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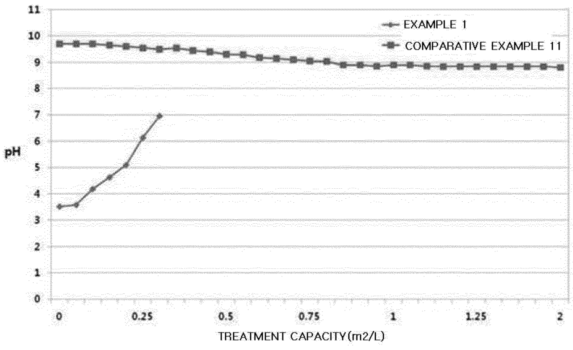
(54) **ALKALINE CONVERSION TREATMENT COMPOSITION FOR MAGNESIUM AND MAGNESIUM ALLOY, AND METHOD FOR PERFORMING SURFACE TREATMENT ON MAGNESIUM AND MAGNESIUM ALLOY MATERIAL BY USING SAME**

(57) An alkali conversion treatment composition for magnesium and magnesium alloy may include 2 to 10% by weight of a phosphoric acid compound, 1 to 5% by weight of an inorganic metal sol, 0.03 to 0.3% by weight of a vanadium compound, 0.5 to 5% by weight of a basic compound, 0.01 to 0.1% of an acrylic resin and a remainder of water soluble solvent. The composition may form a uniform and dense chemical conversion coating on a surface of magnesium or magnesium alloy material, and may provide excellent corrosion resistance, topcoat painting adhesion and water resistance, and may not cause defects on a surface of the topcoat painting.

FIG. 1



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Description

BACKGROUND

1. Field

[0001] Example embodiments relate to an alkali conversion treatment composition for magnesium and magnesium alloy and a surface treating method using the same. More particularly, example embodiments relate to an alkali conversion treatment composition for magnesium and magnesium alloy, which is applied to provide high corrosion resistance to surfaces of magnesium or magnesium alloy, and a surface treating method using the same.

2. Description of the Related Art

[0002] Magnesium is the eighth most abundant metal in the world and lightest metal among practically usable metals. Magnesium has excellent non-strength, machinability and dimensional stability. Magnesium alloy has an advantage of being applicable to electronic devices and transportation equipment aiming at lightweight because of excellent electromagnetic wave shielding property, heat radiation property and vibration absorption property. In recent years, magnesium and magnesium alloy are being applied to automobile structural materials such as handles, cylinder heads, ventilation fans and seat frames, or electronic devices such as computers, cameras, MP3s and mobile phones, and other application fields are expected to increase rapidly.

[0003] Since most of the metal material members (aluminum alloy, steel, magnesium alloy, etc.) used for automobiles, motorcycles, household appliances, etc. is required to have corrosion resistance and aesthetic appearance, they are painted after being subjected to various surface treatments. The purpose of the surface treatment is to remove contaminants such as cutting oil and processing oil remaining on the surface of the workpiece to form a dense chemical film to provide corrosion resistance and coating adhesion.

[0004] The magnesium alloy is painted after surface treatment like steel or aluminum alloy. The magnesium alloy is the most active metal among the practically usable metal and is easily corroded. Furthermore, since the surface of the magnesium alloy is chemically irregular, the magnesium alloy is an extremely difficult material to form a dense and uniform chemical film.

[0005] In order to solve this problem, a chemical conversion treatment liquid containing hexavalent chromium having excellent corrosion resistance has been used to secure corrosion resistance and coating adhesion (Japanese Patent Registration No. 10-0869402). However, use of hexavalent chromium is currently regulated because it is fatal to humans and causes environmental pollution problems. Accordingly, in recent years, a method of forming a dense chemical conversion coating by using a non-chromium conversion treatment composition containing no chromium to provide corrosion resistance and coating adhesion is being applied.

[0006] Known non-chromium conversion treatment may include "Surface treatment method of a metal (Japanese Patent Laid-open Publication No. 9-228062)" using film-forming composition including at least one organometallic compound selected from the group consisting of metal alkoxide, metal acetylacetonate and metal carboxylate, and at least one organic compound selected from the group consisting of an acid, an alkali and a salt thereof, or at least one organic compound containing a hydroxyl group, a carboxyl group or an amino group, and "Phosphate treatment (Japanese Patent Publication No. 7-126858)" based on a magnesium phosphate treatment with a metal other than chromium, such as zirconium, titanium, zinc, etc. However, the chemical conversion treatment composition is impractical due to a long treatment time, and is difficult to provide sufficient corrosion resistance, rust inhibition property and film adhesion property. In addition, these chemical conversion treatment compositions tend to be affected by the non-uniformity of the material, so that the performance may not be stable.

[0007] In order to solve these problems, the present applicant has obtained a patent registration (10-1559285) for a chemical conversion treatment composition for magnesium or magnesium alloy. The present patent has an advantage of forming a high performance chemical conversion coating, however, since the chemical conversion treatment composition has an acidic characteristic, magnesium is rapidly eluted from the chemical conversion treatment composition when the process of forming a chemical conversion coating is repeated. An eluting of magnesium may cause the deterioration of the chemical conversion treatment composition, which may make it difficult to continuously form a chemical conversion coating having excellent corrosion resistance and water resistance.

SUMMARY

[0008] Example embodiments provide an alkali conversion treatment composition for forming a uniform and dense chemical conversion coating on a surface of a magnesium or magnesium alloy material, and having remarkably low aging characteristics compared to conventional acidic chemical conversion solutions.

[0009] Example embodiments provide a surface treating method using an alkali conversion treatment composition to form a uniform and dense chemical conversion coating after removing contaminants and an oxide layer existing on a surface of a magnesium or magnesium alloy.

[0010] An alkali conversion treatment composition for magnesium and magnesium alloy which may include 2 to 10% by weight of a phosphoric acid compound, 1 to 5% by weight of an inorganic metal sol, 0.03 to 0.3% by weight of a vanadium compound, 0.5 to 5% by weight of a basic compound, 0.01 to 0.1% of an acrylic resin and a remainder of water soluble solvent, and may be applied to form a corrosion resistance coating on a surface of magnesium and magnesium alloy materials.

[0011] A method of treating a surface using magnesium and magnesium alloy material may include performing a surface cleaning process on the magnesium and magnesium alloy material, and forming a chemical conversion coating on a surface of the magnesium and magnesium alloy material using an alkali conversion treatment composition. The chemical conversion coating may be formed by using an alkali conversion treatment composition for magnesium and magnesium alloy in which may include 2 to 10% by weight of a phosphoric acid compound, 1 to 5% by weight of an inorganic metal sol, 0.03 to 0.3% by weight of a vanadium compound, 0.5 to 5% by weight of a basic compound, 0.01 to 0.1% of an acrylic resin and a remainder of water soluble solvent.

[0012] The composition described above may form a uniform and dense chemical conversion coating on a surface of magnesium or magnesium alloy material, and may provide corrosion resistance, topcoat painting adhesion and water resistance, and may not cause defects on a surface of the topcoat painting.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013]

FIG. 1 is a graph explaining pH variance of a chemical conversion treatment composition of an Example 1 and Comparative Example 11.

FIG. 2 is an enlarged photograph illustrating a microstructure of a chemical conversion coating formed by using a chemical conversion treatment composition of Example 1.

DESCRIPTION OF EMBODIMENTS

[0014] An alkali conversion treatment composition for magnesium and magnesium alloy and a surface treating method using the same in accordance with example embodiments will be described more fully hereinafter. The inventive concept may, however, be embodied in many different forms and should not be construed as limited to the exemplary embodiments set forth herein.

[0015] The terminology used herein is for the purpose of describing particular exemplary embodiments only and is not intended to be limiting of the invention. As used herein, the singular forms "a," "an" and "the" are intended to include the plural forms as well, unless the context clearly indicates otherwise. It will be further understood that the terms "comprises" and/or "comprising," when used in this specification, specify the presence of stated features, integers, steps, operations, elements, and/or components, but do not preclude the presence or addition of one or more other features, integers, steps, operations, elements, components, and/or groups thereof.

[0016] Unless otherwise defined, all terms (including technical and scientific terms) used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this inventive concept belongs. It will be further understood that terms, such as those defined in commonly used dictionaries, should be interpreted as having a meaning that is consistent with their meaning in the context of the relevant art and will not be interpreted in an idealized or overly formal sense unless expressly so defined herein.

[0017] Hereinafter, an alkali conversion treatment composition of magnesium and magnesium alloy and a surface treating method using the same in accordance with example embodiments will be described more fully.

An alkali conversion treatment composition for magnesium and magnesium alloy

[0018] A conventional chemical conversion treatment composition has an acidic property. Thus, when a magnesium material is dipped in a solution, magnesium ions are continuously eluted from the magnesium material to accelerate aging of the chemical conversion treatment composition. However, in an alkali conversion treatment composition of the present invention, magnesium ions may not be eluted from a magnesium material during chemical conversion treatment, and reactivity with the magnesium material may be well-controlled. Thus, the alkali conversion treatment composition may be capable of forming a chemically treated coating film having excellent characteristics on a surface of the magnesium material even at a room temperature.

[0019] An alkali conversion treatment composition of the present invention having characteristics described above may include a phosphoric acid compound, an inorganic metal sol, a vanadium compound, a basic compound, an acrylic resin and a water-soluble solvent. In example embodiments, the alkali conversion treatment composition for magnesium and magnesium alloy may include 2 to 10% by weight of the phosphoric acid compound, 1 to 5% by weight of the inorganic metal sol, 0.03 to 0.3% by weight of the vanadium compound, 0.5 to 5% by weight of the basic compound, 0.01 to 0.1% by weight of the acrylic resin and a remainder of water-soluble solvent.

[0020] In one embodiment, the phosphoric acid compound included in the alkali conversion treatment composition may be applied to provide corrosion resistance to a chemical conversion coating and to improve film adhesion.

[0021] The phosphoric acid compound may include, e.g., ammonium monophosphate, sodium diphosphate, potassium diphosphate and orthophosphoric acid, etc. These may be used each alone or in combination thereof.

[0022] When the content of the phosphoric acid compound included in the alkali conversion treatment composition is less than 2% by weight, the chemical conversion coating may not be sufficiently formed to secure corrosion resistance and coating adhesion. On the other hand, when the content thereof exceeds 10% by weight, the chemical conversion coating may be excessively formed to improve the corrosion resistance, but it may be difficult to secure the coating adhesion. Thus, the phosphoric acid compound may be preferably used in 2 to 10% by weight, more preferably in 3 to 9% by weight.

[0023] The inorganic metal sol included in the alkali conversion treatment composition may be applied to secure corrosion resistance and to form a uniform chemical conversion coating. The inorganic metal sol may include, e.g., silica sol, alumina sol, titania sol, and zirconia sol, etc. These may be used each alone or in combination thereof.

[0024] In one embodiment, the silica sol of the inorganic metal sol may include, e.g., Ludox HS-30, Ludox HS-40, Ludox TM, Ludox SM, Ludox AM, Ludox AS, Ludox LS, Ludox CL-X, Ludox SK, Ludox TMA, Ludox PG, Ludox CL, Ludox CL-P, Ludox DF, Ludox FM, Ludox HAS marketed by GRACE & Co, SNOWTEX ST-20L, SNOWTEX ST-40, SNOWTEX ST-50, SNOWTEX ST-C, SNOWTEX ST-N, SNOWTEX ST-O, SNOWTEX ST-OL, SNOWTEX ST-ZL, SNOWTEX ST-PS-M, SNOWTEX ST-PS-S, SNOWTEX ST-PS-SO, SNOWTEX ST-OUP, SNOWTEX ST-UP marketed by NISSAN CHEMICAL & Co, and SS-SOL 30SG, SS-SOL 30E, SS-SOL 30, SS-SOL 30F, SS-SOL 100, SS-SOL 30A, SS-SOL 20AM, SS-SOL 300EAC, SS-SOL 300MAC, SS-SOL 300PAC, SS-SOL 20EG, SS-SOL 30EK, SS-SOL 30BK marketed by S-CHEMTECH & Co, etc. The alumina sol of the inorganic metal sol may include, e.g., ALUMINASOL™ AS-100, ALUMINASOL™ AS-200 marketed by NISSAN CHEMICAL & Co, Ultra-Sol 200A, Ultra-Sol 201A/60, Ultra-Sol 201A/280 marketed by GerardKluyskens Co., Inc., Wesol A, Wesol C12, Wesol D30 marketed by WESBOND & Co., etc. These may be used each alone or in combination thereof.

[0025] When the content of the inorganic metal sol included in the alkali conversion treatment composition is less than 1% by weight, the chemical conversion coating may not be uniformly formed, and the corrosion resistance may be reduced. On the other hand, when the content thereof exceeds 5% by weight, water resistance and stability of the chemical conversion treatment composition may be lowered, respectively. Thus, the inorganic metal sol may be preferably used in 1 to 5% by weight, more preferably in 1.5 to 4% by weight.

[0026] The vanadium compound included in the alkali conversion treatment composition may be applied to further improve the corrosion resistance and to provide a self-healing effect to the magnesium alloy material.

[0027] In one embodiment, the vanadium compound may have a vanadium oxidation number of five, four or three. The vanadium compound having a vanadium oxidation number of five may include, e.g., vanadium pentoxide (V_2O_5), metavanadic acid (HVO_3), ammonium metavanadate, sodium metavanadate, vanadium trichloride ($VOCl_3$), etc., the vanadium compound having a vanadium oxidation number of four or three may include, e.g., vanadium trioxide (V_2O_3), vanadium dioxide (VO_2), vanadium oxysulfate ($VOSO_4$), vanadium oxyacetylacetate $VO(OC(=CH_2)CH_2COCH_3))_2$, vanadium acetylacetate $V(OC(=CH_2)CH_2COCH_3))_3$, vanadium trichloride ($VCl_3$), phospho-vanado-molybdate, etc. These may be used each alone or in combination thereof.

[0028] When the content of the vanadium compound included in the alkali conversion treatment composition is less than 0.03% by weight, the corrosion resistance and the self-healing effect may not be obtained. On the other hand, when the content thereof exceeds 0.3% by weight, improvement of performance may not be increased, but a cost may be increased. Thus, the inorganic metal sol may be preferably used in 0.03 to 0.3% by weight, more preferably in 0.05 to 0.2% by weight.

[0029] The basic compound included in the alkali conversion treatment composition may serve to raise pH of the chemical conversion treatment composition to produce more stable alkali conversion treatment composition. The basic compound may include, e.g., sodium hydroxide, potassium hydroxide, calcium hydroxide, barium hydroxide, ammonium hydroxide and lithium hydroxide, etc. These may be used each alone or in combination thereof.

[0030] When the content of the basic compound included in the alkali conversion treatment composition is less than 0.5% by weight, the pH of the chemical conversion treatment composition may not be increased to a desired level. On the other hand, when the content thereof exceeds 5% by weight, the pH of the chemical conversion treatment composition may be excessively increased and a film may not be formed on the surface of the magnesium material during the conversion treatment. Thus, the inorganic metal sol may be preferably used in 0.5 to 5% by weight.

[0031] The acrylic resin included in the alkali conversion treatment composition may improve durability of the chemical conversion coating to be formed, thereby forming a more dense chemical conversion coating and enhancing the water resistance. The acrylic resin may include, e.g., acrylic polyol, acrylic acid copolymer, modified acrylic acid copolymer, polyacrylate, etc. These may be used each alone or in combination thereof.

[0032] When the content of the acrylic resin included in the alkali conversion treatment composition is less than 0.01% by weight, the durability of the chemical conversion coating may be deteriorated to deteriorate the adhesion property and the water resistance. On the other hand, when the content thereof exceeds 0.1% by weight, the chemical conversion coating may be formed to be excessively thick by the excessive resin to deteriorate the adhesion property. Thus, the inorganic metal sol may be preferably used in 0.01 to 0.1% by weight.

[0033] Particularly, the alkali conversion treatment composition in accordance with the example embodiments may preferably have pH of 8.5 to 10.5. When the pH of the alkali conversion treatment composition is less than 8.5, the reactivity of the magnesium alloy material may be increased, and the chemical conversion coating may be actively formed, however, the magnesium ions may be eluted quickly on the surface of the material to accelerate aging of the solution. On the other hand, when the pH thereof exceeds 10.5, the reactivity of the magnesium alloy material may be remarkably reduced, and the chemical conversion coating may be hardly formed on the surface of the magnesium material.

[0034] The alkali conversion treatment composition for magnesium and magnesium alloy may have a low elution property of magnesium ions. Thus, the alkali conversion treatment composition may be prevented from being contaminated by the chemical conversion treating process. Thus, a dense chemical conversion coating may be formed even if the chemical conversion coating is reused by tens of times or more. Accordingly, the magnesium material may have high corrosion resistance, excellent coating adhesion and water resistance, without causing surface defects of a topcoat painting layer formed thereafter.

[0035] Hereinafter, a surface treating method for magnesium and magnesium alloy will be described more fully.

[0036] The surface treating method for magnesium and magnesium alloy may be performed through a surface cleaning process and a chemical conversion treatment process.

[0037] The surface cleaning process may remove contaminants (processing oil, oil, etc.) and an oxide layer existing on a surface of magnesium alloy before a chemical conversion treatment to promote forming a uniform and dense chemical film. The surface cleaning process may include a degreasing (alkali degreasing) process, a first washing process, an etching process, a second washing process, a desmutting process, and a third washing process.

[0038] In the surface cleaning process of the present invention, the degreasing process may be a step of primarily removing oil and processing oil components on the surface of the magnesium alloy prior to the etching process.

[0039] A degreasing solution of the degreasing process may not be particularly limited as long as it can remove organic contaminants, but it is preferable to use an alkaline aqueous solution containing a surfactant. An alkali builder of the degreasing solution may include a hydrate of an alkali metal, a phosphate, a silicate, a carbonate, etc. The surfactant may include any of nonionic, cationic and anionic surfactants. Further, a chelating agent may be added to improve the degreasing efficiency.

[0040] The temperature and time for bringing the degreasing solution into contact with the magnesium alloy may not be particularly limited, but it is preferably within a range of 30 to 70°C for 2 to 10 minutes depending on degree of contamination of the magnesium surface. A concentration of the degreasing solution may also be appropriately adjusted according to the degree of contamination on the surface of the magnesium alloy, the degreasing solution component, etc.

[0041] The first washing process may be a washing step using water to remove the cleaning fluid applied in the degreasing process. The first washing process may be performed by a method, e.g., dipping, spraying, submerging, etc., and may be performed using all kinds of water including, e.g., deionized water, distilled water, pure water, etc. There is no particular limitation on a temperature, however, the first washing process may be performed preferably at a temperature range of 25 to 80°C. When hot water is used, water cleaning may be more efficient, and dehydration drying may be improved. Thus, inflow of water into a next processing tank may be minimized and a treatment liquid may be easily managed. In addition, an ultrasonic vibration may be applied to enhance the cleaning effect during the washing process.

[0042] In the surface cleaning process of the present invention, when the surface of the magnesium alloy to be treated is excessively contaminated by the processing oil or when the oxide layer has grown thereon, the etching process may be performed to remove the processing oil on the surface of the magnesium alloy or to remove the oxide layer. An etching treatment in the etching process may be performed by bringing an acidic aqueous solution into contact with the magnesium alloy material to be treated.

[0043] In one embodiment, the acidic aqueous solution may not be particularly limited so long as the contaminants on the surface of the magnesium alloy can be dissolved and removed, and may be preferable to use one or more of sulfuric acid, phosphoric acid, hydrochloric acid, hydrofluoric acid, nitric acid, and carbonic acid in combination. An organic acid may be mixed to improve an etching efficiency. The conditions such as concentration of the acidic aqueous solution, temperature, and contact time with the surface of the magnesium alloy may not be specifically limited, and may appropriately adjusted according to degree of contamination of the magnesium alloy, components of the acidic aqueous solution used, etc.

[0044] The second washing process may be a cleaning step using water to remove the acidic aqueous solution to be applied in the etching process. The second washing process may be performed by a method such as dipping, spraying, submerging, etc., and may be performed using all kinds of water including deionized water, distilled water, pure water, etc. There is no particular limitation on temperature range.

[0045] In the surface cleaning process of the present invention, the desmutting process may be performed to remove a smut remaining on the surface of the magnesium alloy after the etching process. The desmutting in the desmutting process may be performed by contacting a desmutting solution with the magnesium alloy to be treated.

[0046] In one embodiment, the desmutting solution may not be particularly limited as long as it can remove the smut remaining on the magnesium surface after the etching process, and may be preferable to use a strong alkaline aqueous solution (pH 12 or higher) mixed with one or two kinds of tartaric acid, ascorbic acid, gluconic acid, citric acid and oxalic acid.

[0047] The conditions such as concentration of the desmutting solution, temperature, and contact time with the surface of the magnesium alloy may not be specifically limited, and may be appropriately adjusted according to amount of smut generated after the etching process, component of the desmutting solution, etc.

[0048] The third washing process may be a cleaning step using water to remove the remaining desmutting solution to be applied in the desmutting process. A third washing may be performed by a method such as dipping, spraying, submerging, etc., and may be performed using all kinds of water including deionized water, distilled water, pure water, etc. There is no particular limitation on temperature range.

[0049] In other example embodiments, in a case that the processing oil is not contaminated, or the magnesium and magnesium alloy material is unprocessed, the etching process and the desmutting process may not be performed in the surface cleaning process.

[0050] The chemical conversion treatment process according to the present invention is the process for forming the chemical conversion coating on the surface of the magnesium and the magnesium alloy material having a cleaned surface using the chemical conversion treatment composition. The alkali conversion treatment composition of magnesium and magnesium alloy may include 2 to 10% by weight of the phosphoric acid compound, 1 to 5% by weight of the inorganic metal sol, 0.03 to 0.3% by weight of the vanadium compound, 0.5 to 5% by weight of the basic compound, 0.01 to 0.1% by weight of the acrylic resin and a remainder of water-soluble solvent. A detailed description of the alkali conversion treatment composition is disclosed in the detailed description of the present invention and is omitted in order to avoid redundancy.

[0051] The chemical conversion coating may be preferably formed to have a thickness of 0.1 to 2.5μm. The chemical conversion coating having a thickness of 0.1μm or less may have a good coating adhesion, however, a corrosion resistance and a water resistance may be significantly deteriorated. The chemical conversion coating having a thickness of 2.5μm or more may have a good corrosion resistance, however, the coating adhesion and the water resistance may be deteriorated. The thickness of the chemical conversion coating may be adjusted by adjusting temperature of the chemical conversion solution and time of chemical conversion treatment.

[0052] The magnesium and magnesium alloy materials formed by performing the surface cleaning process described above may be used for replacing automobile parts or other steel after topcoat painting. When moisture on the surface of the magnesium alloy material enters into the paint, the topcoat film formed by an electro-deposition coating may be deteriorated. Thus, a drying process may be preferably performed before the topcoat painting.

[0053] The drying process may not be particularly limited, and it is preferable to perform oven drying with a hot air heater or an infrared heater, and a drying temperature is preferably within a range of 80 to 160°C for 20 to 60 minutes. In addition, drying conditions after the electro-deposition coating may be changed depending on types and characteristics of the electro-deposition paint.

[0054] Also, type of paint used in coating may not be specifically limited, and any of water-based or solvent-based coatings may be used. A method of coating the paint may not be specifically limited, and any conventionally known coating method, e.g., spraying, dipping, powder coating, etc., may be applied.

[0055] Hereinafter, present invention will be described more fully in accordance with example embodiments, comparative examples and evaluation examples. The inventive concept may, however, be embodied in many different forms and should not be construed as limited to the exemplary embodiments set forth herein.

Example 1 and Comparative Examples 1 to 11

[0056] Alkali conversion treatment compositions including the ingredients set forth in Table 1 below in 1L of distilled water were prepared and acidic conversion treatment compositions including the ingredients set forth in Table 2 were prepared.

[Table 1]

	Disodium dihydrogenphosphate	Silica sol	Vanadium oxysulfate	Sodium hydroxide	Acrylic resin	pH
Example 1	3.5	3	0.05	3	0.05	9.5
Comparative Example 1	**1**	3	0.05	3	0.05	9.5
Comparative Example 2	**15**	3	0.05	3	0.05	9.5
Comparative Example 3	3.5	**0.5**	0.05	3	0.05	9.5
Comparative Example 4	3.5	**10**	0.05	3	0.05	9.5
Comparative Example 5	3.5	3	**0.01**	3	0.05	9.5
Comparative Example 6	3.5	3	**1**	3	0.05	9.5
Comparative Example 7	3.5	3	0.05	**0.1**	0.05	**8.0**
Comparative Example 8	3.5	3	0.05	**10**	0.05	**11.0**
Comparative Example 9	3.5	3	0.05	3	**0.005**	9.5
Comparative Example 10	3.5	3	0.05	3	**0.5**	9.5

[Table 2]

	Sodium dihydrogenphosphate	Manganese acetate	Alumina sol	Vanadium oxysulfate	Selenium sulfide	Ammonium fluoride	pH
Comparative Example 11	2	0.3	3	0.05	0.01	0.1	3

[Example 1]

[0057] Each of the magnesium alloy materials (AZ31B plate; ASTM standard product, pneumatic plate, 70mm X 140mm X 0.8mm AZ31B (hot press)) was prepared. A surface of the prepared alloy material was subjected to the surface cleaning process under the conditions shown in Table 3 below. Test specimens were prepared by the processes of forming chemical conversion coatings, washing and electro-deposition coating using the respective chemical conversion treatment compositions prepared in each of Examples and Comparative Examples, respectively. Conditions of electro-deposition coating are as follows

[Table 3]

Surface cleaning process	
a degreasing process	Gardoclean 4292 A solution, B solution [Samyang Chemical Industry Co., Ltd], A solution 30g/L, B solution 3g/L, 50°C, 3 minutes ultrasonic treatment
a first washing process	Using room temperature deionized water
an etching process	Using mixture of 85% phosphoric acid and 1.96g/L hydrochloric acid, pH 1 to 2, 50°C, immersion treatment
a second washing process	Using deionized water of a room temperature
a desmutting process	Using mixture of 50g/L sodium hydroxide and 4.5g/L oxalic acid, 50°C, 3 minutes immersion treatment
a third washing process	Using room temperature deionized water

Conditions of electro-deposition coating

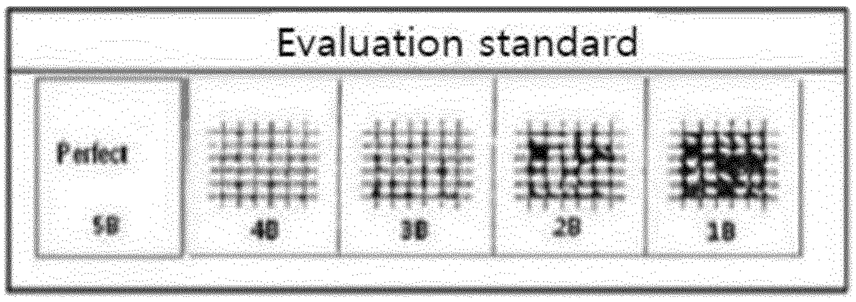
[0058]

- Curing condition : 160°C x 40min
- Coating thickness: 20 ± 5μm
- Paint: RF-6900 F-1, F-2 (Noroo Auto Coating)

Evaluation of coating adhesion

[0059] After the surface cleaning process, the chemical conversion coating formation process, and the electro-deposition coating process of Experimental Example 1 were performed using the alkali conversion treatment compositions of Examples and Comparative Examples, respectively, to prepare samples, the coating adhesion of the samples was evaluated. The coating adhesion was evaluated by the coating adhesion test (ASTM D3359, 1mm X 1mm, 100 pieces) by Cross Cut Test (CCT) method. An evaluation standard is shown in Table 4 below.

[Table 4]



Evaluation of water resistance

[0060] The coating adhesion test (ASTM D3359, 1 mm X 1 mm, 100 pieces) was performed by the Cross Cut Test (CCT) method after the water resistance test (40°C, 240 hours immersion treatment). An evaluation standard is shown in Table 3 below.

Evaluation of corrosion resistance

[0061] The corrosion resistance of each of the specimens was evaluated by a salt spray test in accordance with a method of ASTM B117. Test specimens were placed in X-cut before the salt spray test. A salt spraying time was 800 hours. After a salt spraying was finished, an expansion width atone side of each specimen from the X-cut was measured to evaluate the corrosion resistance after coating. An evaluation standard is shown in Table 5 below.

[Table 5]

Corrosion resistance assessment	
◎	expansion width of one side from the X-cut is less than 1mm
○	expansion width of one side from the X-cut is 1mm or more to less than 3mm
Δ	expansion width of one side from the X-cut is 3mm or more to less than 5mm
X	expansion width of one side from the X-cut is 5mm or more

Evaluation results of Examples and Comparative Examples

[0062] The coating adhesion, the corrosion resistance, and the water resistance were evaluated for each of the specimens prepared by applying the chemical conversion treatment composition of Example 1 and Comparative Examples 1 to 11, and the results are shown in Table 6.

[Table 6]

	Coating adhesion	Corrosion resistance	Water resistance
Comparative Example 11	5B	◎	5B
Example 1	5B	◎	5B
Comparative Example 1	3B	X	3B
Comparative Example 2	1B	Δ	1B
Comparative Example 3	3B	Δ	3B
Comparative Example 4	3B	○	2B
Comparative Example 5	4B	Δ	3B
Comparative Example 6	4B	Δ	3B
Comparative Example 7	2B	Δ	2B
Comparative Example 8	0B	Δ	0B
Comparative Example 9	3B	○	2B
Comparative Example 10	3B	Δ	2B

1) Evaluation of variance of physical properties according to content of phosphate

[0063] As shown in Table 6 above, when the phosphoric acid compound was added (Example 1) as suggested in the present invention, all of the physical properties showed excellent results. On the other hand, when the phosphoric acid compound was added too little (Comparative Example 1), the chemical conversion coating was formed to be too thin and the corrosion resistance was greatly deteriorated. When the phosphoric acid compound was added too much (Comparative Example 2), the chemical conversion coating was formed to be too thick, and the coating adhesion and the water resistance were greatly decreased, respectively. From the above results, it may be noted that the phosphoric acid compound may be very effective in forming the chemical conversion coating, and may also be effective for improving corrosion resistance and other physical properties when used within the scope of the present invention.

2) Evaluation of variance of physical properties according to content of inorganic metal sol

[0064] As shown in Table 6 above, when the inorganic metal sol was added (Example 1) as suggested in the present invention, all of the physical properties showed excellent results. On the other hand, when the inorganic metal sol was added too little (Comparative Example 3), all of the physical properties showed deteriorated results. When the inorganic metal sol was added too much (Comparative Example 4), some of the physical properties showed deteriorated results. From the above results, it may be noted that in order to obtain a uniform film, the inorganic metal sol should be used within the scope of the present invention since the inorganic metal sol may affect the denseness and uniformity of the coating when forming the chemical conversion coating.

3) Evaluation of variance of physical properties according to content of vanadium compound

[0065] As shown in Table 6 above, when the vanadium compound was added (Example 1) as suggested in the present invention, all of the physical properties showed excellent results. On the other hand, when the vanadium compound was added too little (Comparative Example 5), the corrosion resistance was deteriorated as shown in results of Comparative Example 5. When the vanadium compound was added too much (Comparative Example 6), an excessive vanadium coating was formed, so that the water resistance and the corrosion resistance were deteriorated results, as shown in results of Comparative Example 6.

4) Evaluation of variance of physical properties according to the content of basic compound (sodium hydroxide)

[0066] As shown in Table 6 above, when the basic compound (sodium hydroxide) was added (Example 1) as suggested in the present invention, all of the physical properties showed excellent results. On the other hand, when the basic compound (sodium hydroxide) was added too little (Comparative Example 7), magnesium ions were eluted from the magnesium alloy material to accelerate aging of the solution, and all the physical properties were deteriorated since the chemical conversion coating was formed to be too thick. When the basic compound (sodium hydroxide) was added too much (Comparative Example 8), the desired physical properties was not ensured because the pH of the chemical conversion treatment composition was increased to cause no reaction during the chemical conversion treatment.

5) Evaluation of variance of physical properties according to content of acrylic resin

[0067] As shown in Table 6 above, when the acrylic resin was added (Example 1) as suggested in the present invention, all of the physical properties were excellent. On the other hand, when the acrylic resin was added too little (Comparative Example 9), the water resistance was lowered because acrylic resin may be serve as forming a more dense and durable chemical conversion coating on a surface of the magnesium alloy to improve the water resistance. When the acrylic resin was added too much (Comparative Example 10), the effects thereof could not be confirmed, and the corrosion resistance and the water resistance were decreased, respectively.

PH changes of the chemical conversion treatment compositions of Example 1 and Comparative Example 11

[0068] Magnesium alloy material (AZ31B) was treated with the chemical conversion treatment compositions of Example 1 and Comparative Example 11 to measure the pH variance of the solution. The measurement results are shown in FIG. 1.

[0069] A graph of FIG. 1 shows the pH change when the magnesium alloy material was continuously treated using each of the chemical conversion treatment compositions (Example 1 and Comparative Example 11). An X-axis of the graph of FIG. 1 is expressed by converting the amount of the solution (m2/L) per treatment area by continuously treating the magnesium alloy. Comparative Example 11 shows that the pH increases sharply as the treatment capacity of the magnesium alloy increases, however, Example 1 shows that the pH gradually decreases. In the case of Comparative Example 11, as described in the existing patent, when the pH may exceed 5 or more, the physical properties may be deteriorated and the composition may not be used as a chemical conversion treatment composition.

The aging evaluation of the chemical conversion treatment compositions of Example 1 and Comparative Example 11

[0070] A material of AZ31B (25cm x 9cm) was evaluated for a degree of contamination before and after the chemical conversion treatment of the two chemical conversion treatment compositions (Example 1 and Comparative Example

11). Each of the magnesium alloy materials were treated in the chemical conversion treatment composition having the compositions of Example 1 and Comparative Example 11, and then the degree of contamination of the solution was measured by inductively coupled plasma mass spectrometry (ICP) analysis. The results of measurement are shown in Table 7.

[Table 7]

	Comparative Example 11		Example 1	
	Initial state	After 50 sheets	Initial state	After 50 sheets
Na	8800	13900	6600	6800
Si	2100	3700	3100	2400
Mg	N/A	**100**	N/A	N/A
V	90	120	120	90
P	8800	14700	6100	6400

[0071] Referring to Table 7, in each of the chemical conversion treatment compositions (Example 1 and Comparative Example 11) in an initial state, a solution of $0.15m^2/L$ of Comparative Example 11 having a pH of 5 or less and a solution having a treatment capacity of $2.0m^2/L$ of Example 1, Respectively, were analyzed.

[0072] As a result of the measurement, it was noted that although the treatment capacity was at a level of $0.15m^2/L$, a concentration of magnesium ion was rapidly increased in Comparative Example 11, however, the magnesium ion was not detected even at $2.0m^2/L$ in Example 1.

[0073] Each of the initial physical properties of the chemical conversion treatment composition of Comparative Example 11 and Example 1, and the physical properties of the chemical conversion treatment composition after the chemical conversion treatment were measured and compared, respectively. The results are shown in Table 8.

[Table 8]

		Coating adhesion	Corrosion resistance	Water resistance
Comparative Example 1	Initial state	5B	◎	5B
	After 50 sheets	2B	Δ	2B
Example 1	Initial state	5B	◎	5B
	After 50 sheets	5B	◎	5B

[0074] Referring to Table 8, each of the initial physical properties of the chemical conversion treatment composition of Comparative Example 11 and Example 1 were all excellent. However, in Comparative Example 11, the physical properties were equivalent to those of initial properties up to the treatment capacity of $0.15m^2/L$, and after that, the physical properties were lowered. On the other hand, in the Example 1, the physical properties were equivalent to those of initial properties up to the treatment capacity of $2.0m^2/L$. This is because, in the case of Comparative Example 11, the magnesium ions continuously dissolve during the continuous chemical conversion treatment, the pH of the solution was increased, and the solution was rapidly aged. In the case of Example 1, it was noted that the magnesium ions did not dissolve during the conversion treatment, and the aging of the solution were hardly progressed.

[0075] FIG. 2 is an enlarged photograph of a microstructure of a chemical conversion coating formed using the chemical conversion treatment composition of Example 1.

[0076] As shown in FIG. 2, it may be noted that the microstructure of the chemical conversion coating on the surface of the magnesium alloy material (AZ31B) in accordance with Example 1 of the present invention may have a unique structure and a structure similar to that of the Dendrite structure.

Claims

1. An alkali conversion composition for forming a chemical conversion coating having a corrosion resistance on a surface magnesium and magnesium alloy, wherein the alkali conversion composition of magnesium and magnesium alloy includes 2 to 10% by weight of a phosphoric acid compound, 1 to 5% by weight of an inorganic metal sol, 0.03

to 0.3% by weight of a vanadium compound, 0.5 to 5% by weight of a basic compound, 0.01 to 0.1% of an acrylic resin and a remainder of water soluble solvent.

2. The alkali conversion composition of claim 1, wherein the phosphoric acid compound is a compound which generates phosphoric acid ions, and includes at least one selected from the group consisting of ammonium monophosphate, sodium diphosphate, potassium diphosphate and orthophosphoric acid.

3. The alkali conversion composition of claim 1, wherein the basic compound includes at least one selected from the group consisting of sodium hydroxide, potassium hydroxide, calcium hydroxide, barium hydroxide, ammonium hydroxide and lithium hydroxide.

4. The alkali conversion composition of claim 1, wherein the inorganic metal sol includes at least one selected from the group consisting of silica sol, alumina sol, titania sol and zirconia sol.

5. The alkali conversion composition of claim 1, wherein the vanadium compound includes at least one selected from the group consisting of Vanadium pentoxide (V_2O_5), metavanadic acid (HVO_3), ammonium metavanadate, sodium metavanadate, vanadium trichloride ($VOCl_3$), vanadium trioxide (V_2O_3), vanadium dioxide (VO_2), vanadium oxysulfate ($VOSO_4$), vanadium oxyacetylacetate $VO(OC(=CH_2)CH_2COCH_3))_2$, vanadium acetylacetate $V(OC(=CH_2)CH_2COCH_3))_3$, vanadium trichloride ($VCl_3$), phospho-vanado-molybdate.

6. The alkali conversion composition of claim 1, wherein the acrylic resin includes at least one selected from the group consisting of acrylic polyol, acrylic acid copolymer, modified acrylic acid copolymer and polyacrylate.

7. The alkali conversion composition of claim 1, wherein a pH has a value of 8.5 to 10.5.

8. A method of treating a surface for magnesium and magnesium alloy material, the method comprising:

performing a surface cleaning process on the magnesium and magnesium alloy material; and
forming a chemical conversion coating on a surface of the magnesium and magnesium alloy material using an alkali conversion composition; and
wherein the chemical conversion coating is formed by using an alkali conversion composition for magnesium and magnesium alloy, which includes 2 to 10% by weight of a phosphoric acid compound, 1 to 5% by weight of an inorganic metal sol, 0.03 to 0.3% by weight of a vanadium compound, 0.5 to 5% by weight of a basic compound, 0.01 to 0.1% of an acrylic resin and a remainder of water soluble solvent.

9. The method of claim 8, the surface cleaning process comprising:

performing a degreasing process on the magnesium and magnesium alloy material;
performing a first washing process on the degreased magnesium and magnesium alloy material;
performing an etching process using an acidic aqueous solution on the surface of the magnesium and magnesium alloy material;
performing a second washing process on the etched magnesium and magnesium alloy material;
performing a desmutting process to remove a smut on the magnesium and magnesium alloy material; and
performing a third washing process on the desmutted magnesium and magnesium alloy material.

10. The method of claim 8, the surface cleaning process comprising:

performing a degreasing process on the magnesium and magnesium alloy material; and
performing a first washing process on the degreased magnesium and magnesium alloy material.

11. The method of claim 8, wherein the chemical conversion coating is formed to have a thickness of 0.1 to 2.5μm

FIG. 1

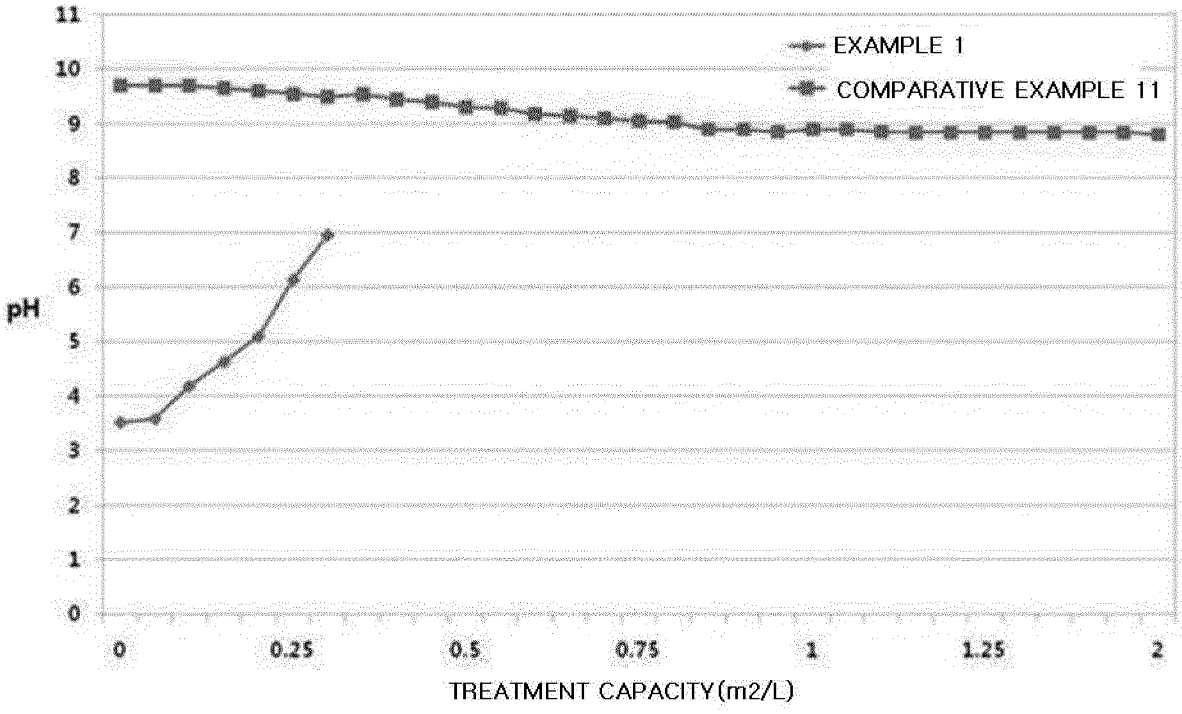
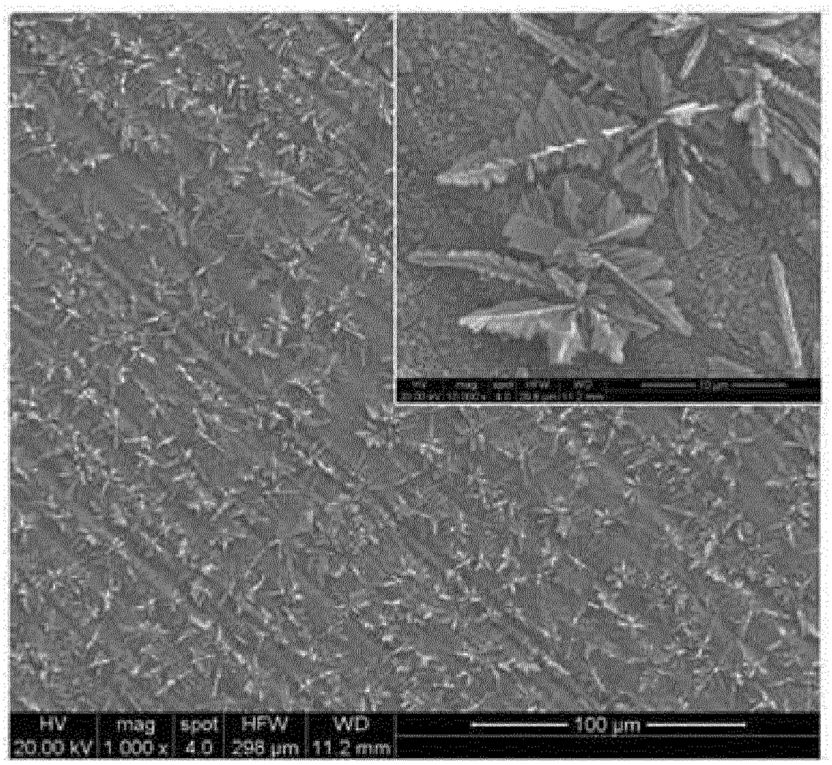

EXAMPLE 1
COMPARATIVE EXAMPLE 11
pH
TREATMENT CAPACITY(m2/L)
0
0.25
0.5
0.75
1
1.25
2
11
10
9
8
7
6
5
4
3
2
1
0

FIG. 2


HV
mag
spot
HFW
WD
20.00 kV
1 000 x
4.0
298 µm
11.2 mm
100 µm

INTERNATIONAL SEARCH REPORT

International application No. **PCT/KR2017/001129**

A. CLASSIFICATION OF SUBJECT MATTER

C23C 22/60(2006.01)i, C23C 22/78(2006.01)i, C23G 1/00(2006.01)i, C23F 1/00(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C23C 22/60; C23C 22/57; C23C 22/34; C23C 22/66; C23C 22/48; C23C 28/00; C23C 22/07; C23F 11/00; C23C 22/78; C23G 1/00; C23F 1/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean Utility models and applications for Utility models: IPC as above
Japanese Utility models and applications for Utility models: IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS (KIPO internal) & Keywords: conversion treatment, magnesium, phosphate, metal sol, vanadium, basic, acryl, solvent, hydroxide

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	KR 10-2009-0104575 A (POSCO et al.) 06 October 2009 See paragraphs [0027]-[0033] and claims 1-10, 31.	1-11
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A	KR 10-2014-0106938 A (NOROO COIL COATINGS CO., LTD.) 04 September 2014 See paragraphs [0026]-[0028] and claims 1-8.	1-11
A	KR 10-2010-0079864 A (POSCO) 08 July 2010 See paragraph [0079] and claims 1-7.	1-11
A	KR 10-2001-0024643 A (NIHON PARKERIZING CO., LTD.) 26 March 2001 See abstract and claims 1-8.	1-11

☐ Further documents are listed in the continuation of Box C.   ☒ See patent family annex.

* Special categories of cited documents:
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 APRIL 2017 (24.04.2017)	**01 MAY 2017 (01.05.2017)**

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Telephone No.

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/KR2017/001129

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