method is difficult particularly to a concrete structure having a complicated shape, and the workability is poor. Further, the overlaid mortar has a problem in its durability, and blistering is likely to result as time passes, and the anode material has a drawback that it is expensive.

Further, as a method for corrosion prevention of a steel plate, a corrosion-preventing method is known wherein an aggregate-containing primer is coated on the surface of a steel plate to form a primer layer having a rough surface, and a metal is metal-sprayed onto the primer layer to form a spray coating layer, for example, in U.S. Patent 4,971,838 or EP 0275083. This corrosion preventing method is capable of effectively protecting the steel plate from corrosion, since a corrosion-preventing film is formed directly on the surface of the steel plate. However, in the case of a reinforced concrete structure, a reinforcing steel is embedded in concrete, and it is impossible by the above corrosion-preventing method to effectively protect the reinforcing steel from corrosion, since a corrosion-preventing film can not directly be formed on such a

reinforcing steel.

It is an object of the present invention to provide a method for corrosion prevention of a reinforced concrete structure, which can easily be applied even to a reinforced concrete structure having a complex shape, and whereby excellent corrosion prevention can be provided efficiently at low costs for a long period of time of at least equal to that attainable by the above-mentioned conventional impressed current methods.

The present inventors have studied the above-mentioned problems inherent to the impressed current method and conducted a research to develop a method for preventing corrosion of a reinforced concrete structure for a long period of time, which is excellent in the workability and can be applied at low costs, while effectively utilizing the feature of the electrolytic protection by the impressed current method. As a result, the present invention has been accomplished.

Thus, the present invention provides a method for preventing corrosion of a reinforced concrete structure having a reinforcing steel embedded therein, which comprises coating an aggregate-containing primer on the surface of the reinforced concrete structure, to form a primer layer having a rough surface, metal-spraying aluminum, an aluminum alloy or a zinc-aluminum pseudo alloy on the primer layer to form a metal spray coating layer, and applying a direct current voltage across the metal spray coating layer as an anode and the reinforcing steel as a cathode to conduct a corrosion preventive current.

In the accompanying drawing, Figure 1 is a cross-sectional side view of a part of a reinforced concrete structure to which corrosion-preventing treatment was applied by the method according to the present invention.

Now, the present invention will be described in detail with reference to the preferred embodiments.

The primer to be used in the present invention is a primer comprising an aggregate and a binder as essential components and having a solvent (or a dispersion medium), a pigment or various additives incorporated as the case requires.

The aggregate to be used in the present invention has an average particle size of from about 10 to 200 μm , preferably from 30 to 100 μm and is the one capable of forming sharp irregularities on the surface of the primer layer.

The aggregate may, for example, be a metal or alloy having the same ionization tendency as the metal-spray coating material, or various metals or alloys having insulation treatment applied at least to their surface, or their oxides (such as aluminum oxide or iron oxide), nitrides or carbides. Further, silicon oxide, silicon carbide, boron nitride or a plastic powder insoluble to a solvent in the primer, may, for example, be mentioned. The amount of such an aggregate to be incorporated, is usually from about 30 to 300 volume %, preferably from 65 to 150 volume %, to the binder, and usually from about 25 to 75%, preferably from 40 to 60% as the pigment volume concentration (PVC). By the aggregate contained in the primer, the surface of the primer layer formed on the concrete structure can be made to have a suitable surface roughness, preferably at a level of a surface roughness (R_z) of from about 40 to 150 μm as prescribed in JIS B 0601. By this surface roughness, it is possible to efficiently form a metal spray coating film excellent in the adhesion on the surface of the reinforced concrete structure without conducting blast treatment.

The binder to be used in the present invention is not particularly limited so long as it is excellent in the drying property, water resistance and adhesion. Conventional binders for coating materials may be used without any particular restriction. For example, one-pack air drying type resin such as chlorinated rubber, an alkyd resin or a vinyl resin, or a two-pack type resin (to be used in combination with a curing agent) such as an epoxy resin, an unsaturated polyester resin, an acryl-urethane resin or a polyester-urethane resin, may be mentioned. In the present invention, a two-pack type epoxy resin excellent in water resistance and adhesion is particularly preferred.

Further, the solvent (or the dispersion medium) to be used as the case requires, may, for example, be a usual organic solvent for a coating material, such as xylene, toluene, butanol, methyl ethyl ketone or butyl acetate, or water. The pigment may, for example, be a filler such as barium sulfate, calcium carbonate or talc, or a coloring pigment such as titanium oxide or carbon black. The additives include a foam-preventing agent, an anti-sagging agent and a dispersant. It is preferred to incorporate from 0 to 50 wt% of the solvent (or the dispersion medium) and from 0 to 30 wt% of the pigment, based on the weight of the primer.

The primer to be used for coating may be of any type such as an organic solvent type, an aqueous type or a liquid non-solvent type.

As the metal spray coating material to form a metal spray coating layer to be used as an anode in the present invention, aluminum, an aluminum alloy or a zinc-aluminum pseudo alloy may be employed. As a metal spray coating material, zinc is known as a typical material, but zinc is likely to wear by e.g. white rust, and even when a protective coating is applied thereon, blistering or the like is likely to form. Therefore, zinc is not suitable for the present invention intended to provide corrosion prevention for a long period of time.

The aluminum alloy is an alloy containing at least 50% by weight of aluminum and having at least one other metal such as Cr, Si, Fe, Ni, Sn, Mg or Zn incorporated.

A metal spray coating formed with aluminum or an aluminum alloy has a merit that wear is little, since the surface of the aluminum itself is oxidized to form a stable and dense coating film.

5 The zinc-aluminum pseudo alloy is a pseudo alloy containing zinc and aluminum in a ratio of Zn:Al = 85:15 to 30:70 (weight ratio).

The metal spray coating formed with such a zinc-aluminum pseudo alloy has a merit that it has a large cohesive force and is highly dense, whereby blistering or the like scarcely occurs.

10 This zinc-aluminum pseudo alloy means a state wherein zinc and aluminum do not form an alloy tissue, and fine zinc particles and fine aluminum particles are overlaid on one another in a non-uniform fashion to present an apparent appearance of a zinc-aluminum alloy. The spray coating film of this zinc-aluminum pseudo alloy can be formed by conducting arc metal-spraying by a low temperature metal-spraying method such as an arc metal-spraying method under reduced pressure, using metal spray wire materials of zinc and aluminum.

15 Figure 1 is a cross-sectional side view of a characteristic part of a typical reinforced concrete structure to which corrosion preventing treatment was applied by the method according to the present invention. Referring to this Figure, the method for preventing corrosion of a reinforced concrete structure of the present invention will be described.

20 The surface of a concrete structure 1 having a reinforcing steel 2 embedded as a reinforcing material, is cleaned to remove deposits such as dusts or oils, as the case requires. Then, the above-mentioned primer is coated thereon and dried to form a primer layer 3. Coating of the primer is conducted by a conventional coating method such as spraying, brush coating or roller coating. The coating amount is adjusted to be usually from about 20 to 400 g/m², preferably from 40 to 200 g/m².

25 Heretofore, in order to improve the adhesion of the spray coating metal film, it has been common to adopt a method wherein the surface of the substrate to be metal-sprayed is subjected to blast treatment to make a rough surface. However, if this blast treatment is applied to the surface of a concrete structure, a dust will be formed, and the working environment and surrounding environment will be thereby polluted. Further, the surface hardness of the concrete structure is relatively low as compared with e.g. steel material, and aggregate material of concrete is likely to fall off from the surface, whereby it is hardly possible to
30 obtain such a sharp roughened surface as is obtainable by the blast treatment of a steel surface, and consequently it has been impossible to form a metal spray coating film excellent in the adhesion. According to the present invention, this problem has been overcome by coating an aggregate-containing primer instead of conducting such blast treatment.

35 On the semi-dried or completely dried primer layer 3 thus obtained, aluminum, an aluminum alloy or a zinc-aluminum pseudo alloy is metal-sprayed to form a spray - coating layer 4 which will serve as an anode.

40 As the method of metal-spraying aluminum or an aluminum alloy, a gas flame-spraying method, an electrical arc spraying method or a low temperature metal-spraying method by means of a reduced pressure arc spraying machine may be mentioned. In the present invention, any one of these methods may be employed. In a case where the primer layer is likely to be burned out if the temperature of sprayed metal particles is high, it is preferred to employ a low temperature metal-spraying method by a reduced pressure arc spraying machine as disclosed in e.g. Japanese Examined Patent Publication No. 24859/1972 or Japanese Unexamined Patent Publication No. 167472/1986.

45 This low temperature metal-spraying method by means of a reduced pressure arc spraying machine is a method wherein a metal wire material is continuously electrically arc-melted under an environment where the central portion is depressurized than the peripheral portion by means of a low temperature air stream jetted in a cylindrical shape, and at the same time, the melted metal is suctioned into a forward jet stream, pulverized and quenched, whereupon the metal particles in a super cooled liquid state are sprayed on the primer layer. In the case of the zinc-aluminum pseudo alloy, metal spraying is conducted by this low
50 temperature metal spraying method.

The thickness of the metal spray coating layer 4 formed on the primer layer 3 is preferably from about 20 to 200 μm, more preferably from 30 to 150 μm. However, the thickness may be as thick as e.g. 1000 μm.

55 The metal spray coating layer 4 thus formed and the reinforcing steel 2 will then be connected by an electrically conductive material 5 having the surface coated with an insulating material, via a power source 6.

According to the present invention, a metal spray coating layer constituting an anode is thus formed on the reinforced concrete surface with the primer layer interposed, and using the reinforcing steel as a

cathode, a direct current voltage is applied by a power source across the reinforcing steel and the metal spray coating layer to conduct a corrosion preventive current, thereby to prevent corrosion of the reinforcing steel embedded in the concrete structure. The direct current voltage is applied so that the potential of the reinforcing steel will be from -1,000 mV to -550 mV (based on a saturated Ag/AgCl electrode), preferably from -900 mV to -600 mV.

In Figure 1, reference numeral 7 is an electrode such as a saturated calomel electrode or a Ag/AgCl electrode, and numeral 8 indicates a voltmeter, and they were provided to measure the potential of the reinforcing steel.

The method for preventing corrosion of a reinforced concrete structure of the present invention is as described in the foregoing. However, in order to prevent wear by rusting of the metal spray coating film, it is advisable to coat a corrosion preventive paint or polymer cement on the metal spray coating layer to provide a protective coating film.

The method of the present invention is applicable not only to newly built or existing marine reinforced concrete structures but also to various reinforced concrete structures such as bridges or tunnels on land.

According to the method of the present invention, the operation will be easy even to a reinforced concrete structure having a complicated shape, and electrolytic corrosion prevention by an impressed current method can be efficiently conducted at low costs, whereby it is possible to obtain a reinforced concrete structure excellent in the corrosion prevention for a long period of time of at least equal to that attainable by electrolytic corrosion prevention by the conventional impressed current methods.

Further, according to the present invention, a rough surface is formed by the primer coating on the surface of the reinforced concrete structure, whereby the adhesion of the metal spray coating layer is excellent, and it is unnecessary to roughen the surface of the reinforced concrete structure by blast treatment which used to be conducted prior to metal-spraying, whereby environmental pollution by a dust generated by such blast treatment can be avoided and the operational time required for such treatment can be saved.

Now, the present invention will be described in further detail with reference to Examples. However, it should be understood that the present invention is by no means restricted by such specific Examples.

Primer

275 g (volume of the solid resin content: 100 cm³) of an epoxy-polyamide resin having 40% nonvolatile, which was prepared by dissolving 100 g of an epoxy resin (Epichlon 4051, trade name, manufactured by Dainippon Ink and Chemicals, Inc.; epoxy equivalent: 950) in 80 g of xylene, 60 g of methyl ethyl ketone and 25 g of butanol and adding 10 g of a polyamide resin (Epicure 892, trade name, manufactured by Ceranese; active hydrogen equivalent: 133) thereto, and 221 g (volume of particles: 70 cm³, PVC: 41%) of silicon carbide having an average particles size of 48 μm (green silicon carbide CG320, trade name, manufactured by Nagoya Kenmakizai Kogyo K.K.; specific gravity: 3.16) were thoroughly stirred to obtain a primer.

Reinforced concrete test specimen

A reinforced concrete test specimen (height × length × width = 900 mm × 900 mm × 100 mm) was used which was prepared by embedding a total of 12 deformed reinforcing steel bars so-called D13 as prescribed by JIS G3112, i.e. 12 bars in a covering depth of 20 mm in concrete, attaching a lead wire to the end of each steel bar and embedding a Ag/AgCl electrode, as shown in Figure 1.

The concrete was prepared by using normal Portland cement at a ratio of water/cement = 60/40 (weight ratio) at a ratio of sand/concrete aggregate = 54/46 (weight ratio) and in a unit amount of cement of 320 kg/m³. To avoid an influence of the effects of the end portions, the four side surfaces other than the surface on which a metal spray coating film was to be applied, were sealed by coating a solventless epoxy resin coating material thereon. However, the rear side surface opposite to the surface on which the metal spray coating was applied, was non-treated.

EXAMPLE 1

The surface of the reinforced concrete test specimen was cleaned by high pressure water washing. Then, the primer was coated thereon by an air spray in an amount of 50 g/m² and dried in air for 2 hours to form a primer layer having a surface roughness (R_z) of 60 μm.

Then, an aluminum wire material was metal-sprayed onto the primer layer by a reduced pressure arc spraying machine (PA-100, manufactured by Pan Art Craft Co.) to form a metal spray coating layer having a thickness of 80 μm . The metal spray coating layer as an anode was connected to the lead wires attached to the ends of steel bars as a cathode via a power source as shown in Figure 1.

The metal-spraying was conducted by low temperature metal-spraying by using an aluminum wire having a diameter of 1.1 mm at a wire conveying speed of 5 m/min at a voltage of 17 V at a current of 120 A under an air pressure of 6 kg/cm² at an air flow rate of 1 m³/min at a spray distance of 20 cm.

EXAMPLE 2

A test specimen was prepared in the same manner as in Example 1 except that after forming a primer layer in the same manner as in Example 1, a metal spray coating of a zinc-aluminum pseudo alloy [Zn/Al = 72/28 (weight ratio)] was formed on the primer layer by means of a reduced pressure arc spraying machine (PA-100, manufactured by Pan Art Craft Co.), and an acrylic resin polymer cement paint was further coated thereon to form a protective coating film of 100 μm . The metal-spraying was conducted by low temperature metal-spraying using a zinc wire and an aluminum wire each having a diameter of 1.1 mm at a wire conveying speed of 6 m/min at a voltage of 15 V at a current of 120 A under an air pressure of 6 kg/cm² at an air flow rate of 1 m³/min at a spray distance of 20 cm.

COMPARATIVE EXAMPLE 1

In the same manner as in Example 1, an aluminum spray coating layer was formed, and the spray coating layer as an anode was connected to the lead wires attached to the ends of steel bars as a cathode via a power source, except that the surface was roughened by sand blast treatment instead of forming a primer layer on the surface of the reinforced concrete test specimen.

COMPARATIVE EXAMPLE 2

A titanium mesh (aperture : 35 \times 70 mm) having a platinum-type metal oxide coating applied thereto, was put on the surface of a reinforced concrete test specimen, and an acrylic resin type polymer cement mortar was coated thereon to form a protective layer of 20 mm. The mesh as an anode was connected to lead wires attached to the ends of steel bars as a cathode via a power source.

With respect to the test specimens obtained in Examples 1 and 2 and Comparative Examples 1 and 2, the potentials of steel bars were monitored by Ag/AgCl electrodes preliminarily embedded at the positions of the steel bars, and an electric current was conducted while adjusting the current so that the monitored value would always be -800 mV, and the following cycle test was conducted.

Cycle test method

A specimen was left to stand in a constant temperature chamber at a temperature of 20 °C under a relative humidity of 60% for 24 hours and then immersed in a 3% sodium chloride aqueous solution at 50 °C for 24 hours. This process was regarded as one cycle and repeated 100 cycles.

Measurement of the natural potential after the 100 cycle test, measurement of the current density (using a small current ampere meter) and inspection of the outer appearance after each cycle and inspection of the rusted area (%) of the steel bars after the 100 cycle test, were conducted. The results are shown in Table 1.

Table 1

Test items	Examples		Comparative Examples		
	1	2	1	2	Non-treated
Natural potential after 100 cycle test (unit: mV)	-165	-170	-500	-180	-485
Current density (unit: $\mu\text{A}/\text{cm}^2$)					
5 cycles	12	12	11	12	-
10 cycles	12	11	12	10	-
20 cycles	10	10	11	11	-
40 cycles	8	9	9	10	-
60 cycles	9	8	7	8	-
80 cycles	8	8	6	8	-
100 cycles	7	8	4	8	-

Table 1 (continued)

Test items	Example		Comparative Example		
	1	2	1	2	Non-treated
Outer appearance					
5 cycles	No change	No change	No change	No change	No change
10 cycles	No change	No change	No change	No change	No change
20 cycles	No change	No change	No change	No change	Dotted rust appeared
40 cycles	No change	No change	No change	No change	Little cracks
60 cycles	No change	No change	Less than 5% of metal spray coating peeled	No change	Many cracks
80 cycles	No change	No change	About 10% of metal spray coating peeled	No change	Cracks enlarged
100 cycles	No change	No change	About 20% of metal spray coating peeled	No change	Cracks enlarged
Rusted area of steel bars (unit: %)	5>	5>	About 15	5>	95<

It is evident from Table 1 that in Examples 1 and 2 wherein corrosion prevention was conducted by the method of the present invention, the operation was efficient and inexpensive, and corrosion prevention was substantially equal, as compared with Comparative Example 2 wherein corrosion prevention was conducted by a conventional mesh anode system.

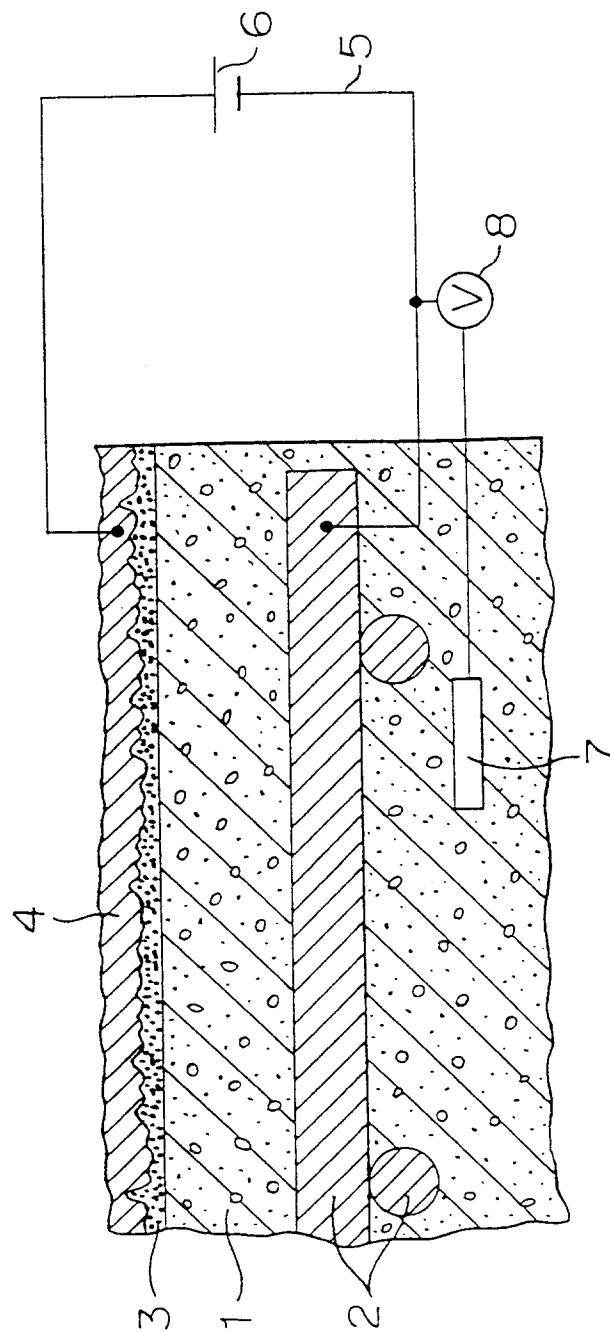
In Comparative Example 1 wherein blast treatment was conducted, the metal spray coating film had poor adhesion and peeled off, and the specimen was poor in corrosion prevention for a long period of time.

Further, the non-treated test specimen showed cracking in the concrete, and rust formed substantially over the entire surface of the steel bars.

Claims

- 5 1. A method for preventing corrosion of a reinforced concrete structure having a reinforcing steel embedded therein, which comprises coating an aggregate-containing primer on the surface of the reinforced concrete structure, to form a primer layer having a rough surface, metal-spraying aluminum,
10 an aluminum alloy or a zinc-aluminum pseudo alloy on the primer layer to form a metal spray coating layer, and applying a direct current voltage across the metal spray coating layer as an anode and the reinforcing steel as a cathode to conduct a corrosion preventive current.
- 15 2. The method for preventing corrosion of a reinforced concrete structure according to Claim 1, wherein the primer layer is a layer having a surface roughness (Rz) of from 40 to 150 μm .
3. The method for preventing corrosion of a reinforced concrete structure according to Claim 1, wherein a protective coating film is formed on the metal spray coating layer.

FIGURE 1





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EUROPEAN SEARCH REPORT

Application Number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 93115369.6
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	<u>US - A - 4 931 156</u> (DOWD et al.) * Totality * --	1	C 23 F 13/00 C 23 F 13/16
A	<u>DE - A - 3 826 926</u> (HERAEUS ELEKTRODEN) * Totality * --	1	
P, A	<u>US - A - 5 225 058</u> (BAZZONI et al.) * Example 1; claim 13 * ----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 23 F E 04 B E 02 D H 01 B
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 30-12-1993	Examiner SEIRAFI
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	