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Remarks:
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(54) Electrodeposition medium

(57) The present invention relates to a cathodic electrodeposition medium for forming a deposit on the surface of a metallic or conductive surface. The medium comprises a combination of water, silica, at least one water soluble silicate, and at least one water soluble dopant wherein the medium has a basic pH. The resulting deposit imparts improved corrosion resistance to the underlying substrate. In the preferred embodiment, the medium comprises sodium silicate and has a pH of greater than approximately 10.

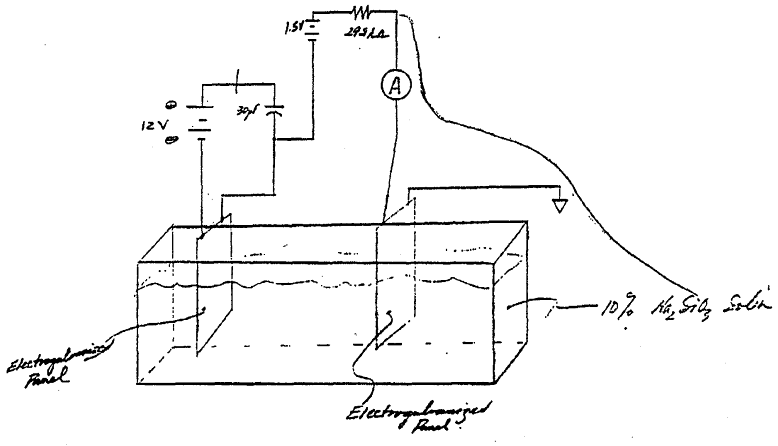

Fig 1

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Description

FIELD OF THE INVENTION

[0001] The instant invention relates to a medium for forming a deposit on the surface of a metallic or conductive surface. The medium deposits a mineral containing coating or film upon a metallic or conductive surface.

BACKGROUND OF THE INVENTION

[0002] Silicates have been used in electrocleaning operations to clean steel, tin, among other surfaces. Electrocleaning is typically employed as a cleaning step prior to an electroplating operation. Using "Silicates As Cleaners In The Production of Tinplate" is described by L.J. Brown in February 1966 edition of Plating.

[0003] Processes for electrolytically forming a protective layer or film by using an anodic method are disclosed by U.S. Patent No. 3,658,662 (Casson, Jr. et al.), and United Kingdom Patent No. 498,485; both of which are hereby incorporated by reference.

[0004] U.S. Patent No. 5,352,342 to Riffe, which issued on October 4, 1994 and is entitled "Method And Apparatus For Preventing Corrosion Of Metal Structures" that describes using electromotive forces upon a zinc solvent containing paint.

SUMMARY OF THE INVENTION

[0005] The instant invention solves problems associated with conventional practices by providing a medium for a cathodic method for forming a protective layer upon a metallic substrate. The cathodic method is normally conducted by immersing a electrically conductive substrate into a silicate containing bath wherein a current is pased through the bath and the substrate is the cathode. A mineral layer comprising an amorphous matrix surrounding or incorporating metal silicate crystals forms upon the substrate. The mineral layer imparts improved corrosion resistance, among other properties, to the underlying substrate.

[0006] The inventive medium is also a marked improvement as solvents or solvent containing systems are not required to form a corrosion resistant layer, i.e., a mineral layer. In contrast, to conventional compositions the inventive medium is substantially solvent free. By "substantially solvent free" it is meant that less than about 5 wt.%, and normally less than about 1 wt.% volatile organic compounds (V.O.C.s) are present in the electrolytic environment.

[0007] Conventional electrocleaning processes sought to avoid formation of oxide containing products such as greenalite whereas the instant invention relates to a medium for forming a mineral layer.

BRIEF DESCRIPTION OF THE DRAWING

[0008]

Figure 1 is a schematic drawing of the circuit and apparatus which can be employed for contacting an embodiment of a medium in accordance with the present invention with a metal surface.

DETAILED DESCRIPTION

[0009] The instant invention relates to a medium according to Claim 1. The medium is employed in a process an electrically enhanced method to obtain a mineral coating or film upon a metallic or conductive surface. By "mineral containing coating," it is meant to refer to a relatively thin coating or film which is formed upon a metal or conductive surface wherein at least a portion of the coating or film includes at least one of metal atom containing mineral, e.g., an amorphous phase or matrix surrounding or incorporating crystals comprising a zinc disilicate. Mineral and Mineral Containing are defined in the previously identified Copending and Commonly Assigned Patents and Patent Applications; incorporated by reference. By "electroyltic" or "electrodeposition" or "electrically enhanced", it is meant to refer to an environment created by passing an electrical current through a silicate containing medium while in contact with an electrically conductive substrate wherein the substrate functions as the cathode.

[0010] The electroyltic environment can be established in any suitable manner including immersing the substrate, applying a silicate containing coating upon the substrate and thereafter applying an electrical current, among others. The preferred method for establishing the environment will be determined by the size of the substrate, electroplating time, among other parameters known in the electrodeposition art.

[0011] The silicate containing medium can be a fluid bath, gel, spray, among other methods for contacting the substrate with the silicate medium. Examples of the silicate medium comprise a bath containing at least one alkali silicate, a gel comprising at least one alkali silicate and a thickener, among others. Normally, the medium comprises a bath of sodium silicate.

[0012] The metal surface refers to a metal article as well as a non-metallic or an electrically conductive member having an adhered metal or conductive layer. Examples of suitable metal surfaces comprise at least one member selected from the group consisting of galvanized surfaces, zinc, iron, steel, brass, copper, nickel, tin, aluminum, lead, cadmium, magnesium, alloys thereof, among others. The mineral layer can be formed on a nonconductive substrate having at least one surface coated with an electrically conductive material, e.g., a ceramic material encapsulated within a metal. Conductive surfaces can also include carbon or graphite as well as conductive polymers (polyaniline for example).

[0013] The mineral coating can enhance the surface characteristics of the metal or conductive surface such as resistance to corrosion, protect carbon (fibers for example) from oxidation and improve bonding strength in composite materials, and reduce the conductivity of conductive polymer surfaces including potential application in sandwich type materials.

[0014] In one embodiment of the invention, the silicate medium is modified to include one or more dopant materials. While the cost and handling characteristics of sodium silicate are desirable, at least one member selected from the group of water soluble salts and oxides of tungsten, molybdenum, chromium, titanium, zircon, vanadium, phosphorus, aluminum, iron, boron, bismuth, gallium, tellurium, germanium, antimony, niobium (also known as columbium), magnesium and manganese, mixtures thereof, among others, and usually, salts and oxides of aluminum and iron can be employed along with or instead of a silicate. The dopant materials can be introduced to the metal or conductive surface in pretreatment steps prior to electrodeposition, in post treatment steps following electrodeposition, and/or by alternating electrolytic dips in solutions of dopants and solutions of silicates if the silicates will not form a stable solution with the water soluble dopants. When sodium silicate is employed as a mineral solution, desirable results can be achieved by using N grade sodium silicate supplied by Philadelphia Quartz (PQ) Corporation. The presence of dopants in the mineral solution can be employed to form tailored mineral containing surfaces upon the metal or conductive surface, e.g, an aqueous sodium silicate solution containing aluminate can be employed to form a layer comprising oxides of silicon and aluminum.

[0015] The silicate solution can also be modified by adding water soluble polymers, and the elctrodeposition solution itself can be in the form of a flowable gel consistency. A suitable composition can be obtained in an aqueous composition comprising 3 wt% N-grade Sodium Silicate Solution (PQ Corp), 0.5 wt% Carbopol EZ-2 (BF Goodrich), about 5 to 10 wt.% fumed silica, mixtures thereof, among others . Furthers the aqueous silicate solution can be filled with a water dispersible polymer such as polyurethane to electro deposit a mineral-polymer composite coating. The characteristics of the electrodeposition solution can be modified or tailored by using an anode material as a source of ions which can be available for codeposition with the mineral anions and/or one or more dopants. The dopants can be useful for building additional thickness of the electrodeposited mineral layer.

[0016] The following sets forth the parameters which may be employed for tailoring the process to obtain a desirable mineral containing coating :

1. Voltage
2. Current Density
3. Apparatus or Cell Design
4. Deposition Time
5. Concentration of the N-grade sodium silicate solution
7. Type and concentration of anions in solution
8. Type and concentration of cations in solution
9. Composition of the anode
10. Composition of the cathode
11. Temperature
12. Pressure
13. Type and Concentration of Surface Active Agents

[0017] The specific ranges of the parameters above depend on the substrate to be deposited on and the intended composition to be deposited. Items 1, 2, 7, and 8 can be especially effective in tailoring the chemical and physical characteristics of the coating. That is, items 1 and 2 can affect the deposition time and coating thickness whereas items 7 and 8 can be employed for introducing dopants that impart desirable chemical characteristics to the coating. The differing types of anions and cations can comprise at least one member selected from the group consisting of Group I metals, Group II metals, transition and rare earth metal oxides, oxyanions such as mineral, molybdate, phosphate, titanate, boron nitride, silicon carbide, aluminum nitride, silicon nitride, mixtures thereof, among others.

[0018] The x-ray photoelectron spectroscopy (ESCA) data in the following Examples demonstrate the presence of a unique metal disilicate species within the mineralized layer, e.g., ESCA measures the binding energy of the photoelectrons of the atoms present to determine bonding characteristics.

[0019] The following Examples are provided to illustrate certain aspects of the invention and it is understood that such an Example does not limit the scope of the invention as defined in the appended claims.

EXAMPLE 1

[0020] The following apparatus and materials were employed in this Example:

Standard Electrogalvanized Test Panels, ACT Laboratories
10% (by weight) N-grade Sodium Mineral solution
12 Volt EverReady battery
1.5 Volt Ray-O-Vac Heavy Duty Dry Cell Battery
Triplett RMS Digital Multimeter
30 µF Capacitor
29.8 kΩ Resistor

[0021] A schematic of the circuit and apparatus which were employed for practicing the Example are illustrated in Figure 1. Referring now to Figure 1, the aforementioned test panels were contacted with a solution comprising 10% sodium mineral and deionized water. A current was passed through the circuit and solution in the manner illustrated in Figure 1. The test panels was exposed for 74 hours under ambient environmental conditions. A visual inspection of the panels indicated that a light-grey colored coating or film was deposited upon the test panel.

[0022] In order to ascertain the corrosion protection afforded by the mineral containing coating, the coated panels were tested in accordance with ASTM Procedure No. B 117. A section of the panels was covered with tape so that only the coated area was exposed and. thereafter, the taped panels were placed into salt spray. For purposes of comparison, the following panels were also tested in accordance with ASTM Procedure No. B117, 1) Bare Electrogalvanized Panel, and 2) Bare Electrogalvanized Panel soaked for 70 hours in a 10% Sodium Mineral Solution. In addition, bare zinc phosphate coated steel panels(ACT B952, no Parcolene) and bare iron phosphate coated steel panels (B1000, no Parcolene) were subjected to salt spray for reference.

[0023] The results of the ASTM Procedure are listed in the Table below:

Panel Description	Hours in B117 Salt Spray
Zinc phosphate coated steel	1
Iron phosphate coated steel	1
Standard Bare Electrogalvanize Panel	≈ 120
Standard Panel with Sodium Mineral Soak	≈ 120
Coated Cathode of the Invention	240+

[0024] The above Table illustrates that the instant invention forms a coating or film which imparts markedly improved corrosion resistance. It is also apparent that the process has resulted in a corrosion protective film that lengthens the life of electrogalvanized metal substrates and surfaces.

[0025] ESCA analysis was performed on the zinc surface in accordance with conventional techniques and under the following conditions:

Analytical conditions for ESCA:

[0026]

Instrument	Physical Electronics Model 5701 LSci
X-ray source	Monochromatic aluminum
Source power	350 watts
Analysis region	2 mm X 0.8 mm

(continued)

Exit angle*	50°
Electron acceptance angle	±7°
Charge neutralization	electron flood gun
Charge correction	C-(C,H) in C 1s spectra at 284.6 eV

* Exit angle is defined as the angle between the sample plane and the electron analyzer lens.

[0027] The silicon photoelectron binding energy was used to characterized the nature of the formed species within the mineralized layer that was formed on the cathode. This species was identified as a zinc disilicate modified by the presence of sodium ion by the binding energy of 102.1 eV for the Si(2p) photoelectron.

EXAMPLE 2

[0028] This Example illustrates performing the electrodeposition process at an increased voltage and current in comparison to Example 1.

[0029] Prior to the electrodeposition, the cathode panel was subjected to preconditioning process:

1) 2 minute immersion in a 3:1 dilution of Metal Prep 79 (Parker Amchem),
2) two deionized rinse,
3) 10 second immersion in a pH 14 sodium hydroxide solution,
4) remove excess solution and allow to air dry,
5) 5 minute immersion in a 50% hydrogen peroxide solution,
6) Blot to remove excess solution and allow to air dry.

[0030] A power supply was connected to an electrodeposition cell consisting of a plastic cup containing two standard ACT cold roll steel (clean, unpolished) test panels. One end of the test panel was immersed in a solution consisting of 10% N grade sodium mineral (PQ Corp.) in deionized water. The immersed area (1 side) of each panel was approximately 8 cm by 10 cm (80 cm^2)(3 inches by 4 inches (12 sq. in.)) for a 1:1 anode to cathode ratio. The panels were connected directly to the DC power supply and a voltage of 6 volts was applied for 1 hour. The resulting current ranged from approximately 0.7-1.9 Amperes. The resultant current density ranged from 0.008-0.02 amps/cm (0.05-0.16 amps/in^2).

[0031] After the electrolytic process, the coated panel was allowed to cry at ambient conditions and then evaluated for humidity resistance in accordance with ASTM Test No. D2247 by visually monitoring the corrosion activity until development of red corrosion upon 5% of the panel surface area. The coated test panels lasted 25 hours until the first appearance of red corrosion and 120 hours until 5% red corrosion. In comparison, conventional iron and zinc phosphated steel panels develop first corrosion and 5% red corrosion after 7 hours in ASTM D2247 humidity exposure. The above Examples, therefore, illustrate that the inventive process offers an improvement in corrosion resistance over iron and zinc phosphated steel panels.

EXAMPLE 3

[0032] Two lead panels were prepared from commercial lead sheathing and cleaned in 6M HCl for 25 minutes. The cleaned lead panels were subsequently placed in a solution comprising 1 wt.% N-grade sodium silicate (supplied by PQ Corporation).

[0033] One lead panel was connected to a DC power supply as the anode and the other was a cathode. A potentional of 20 volts was applied initially to produce a current ranging from 0.9 to 1.3 Amperes. After approximately 75 minutes the panels were removed from the sodium silicate solution and rinsed with deionized water.

[0034] ESCA analysis was performed on the lead surface. The silicon photoelectron binding energy was used to characterized the nature of the formed species within the mineralized layer. This species was identified as a lead disilicate modified by the presence of sodium ion by the binding energy of 102.0 eV for the Si(2p) photoelectron.

EXAMPLE 4

[0035] This Example demonstrates forming a mineral surface upon an aluminum substrate. Using the same apparatus in Example 1, aluminum coupons (3" x 6") were reacted to form the metal silicate surface. Two different alloys of aluminum were used, A1 2024 and A17075. Prior to the panels being subjected to the electrolytic process, each panel was prepared using the methods outlined below in Table A. Each panel was washed with reagent alcohol to remove any excessive dirt and oils. The panels were either cleaned with Alumiprep 33, subjected to anodic cleaning or both. Both forms of cleaning are designed to remove excess aluminum oxides. Anodic cleaning was accomplished by placing the working panel as an anode into an aqueous solution containing 5% NaOH, 2.4% Na_2CO_3, 2% Na_2SiO_3, 0.6% Na_3PO_4, and applying a potential to maintain a current density of 100mA/cm^2 across the immersed area of the panel for one minute.

[0036] Once the panel was cleaned, it was placed in a 1 liter beaker filled with 800 mL of solution. The baths were prepared using deionized water and the contents are shown in the table below. The panel was attached to the negative lead of a DC power supply by a wire while another panel was attached to the positive lead. The two panels were spaced 5 cm(2inches) apart from each other. The potential was set to the voltage shown on the table and the cell was run for one hour.

TABLE A

Example	A	B	C	D	E	F	G	H
Alloy type	2024	2024	2024	2024	7075	7075	7075	7075
Anodic Cleaning	Yes	Yes	No	No	Yes	Yes	No	No
Acid Wash	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Bath Solution								
Na_2SiO_3	1%	10%	1%	10%	1%	10%	1%	10%
H_2O_2	1%	0%	0%	1%	1%	0%	0%	1%
Potential	12V	18V	12V	18V	12V	18V	12V	18V

[0037] ESCA was used to analyze the surface of each of the substrates. Every sample measured showed a mixture of silica and metal silicate. Without wishing to be bound by any theory or explanation, it is believed that the metal silicate is a result of the reaction between the metal cations of the surface and the alkali silicates of the coating. It is also believed that the silica is a result of either excess silicates from the reaction or precipitated silica from the coating removal process. The metal silicate is indicated by a Si (2p) binding energy (BE) in the low 102 eV range, typically between 102.1 to 102.3. The silica can be seen by Si(2p) BE between 103.3 to 103.6 eV. The resulting spectra show overlapping peaks, upon deconvolution reveal binding energies in the ranges representative of metal silicate and silica.

EXAMPLE 5

[0038] This Example illustrates an alternative to immersion for creating the silicate containing medium.

[0039] An aqueous gel made from 5% sodium silicate and 10% fumed silica was used to coat cold rolled steel panels. One panel was washed with reagent alcohol, while the other panel was washed in a phosphoric acid based metal prep, followed by a sodium hydroxide wash and a hydrogen peroxide bath. The apparatus was set up using a DC power supply connecting the positive lead to the steel panel and the negative lead to a platinum wire wrapped with glass wool. This setup was designed to simulate a brush plating operation. The "brush" was immersed in the gel solution to allow for complete saturation. The potential was set for 12V and the gel was painted onto the panel with the brush. As the brush passed over the surface of the panel, hydrogen gas evolution could be seen. The gel was brushed on for five minutes and the panel was then washed with DI water to remove any excess gel and unreacted silicates.

[0040] ESCA was used to analyze the surface of each steel panel. ESCA detects the reaction products between the metal substrate and the environment created by the electrolytic process. Every sample measured showed a mixture of silica and metal silicate. The metal silicate is a result of the reaction between the metal cations of the surface and the alkali silicates of the coating. The silica is a result of either excess silicates from the reaction or precipitated silica from the coating removal process. The metal silicate is indicated by a Si (2p) binding energy (BE) in the low 102 eV range, typically between 102.1 to 102.3. The silica can be seen by Si(2p) BE between 103.3 to 103.6 eV. The resulting spectra show overlapping peaks, upon deconvolution reveal binding energies in the ranges representative of metal silicate and silica.

EXAMPLE 6

[0041] Using the same apparatus in Example 1, cold rolled steel coupons (ACT laboratories) were reacted to form the metal silicate surface. Prior to the panels being subjected to the electrolytic process, each panel was prepared using the methods outlined below in Table B. Each panel was washed with reagent alcohol to remove any excessive dirt and oils. The panels were either cleaned with Metalprep 79 (Parker Amchem), subjected to anodic cleaning or both. Both forms of cleaning are designed to remove excess metal oxides. Anodic cleaning was accomplished by placing the working panel as an anode into an aqueous solution containing 5% NaOH, 2.4% Na_2CO_3, 2% Na_2SiO_3, 0.6% Na_3PO_4, and applying a potential to maintain a current density of 100mA/cm^2 across the immersed area of the panel for one minute.

[0042] Once the panel was cleaned, it was placed in a 1 liter beaker filled with 800 mL of solution. The baths were prepared using deionized water and the contents are shown in the table below. The panel was attached to the negative lead of a DC power supply by a wire while another panel was attached to the positive lead. The two panels were spaced inches apart from each other. The potential was set to the voltage shown on the table and the cell was run for one hour.

TABLE B

Example	AA	BB	CC	DD	EE
Substrate type	CRS	CRS	CRS	CRS[1]	CRS[2]
Anodic Cleaning	No	Yes	No	No	No
Acid Wash	Yes	Yes	Yes	No	No
Bath Solution					
Na_2SiO_3	1%	10%	1%	-	-
Potential (V)	14-24	6 (CV)	12V (CV)	-	-
Current Density	23 (CC)	23-10	85-48	-	-
(mA/cm^2) B177	2hrs	1 hr	1 hr	0.25 hr	0.25 hr

[1] Cold Rolled Steel Control- No treatment was done to this panel.

[2] Cold Rolled Steel with iron phosphate treatment (ACT Laboratories)- No further treatments were performed

[0043] The electrolytic process was either run as a constant current or constant voltage experiment, designated-by the CV or CC symbol in the table. Constant Voltage experiments applied a constant potential to the cell allowing the current to fluctuate while Constant Current experiments held the current by adjusting the potential. Panels were tested for corrosion protection using ASTM B117. Failures were determined at 5% surface coverage of red rust.

[0044] ESCA was used to analyze the surface of each of the substrates. ESCA detects the reaction products between the metal substrate and the environment created by the electrolytic process. Every sample measured showed a mixture of silica and metal silicate. The metal silicate is a result of the reaction between the metal cations of the surface and the alkali silicates of the coating. The silica is a result of either excess silicates from the reaction or precipitated silica from the coating removal process. The metal silicate is indicated by a Si (2p) binding energy (BE) in the low 102 eV range, typically between 102.1 to 102.3. The silica can be seen by Si(2p) BE between 103.3 to 103.6 eV. The resulting spectra show overlapping peaks, upon deconvolution reveal binding energies in the ranges representative of metal silicate and silica.

EXAMPLE 7

[0045] Using the same apparatus in Example 1, zinc galvanized steel coupons (EZG 60G ACT Laboratories) were reacted to form the metal silicate surface. Prior to the panels being subjected to the electrolytic process, each panel was prepared using the methods outlined below in Table C. Each panel was washed with reagent alcohol to remove any excessive dirt and oils.

[0046] Once the panel was cleaned, it was placed in a 1 liter beaker filled with 800 mL of solution. The baths were prepared using deionized water and the contents are shown in the table below. The panel was attached to the negative lead of a DC power supply by a wire while another panel was attached to the positive lead. The two panels were spaced approximately 5 cm (2 inches) apart from each other. The potential was set to the voltage shown on the table and the cell was run for one hour.

TABLE C

Example	A1	B2	C3	D5
Substrate type	GS	GS	GS	GS[1]
Bath Solution Na_2SiO_3	10%	1%	10%	-

[1] IGalvanized Steel Control- No treatment was done to this panel.

TABLE C (continued)

Example	A1	B2	C3	D5
Potential (V)	6 (CV)	10 (CV)	18 (CV)	-
Current Density (mA/cm^2)	22-3	7-3	142-3	-
B177	336 hrs	224 hrs	216 hrs	96 hrs

[0047] Panels were tested for corrosion protection using ASTM B117. Failures were determined at 5% surface coverage of red rust.

[0048] ESCA was used to analyze the surface of each of the substrates. ESCA detects the reaction products between the metal substrate and the environment created by the electrolytic process. Every sample measured showed a mixture of silica and metal silicate. The metal silicate is a result of the reaction between the metal cations of the surface and the alkali silicates of the coating. The silica is a result of either excess silicates from the reaction or precipitated silica from the coating removal process. The metal silicate is indicated by a Si (2p) binding energy (BE) in the low 102 eV range, typically between 102.1 to 102.3. The silica can be seen by Si(2p) BE between 103.3 to 103.6 eV. The resulting spectra show overlapping peaks, upon deconvolution reveal binding energies in the ranges representative of metal silicate and silica.

EXAMPLE 8

[0049] Using the same apparatus in Example 1, copper coupons (C 110 Hard, Fullerton Metals) were reacted to form the metal silicate surface. Prior to the panels being subjected to the electrolytic process, each panel was prepared using the methods outlined below in Table D. Each panel was washed with reagent alcohol to remove any excessive dirt and oils.

[0050] Once the panel was cleaned, it was placed in a 1 liter beaker filled with 800 mL of solution. The baths were prepared using deionized water and the contents are shown in the table below. The panel was attached to the negative lead of a DC power supply by a wire while another panel was attached to the positive lead. The two panels were spaced 5 cm (2 inches)apart from each other. The potential was set to the voltage shown on the table and the cell was run for one hour.

TABLE D

Example	AA1	BB2	CC3	DD4	EE5
Substrate type	Cu	Cu	Cu	Cu	Cu[1]
Bath Solution					
Na_2SiO_3	10%	10%	1%	1%	-
Potential (V)	12 (CV)	6 (CV)	6 (CV)	36 (CV)	-
Current Density (mA/cm^2)	40-17	19-9	4-1	36-10	-
B117	11 hrs	11hrs	5 hrs	5 hrs	2hrs

[1] Copper Control- No treatment was done to this panel.

[0051] Panels were tested for corrosion protection using ASTM B117. Failures were determined by the presence of copper oxide which was indicated by the appearance of a dull haze over the surface.

[0052] ESCA was used to analyze the surface of each of the substrates. ESCA allows us to examine the reaction products between the metal substrate and the environment set up from the electrolytic process. Every sample measured showed a mixture of silica and metal silicate. The metal silicate is a result of the reaction between the metal cations of the surface and the alkali silicates of the coating. The silica is a result of either excess silicates from the reaction or precipitated silica from the coating removal process. The metal silicate is indicated by a Si (2p) binding energy (BE) in the low 102 eV range, typically between 102.1 to 102.3. The silica can be seen by Si(2p) BE between 103.3 to 103.6 eV. The resulting spectra show overlapping peaks, upon deconvolution reveal binding energies in the ranges representative of metal silicate and silica.

Claims

1. A cathodic electrodeposition medium comprising a combination comprising water, silica, at least one water soluble silicate, and at least one water soluble dopant wherein the medium has a basic pH.

2. The medium of claim 1 wherein the water soluble silicate comprises sodium silicate.

3. The medium of claim 1 or claim 2 wherein the medium further comprises a cathode comprising at least one member selected from the group consisting of lead, copper, zinc, aluminum, stainless steel and steel.

4. The medium of any one of claims 1 to 3 wherein the medium comprises at least one member from the group consisting of a fluid bath, gel or spray.

5. The medium of any one of the preceding claims wherein the dopant comprises at least one member selected from the group consisting of molybdenum, chromium, titanium, zirconium, vanadium, phosphorus, aluminum, iron, boron, bismuth, gallium, tellurium, germanium, antimony, niobium, magnesium, manganese, and their oxides and salts.

6. The medium of any one of the preceding claims wherein the medium further comprises a water dispersible polymer.

7. The medium of any one of the preceding claims wherein said medium has a pH of greater than about 10.

8. The medium of any one of the preceding claims comprising greater than about 3wt% of at least one water soluble silicate.

9. The medium of any one of the preceding claims wherein said medium further comprises at least one anode chosen from the group consisting of platinum, zinc, steel, tantalum, niobium, titanium, nickel and alloys thereof.

10. The medium of any one of the preceding claims wherein said medium has a temperature of about 25 to about 95°C.

11. The medium of any one of the preceding claims wherein said medium is electrically conductive when exposed to a voltage of greater than about 12V.

12. The medium of any one of the preceding claims wherein said medium is substantially free of VOCs.

13. The medium of any one of the preceding claims further comprising ions from at least one member selected from the group of platinum, zinc, iron, tantalum, niobium and titanium.

14. The medium of claim 13 wherein the ions comprises at least one of zinc and iron.

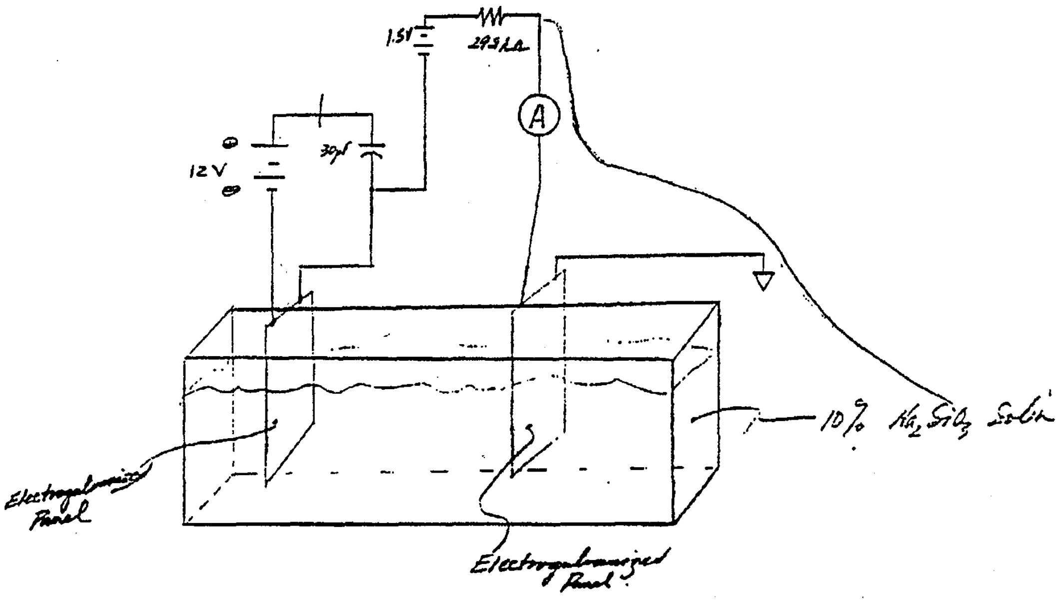
1.5V
293kΩ
A
⊕
12V
⊖
30μf
10% Na₂SiO₃ Sol'n
Electrogalvanized Panel
Electrogalvanized Panel

Fig 1

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 03 07 6855

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X Y	EP 0 608 107 A (NIPPON PAINT CO LTD) 27 July 1994 (1994-07-27) * page 9, line 50 - page 10, line 3 * * page 11, line 10-29; claim 5; examples 1-4; tables 1,2 *	1,3-6, 10,12-14 2,7-9,11	C25D9/04
Y	GB 2 027 055 A (NIPPON STEEL CORP) 13 February 1980 (1980-02-13) * page 8, line 46 - page 9, line 11; table 5 *	2,7-9,11	
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
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Application Number
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