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(54) Method of non-chromate pretreatment for metal alloys

Chromatfreies Vorbehandlungsverfahren für Metallegierungen

Procédé de prétraitement non-chromate pour alliages métalliques

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Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] This invention relates to a method of non-chromate pretreatment for magnesium alloys, particularly to one in which film treatment is carried out after an alloy surface is degreased and cleaned. The process of film treatment is to have the alloy surface coated with coating liquid which will bond with the alloy surface to form a film thereon, impossible to produce industrial waste water with heavy metallic ion, reducing environmental pollution to the minimum, simple in handling, and able to elevate producing efficiency and lower producing cost.

2. Description of the Prior Art

[0002] For the present, communication electronic products, such as portable computers, mobile phones, radars and the like, have a tendency to become comparatively light, thin and small. An alloy which is thin and light and has great strength (unit weight), high vibration-resisting force, good conductivity and a function of isolating EMI, most meet the requirements of the foresaid products, including magnesium alloy, aluminum alloy, titanium alloy, zinc alloy or copper alloy.

[0003] In a conventional process for treating an alloy surface, acid conversion or anodizing in acid liquid has to be carried out in order to produce a rough and porous oxidized layer on the alloy surface for facilitating gluing or lacquering. The process of treating the alloy surface, as shown in Fig. 1, is to have an alloy surface degreased and cleaned first and then water washed through two stages to ensure its cleanness and then pickled to remove dissociative agent, and then water rinsing again so as to remove pickling liquid from the alloy surface for carrying out sequent film forming. Subsequently, the alloy has its surface treated with dip coating, spray coating or roll coating with film forming agent, which will react to the alloy surface for preventing corrosion and sequent lacquering with excellent physical adhesion. Although this conventional method has been employed for many years and proved effective, yet it is too complicated and acid used for treating an alloy surface is mostly inclusive of chromium ion (six valence chromium), phosphorous ion vanadium ion, manganese ion of heavy metal, seriously polluting environment, wasting much water and increasing producing cost.

[0004] EP 0 358 338 A2 discloses a method of pretreatment for metals like titanium, copper, zinc, aluminium and their alloys. This method includes the steps of degreasing and water rinsing. Afterwards the surface is treated by a pretreatment solution which is an aqueous composition comprising an inorganic hydrous oxide sol in order to form a protective coating. This aqueous composition may contain an adhesion promoter, for instance one or more silane coupling agents.

[0005] JP 57023057 A discloses a method of treating the surface of magnesium or magnesium alloys by a coating composition containing a silane coupling agent like vinyl trichlorosilane.

[0006] JP 02034790 A discloses a method for treating steel sheets by applying a solution containing one or more of (1) an alkoxide of Al, Zr, Ti, (2) monomethyl alkoxide of the metals, and (3) one or more of acetylacetonate salts, and an amount of silane coupling agent.

SUMMARY OF THE INVENTION

[0007] One objective of the invention is to offer a method of non-chromate pretreatment for metal alloys, impossible to produce heavy metallic waste water to pollute environment and able to reduce producing cost.

[0008] Another objective of the invention is to offer a method of non-chromate pretreatment for metal alloys, able to let a treated alloy surface have high adhesion, high conductivity, and anti-rust, anti-corrosion, anti-finger, anti-dust and water repellence functions.

[0009] The main feature of the invention is a treating process including degreasing, water rinsing acid pretreatment and film treatment as specified in claim 1. The film treatment is to have an alloy surface coated with coating liquid to carry out continuously a coating reaction on the alloy surface until the coating liquid bonds with the alloy surface and forms a film thereon. The film coating liquid applies aluminum sec-butoxide or a combination freely composed of more than one of the following chemicals: vinyltrimethoxysilane, tetraethoxysilane, methyltrimethoxysilane, γ-methacryloxypropyl-trimethoxysilane, γ-chloropropyl-trimethoxysilane, dimethyldiethoxysilane, phenyltriethoxysilane, decyltrimethoxysilane, isobutyltrimethoxysilane, 3-aminopropyltrimethoxysilane, tert-butyldimethylchlorosilane, vinyltrichlorosilane, γ-mercaptopropyl-trimethoxysilane, diphenyldichlorosilane, hexamethyldisilane, vinyltrisilane, zirconiumpropoxide, ethylsilicate, 1,1,2,2-tetrahydroctyl-1-triethoxysilane, titanium(IV)propoxide, titanium(IV)isopropoxide, titanium(IV)butoxide, titanium(IV)sec-butoxide, or titanium(IV)tert-butoxide.

[0010] The invention is a method of non-chromate pretreatment especially for magnesium alloy. The treating step is to have the magnesium alloy surface degreased and water rinsed first and then acid treatment before carrying out film coating. The alloy surface is treated with a mixed solution of organic and inorganic acid to let the alloy surface present metal original color or gray or black and become activated to form a thin film afterward. In reality, the treatment on metal surface with a mixed solution of organic and inorganic acid can remove oxidization layer from the metal surface and form hydroxyl group thereon to facilitate sequent film treatment.

BRIEF DESCRIPTION OF DRAWINGS

[0011] This invention will be better understood by referring to the accompanying drawings, wherein:

Fig.1 is a block diagram of a flowing process of a conventional method for treating the surface of magnesium alloy;
Fig.2 is a block diagram of a flowing process of a method of non-chromate pretreatment for metal alloys; and,
Fig.3 is a block diagram of a flowing process of a method of non-chromate pretreatment for magnesium alloy in the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0012] A method of non-chromate pretreatment for metal alloys, inclusive of aluminum alloy, titanium alloy, zinc alloy or copper alloy as shown in Fig. 2, is to have the alloy surface degreased and cleaned first and then carry out spray coating, dip coating or roller coating and then bake it for five to thirty minutes at a temperature 150°C ~200°C to get a film with a thickness around 0.5~1 μm. The steps of treating the alloy surface are as follows.

1. Degreasing: A primary alloy is treated with degreasing agent to remove superficial oily dirt from the alloy surface.
2. Water rinsing: The degreased alloy surface is rinsed to keep it clean.
3. Thin film treatment: The alloy surface is treated with dip coating, spray coating or roller coating with coating liquid which will bond with the alloy surface and form a film on the alloy surface.
The coating liquid employs aluminum sec-butoxide or a compound freely composed of more than one of the following chemicals: vinyltrimethoxysilane, tetraethoxysilane, methyltrimethoxysilane, γ-methacryloxypropyl-trimethoxysilane, γ-chloropropyl-trimethoxysilane, dimethyldiethoxysilane, phenyltriethoxysilane, decyltrimethoxysilane, isobutyltrimethoxysilane, 3-aminopropyltrimethoxysilane, tert-butyldimethylchlorosilane, vinyltrichlorosilane, γ-mercaptopropyltrimethoxysilane,diphenyldichlorosilane, hexamethyldisilane, vinyltrisilane, zirconiumpropoxide, ethylsilicate, 1,1,2,2-tetrahydroctyl-1-triethoxysilane, titanium(IV)propoxide, titanium (IV)isopropoxide, titanium(IV)butoxide, titanium (IV)sec-butoxide, or titanium(IV)tert-butoxide.
4. Painting: apply lacquer or adhesives to the surface of the film formed on the alloy surface, but whether this step is necessary or not depends on forming quality of the film and requirement of the product.

[0013] A preferred embodiment of a method of non-chromate pretreatment for magnesium alloy in the present invention, as shown in Fig.3, includes the following steps:

1. Degreasing: Primary magnesium alloy is degreased with a degreasing agent to remove superficial oily dirt from its surface.
2. Water rinsing: The degreased magnesium alloy is rinsed to keep its surface clean.
3. Acid treatment: The alloy surface is treated with a mixed solution of organic and inorganic acid to let the alloy surface present metal original color or gray or black and become activated to enhance forming a thin film afterward. The mixed solution of organic-inorganic acid can be an inorganic acid or an organic acid singly, or a mixed solution of both. The organic acid in the solution can be selected from more than one of the followings: acid, alcoholic acid, diacid and phosphonic acid, while the inorganic acid can be selected from more than one of the followings: hydrochloric acid, phosphoric acid, boric acid or nitric acid. The general formula of the organic acid is R-(COOH):

when R is alkyl, the organic acid is alkanoic acid;
when R is alkenyl, the organic acid is alkene acid;
when R is aryl, the organic acid is aromatic acid;
when R is alkylhalide, the organic acid is halidealkanoic acid;
when R is hydrogen, the organic acid is formic acid; and,
when R is alkynyl, the organic acid is alkyne acid.

The general formula of the organic alcohol acid is (HO)-R-(COOH):

when R is alkyl, the organic acid is hydroxyalkanoicacid;
when R is alkenyl, the organic acid is hydroxyalkenoicacid;
when R is aryl, the organic acid is aryl alcoholic acid; and,
when R is alkynyl, the organic acid is hydroxyalkynoicacid.

The general formula of the organic diacid is (HOOC)-R-(COOH):

when R is alkyl, the organic acid is alkyl diacid;
when R is alkenyl, the organic acid is alkene diacid;
when R is aryl, the organic acid is aryl diacid; and,
when R is alkynyl, organic acid is alkyne diacid.

The general formula of the organic phosphoric acid is $(R_1O), (R_2O)\text{-}(POOH)$:

when R is alkyl, the organic acid is dialkylphosphoric acid;
when R is alkenyl, the organic acid is dialkene phosphoric acid;
when R is alkylhalide, the organic is halidedialkylphosphoric acid;
when R is hydrogen, the organic is phosphoric acid; and,
when R is alkynyl, the organic is dialkyne phosphoric acid.

4. Water rinsing: All acid residuals are removed from alloy surface by water rinsing.
5. Removing of oxide on the alloy surface: After acid treatment, the alloy is put in a solution of acidity or alkalinity to remove oxide from the alloy surface. Meanwhile in this process, the alloy surface produces hydroxyl.
6. The acidic or alkaline solution left on the alloy surface is cleaned up by water.
7. Thin film treatment: The alloy surface formed with hydroxyl group is treated by dip coating, spray coating or roller coating with coating liquid which will bond with the hydroxyl group on the alloy surface and form a film thereon. The coating liquid employs aluminum sec-butoxide or a compound freely composed of more than one of the ingredients listed in the first preferred embodiment of the invention.
8. Curing: The alloy formed with a film on the surface is cured for five to thirty minutes at a temperature around 150°C~200°C to finish thin film coating on the alloy surface.

[0014] In addition, the modes of the film treatment in the steps of the preferred embodiment mentioned above may have the following processes.

(A). Dip coating with coating liquid:
The ingredient of the coating liquid forms an extremely thin film on an alloy surface, and then the alloy is centrifugated by a centrifugal machine. Then, the alloy formed with a film on the surface is cured for about five to thirty minutes at a temperature around 150°C~200°C to obtain a film with a thickness around 0.5~1 μm, thus finishing coating a film on the alloy surface.
(B). Heat the alloy with coating liquid: The coating liquid is first reacts with the alloy surface which immersed in the liquid, and also the nano-particle ingredients in the coating liquid will penetrate into the alloy surface to make up an extremely thin film thereon and then cured. The thin film thickness is around 0.5~1μm.

[0015] Subsequently, the alloy surface formed with a thin film and treated through the above-mentioned processes is tested by salt spraying for twenty four hours, The result is that less than 5% corrosion area of the alloy surface that means the treated alloy performming well in quality.

[0016] Besides, the alloy treated through the foresaid processes passes the adhesion tested per ASTM D3359-97 by over coat on the treated alloy surface. Further, the alloy treated through the foresaid processes is tested in conductivity by means of a HP milliohmer (HP4338) and the result is less than 0.3 mΩ, it means that the alloy surface has good conductivity.

[0017] As can be noted from the above description, the method of non-chromate pretreatment for magnesium alloys in the invention has the following advantages.

1. Promotion of anti-corrosion : In the process of thin film forming, chemical bonding takes the place of physical engagement, able to make up a strong adhesion and extreme thin film with anti-corrosion performance.
2. Increasing adhesion in coating or gluing: By adhesion test, it is proved that the paint on the alloy surface treated through the process of this invention is performing well. Besides, there is a variety of coating liquids, so chemical ingredients for coating on an alloy surface can be freely selected and adjusted for use, able to acquire different capacities in adhesion, anti-rust, anti-corrosion, anti-finger, anti-dust conductivity and in water repellence.
3. Having good conductivity: The conductivity of the treated alloy, tested by a HP milliohmer (HP4338), is less than 0.3mΩ, indicating that the alloy treated through the process of this invention has excellent conductibility.
4. The alloy surface treated by the method of this invention is able to reduce adherence of fingerprint and dust.
5. No water rinsing process is used after thin film formed on the alloy surface and no heavy metallic ion in the agents employed for treating the alloy surface, impossible to waste and pollute water.
6. The film is formed on the alloy surface by means of dip coating, spray coating or roller coating, simple and easy in handling, greatly lowering cost in equipment and able to produce products with high throughput.

[0018] While the preferred embodiments of the invention have been described above, it will be recognized and understood that various modifications may be made therein and the appended claims are intended to cover all such modifications that may fall within the scope of said claims.

Claims

1. Method of non-chromate pretreatment for magnesium alloys comprising:

(a) a first step of degreasing: an alloy is primarily treated with a degreasing agent to remove superficial oily dirt from the surface of said alloy:
(b) a second step of water rinsing: said alloy surface finished in step (a) is rinsed with water to make it clean;
(c) a third step of acid pretreatment: a mixed solution of organic-inorganic acid is applied on the surface of said magnesium alloy to let the surface of said magnesium alloy present its original color or gray or black and make its surface activated to enhance a film's formation; using said mixed solution of said organic-inorganic acid for acid pretreatment on an alloy surface can activate a metal and remove oxide from its surface and form hydroxyl group thereon so as to enhance sequent film treatment;
(d) a fourth step of film treatment: said alloy surface is coated with coating liquid, said coating liquid carrying out reaction on said alloy surface, said coating liquid bonding with said alloy surface and forming a film on said alloy surface, said coating liquid using aluminium sec-butoxide or a compound freely composed of more than one of the following chemicals: vinyltrimethoxysilane, tetraethoxysilane, methyltrimethoxysilane, γ-methacryloxypropyl-trimethoxysilane, γ-chloropropyl-trimethoxysilane, dimethyldiethoxysilane, phenyltriethoxysilane, decyltrimethoxysilane, isobutyltrimethoxysilane, 3-aminopropyltrimethoxysilane, tert-butyldimethylchlorosilane, vinyltrichlorosilane, γ-mercaptopropyltrimethoxysilane, diphenyldichlorosilane, hexamethyldisilane, vinyltrisilane, zirconiumpropoxide, ethylsilicate, 1,1,2,2-tetrahydroctyl-1-triethoxysilane, titanium(IV) propoxide, titanium(IV)isopropoxide, titanium (IV)butoxide, titanium(IV)sec-butoxide, or titanium(IV)tert-butoxide.

2. Method according to claim 1, **characterized in that** after film treatment, said film formed on said alloy surface can be lacquered or stuck thereon with adhesives, and the way of applying said coating liquid on said alloy surface is dip coating, spray coating or roller coating.

3. Method according to claim 1 or 2, **characterized in that** activation treatment is carried out after said alloy surface finishes acid treatment; said activation treatment is to have said alloy dipped in an acidic or alkaline solution to let said alloy surface produce hydroxyl group, and said mixed solution of said organic-inorganic acid used for acid treatment is inorganic acid or organic acid singly, or a mixed solution of both; said organic acid can be selected from more than one of the followings, acid, alcohol acid, diacid and phosphonic acid, while said inorganic acid can be selected from more than one of the followings, hydrochloric acid, phosphoric acid, boric acid or nitric acid; and,
the general formula of said organic acid being R-(COOH):

when R is alkyl, said organic acid being alkanoic acid;
when R is alkenyl, said organic acid being alkene acid;
when R is aryl, said organic acid being aromatic acid;
when R is alkylhalide, said organic acid being halidealkanoic acid;
when R is hydrogen, said organic acid being formic acid;
when R is alkynyl, said organic acid being alkyne acid; and,

the general formula of organic alcohol acid being (HO)-R-(COOH):

when R is alkyl, said organic acid being hydroxyalkanoic acid;
when R is alkenyl, said organic acid being hydroxyalkenoic acid;
when R is aryl, said organic acid being aryl alcohol acid;
when R is alkynyl, said organic acid being hydroxyalkynoic acid; and

the general formula of organic diacid being (HOOC)-R-(COOH):

when R is alkyl, said organic acid being alkyl diacid;
when R is alkenyl, said organic acid being alkene diacid;
when R is aryl, said organic acid being aryl diacid;
when R is alkynyl, said organic acid being alkyne diacid; and,

the general formula of organic phosphoric acid being (R_1O), (R_2O)-(POOH):

when R is alkyl, said organic acid being dialkyl phosphoric acid;
when R is alkenyl, said organic acid being dialkene phosphoric acid;
when R is alkylhalide, said organic acid being halidedialkyl phosphoric acid;
when R is hydrogen, said organic acid being

phosphoric acid;
when R is alkynyl, said organic acid being dialkyne phosphoric acid.

Patentansprüche

1. Verfahren zur nicht-Chromat-Vorbehandlung für Magnesiumlegierungen, umfassend:

(a) einen ersten Schritt des Entfettens, bei dem eine Legierung primär mit einem Entfettungsmittel zur Entfernung von oberflächlichem öligen Schmutz von der Oberfläche der Legierung behandelt wird,
(b) einen zweiten Schritt des Spülens mit Wasser, bei dem die im Schritt (a) fertiggestellte Legierungsoberfläche mit Wasser gespült wird, um sie zu säubern,
(c) einen dritten Schritt einer Säurevorbehandlung, bei dem eine Mischlösung aus einer organischen-anorganischen Säure auf die Oberfläche der Magnesiumlegierung aufgebracht wird, so dass die Oberfläche der Magnesiumlegierung ihre ursprüngliche Farbe zeigt oder grau oder schwarz ist und deren Oberfläche aktiviert wird, um die Bildung eines Films zu verstärken, wobei die Verwendung der Mischlösung der organischen-anorganischen Säure für eine Säurevorbehandlung auf einer Legierungsoberfläche ein Metall aktivieren und Oxid von dessen Oberfläche entfernen und Hydroxylgruppen darauf bilden kann, so dass eine anschließende Filmbehandlung verstärkt wird,
(d) einen vierten Schritt einer Filmbehandlung, bei dem die Legierungsoberfläche mit einer Beschichtungsflüssigkeit beschichtet wird, wobei die Beschichtungsflüssigkeit eine Reaktion auf der Legierungsoberfläche ausführt, wobei die Beschichtungsflüssigkeit mit der Legierungsoberfläche bindet und einen Film auf der Legierungsoberfläche bildet, wobei in der Beschichtungsflüssigkeit Aluminium-sec-butoxid oder eine Verbindung verwendet wird, die beliebig aus mehr als einer der folgenden Chemikalien zusammengesetzt ist: Vinyltrimethoxysilan, Tetraethoxysilan, Methyltrimethoxysilan, γ-Methacryloxypropyltrimethoxysilan, γ-Chlorpropyltrimethoxysilan, Dimethyldiethoxysilan, Phenyltriethoxysilan, Decyltrimethoxysilan, Isobutyltrimethoxysilan, 3-Aminopropyltrimethoxysilan, tert-Butyldimethylchlorsilan, Vinyltrichlorsilan, γ-Mercaptopropyltrimethoxysilan, Diphenyldichlorsilan, Hexamethyldisilan, Vinyltrisilan, Zirkoniumpropoxid, Ethylsilikat, 1,1,2,2-Tetrahydroctyl-1-triethoxysilan, Titan(IV)-propoxid, Titan(IV)-isopropoxid, Titan(IV)-butoxid, Titan (IV)-sec-butoxid oder Titan(IV)-tert-butoxid.

2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** nach der Filmbehandlung der auf der Legierungsoberfläche gebildete Film lackiert oder mit Haftmitteln versehen werden kann, wobei die Beschichtungsflüssigkeit mittels Tauchbeschichten, Sprühbeschichten oder Walzenbeschichten auf die Legierungsoberfläche aufgebracht wird.

3. Verfahren nach Anspruch 1 oder 2, **dadurch gekennzeichnet, dass** die Aktivierungsbehandlung nach dem Ende der Säurebehandlung der Legierungsoberfläche durchgeführt wird, wobei bei der Aktivierungsbehandlung die Legierung in eine saure oder alkalische Lösung getaucht wird, so dass die Legierungsoberfläche Hydroxylgruppen erzeugt, und wobei die Mischlösung aus einer organischen-anorganischen Säure, die für die Säurebehandlung verwendet wird, eine einzelne anorganische Säure oder organische Säure oder eine Mischlösung aus beiden ist, wobei die organische Säure aus mehr als einer der folgenden ausgewählt werden kann: Säure, Alkoholsäure, Disäure und Phosphonsäure, während die anorganische Säure aus mehr als einer der folgenden ausgewählt werden kann: Chlorwasserstoffsäure, Phosphorsäure, Borsäure oder Salpetersäure, und wobei
die allgemeine Formel der organischen Säure R-(COOH) ist,
wobei dann, wenn R Alkyl ist, die organische Säure eine Alkansäure ist,
wobei dann, wenn R Alkenyl ist, die organische Säure eine Alkensäure ist,
wobei dann, wenn R Aryl ist, die organische Säure eine aromatische Säure ist,
wobei dann, wenn R Alkylhalogenid ist, die organische Säure eine Halogenalkansäure ist,
wobei dann, wenn R Wasserstoff ist, die organische Säure Ameisensäure ist,
wobei dann, wenn R Alkinyl ist, die organische Säure eine Alkinsäure ist, und
die allgemeine Formel der organischen Alkoholsäure (HO)-R-(COOH) ist,
wobei dann, wenn R Alkyl ist, die organische Säure eine Hydroxyalkansäure ist,
wobei dann, wenn R Alkenyl ist, die organische Säure eine Hydroxyalkensäure ist,
wobei dann, wenn R Aryl ist, die organische Säure eine Arylalkoholsäure ist,
wobei dann, wenn R Alkinyl ist, die organische Säure eine Hydroxyalkinsäure ist, und
die allgemeine Formel der organischen Disäure (HOOC)-R-(COOH) ist,
wobei dann, wenn R Alkyl ist, die organische Säure eine Alkyldisäure ist,
wobei dann, wenn R Alkenyl ist, die organische Säure eine Alkendisäure ist,
wobei dann, wenn R Aryl ist, die organische Säure eine Aryldisäure ist,

wobei dann, wenn R Alkinyl ist, die organische Säure eine Alkindisäure ist, und
die allgemeine Formel der organischen Phosphorsäure (R_1O), (R_2O)-(POOH) ist,
wobei dann, wenn R Alkyl ist, die organische Säure eine Dialkylphosphorsäure ist,
wobei dann, wenn R Alkenyl ist, die organische Säure eine Dialkenphosphorsäure ist,
wobei dann, wenn R Alkylhalogenid ist, die organische Säure eine Halogendialkylphosphorsäure ist,
wobei dann, wenn R Wasserstoff ist, die organische Säure Phosphorsäure ist,
wobei dann, wenn R Alkinyl ist, die organische Säure eine Dialkinphosphorsäure ist.

Revendications

1. Procédé pour le prétraitement d'alliage de magnésium sans chromate, comprenant :

(a) une première étape de dégraissage dans laquelle un alliage est principalement traité avec un agent de dégraissage pour supprimer les saletés huileuses superficielles depuis la surface dudit alliage ;
(b) une seconde étape de rinçage à l'eau dans laquelle la surface de l'alliage finie dans l'étape (a) est rincée avec de l'eau pour la rendre propre,
(c) une troisième étape de prétraitement à l'acide dans laquelle une solution mixte d'acides organiques/inorganiques est appliquée sur la surface dudit alliage de magnésium pour amener la surface dudit alliage de magnésium à présenter sa couleur, grise ou noire, d'origine et rendre sa surface activée pour améliorer la formation d'un film ; et on utilise ladite solution mixte d'acides organiques/inorganiques pour un prétraitement à l'acide sur une surface de l'alliage pour pouvoir activer un métal et supprimer les oxydes depuis sa surface et former sur celui-ci un groupe hydroxyle de manière à améliorer le traitement du film ultérieur ;
(d) une quatrième étape de traitement du film dans laquelle ladite surface de l'alliage est revêtue avec un liquide de revêtement, ledit liquide de revêtement effectuant une réaction sur ladite surface de l'alliage, ledit liquide de revêtement s'alliant avec ladite surface de l'alliage et formant un film sur ladite surface, ledit liquide revêtement utilisant de l'aluminium sec-butoxide ou un composé constitué librement de plus d'un des produits chimiques suivants : vinyltriméthoxysilane, tétraéthoxysilane, méthyltriméthoxysilane, γ-méthacryloxypropyl-triméthoxysilane, γ-chloropropyltriméthoxysilane, diméthyldiéthoxysilane, phényltriéthoxysilane, décyltriméthoxysilane, isobutyltriméthoxysilane, 3-aminopropyltriméthoxysilane, tert-butyldiméthylchlorosilane, vinyltrichlorosilane, γ-mercaptopropyltriméthoxysilane, diphényldichlorosilane, hexaméthyldisilane, vinyltrisilane, propoxide de zirconium, éthylsilicate, 1,1,2,2-tétrahydroctyl-1-triméthoxysilane, propoxide de titane (IV), isopropoxide de titane (IV), butoxide de titane (IV), sec-butoxide de titane (IV), ou butoxide de tertiaire de titane (IV).

2. Procédé selon la revendication 1, **caractérisé en ce que**, après traitement du film, ledit film formé sur ladite surface de l'alliage peut être appliqué par peinture ou par collage sur celle-ci avec des adhésifs, et la méthode d'application dudit liquide revêtement sur ladite surface de l'alliage a lieu par revêtement au plonger, revêtement par pulvérisation, ou revêtement au rouleau.

3. Procédé selon la revendication 1 ou 2, **caractérisé en ce que** le traitement d'activation est effectué après terminaison du traitement acide de ladite surface de l'alliage ; ledit traitement d'activation consistant à plonger ledit alliage dans une solution acide ou alcaline pour amener ladite surface de l'alliage à produire un groupe hydroxyle, et ladite solution mixte d'acides organiques/inorganiques utilisée pour le traitement acide est constituée uniquement d'acide inorganique ou d'acide organique, ou d'une solution mixte des deux ; ledit acide organique pouvant être choisi parmi plusieurs des acides suivants :

acides dérivé d'alcool, diacide et acide phosphorique, alors que ledit acide inorganique peut être choisi parmi plusieurs des acides suivants :

acide chlorhydrique, acide phosphorique, acide borique ou acide nitrique ; et

la formule générale dudit acide organique étant R-(COOH) :

quand R est un alkyle, ledit acide organique est de l'acide alcanoïque ;
quand R est un alcényle, ledit acide organique est de l'acide alcénique ;
quand R est un aryle, ledit acide organique est un acide aromatique ;
quand R est un halogénure alkyle, ledit acide organique est un acide halogénure alkanoïque ;
quand R est de l'hydrogène, ledit acide organique est de l'acide formique ;
quand R est un alkynyle, ledit acide organique est de l'acide alkyne ; et
la formule générale de l'acide organique d'alcool étant (HO)-R-(COOH) :
quand R est un alkyle, ledit acide organique est

de l'acide hydroxyalkanoïque ;
quand R est un alkényle, ledit acide organique est de l'acide hydroxyalkénoïque ;
quand R est un aryle, ledit acide organique et de l'acide aryle-alcool ;
quand R est un alkynyle, ledit acide organique est de l'acide hydroxyalkynoïque ; et

la formule générale du diacide organique étant (HOOC)-R-(COOH) :

quand R est un alkyle, ledit acide organique est du diacide alkyle ;
quand R est un alkényle, ledit acide organique est du diacide alkénique ;
quand R est un aryle, ledit acide organique est du diacide aryle ;
quand R est un alkynyle, ledit acide organique est du diacide alkyne ; et
la formule générale de l'acide organique phosphorique étant (R1O), (R2O)-(POOH) :
quand R est un alkyle, ledit acide organique est de l'acide phosphorique dialkyle ;
quand R est un alkényle, ledit acide organique est de l'acide phosphorique dialkénique ;
quand R est un halogénure alkyle, ledit acide organique est de l'acide phosphorique halogénure dialkyle ;
quand R est de l'hydrogène, ledit acide organique est de l'acide phosphorique ;
quand R est un alkynyle, ledit acide organique est de l'acide phosphorique dialkyne.

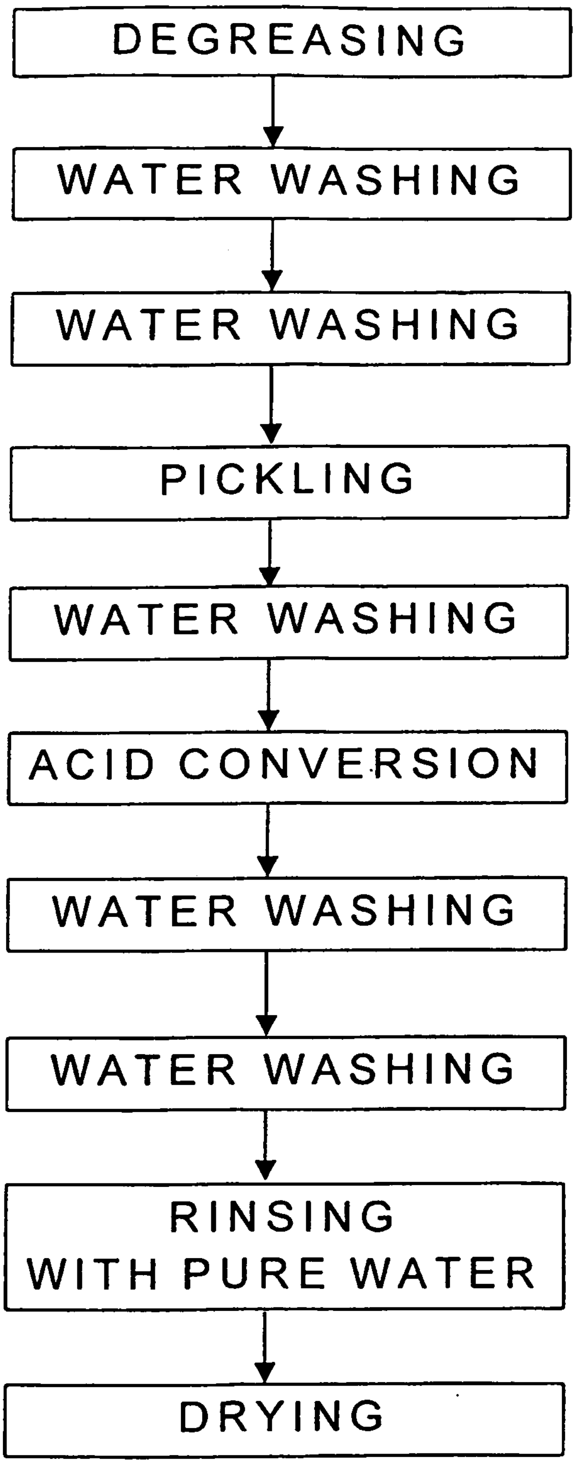

FIG. 1
(PRIOR ART)

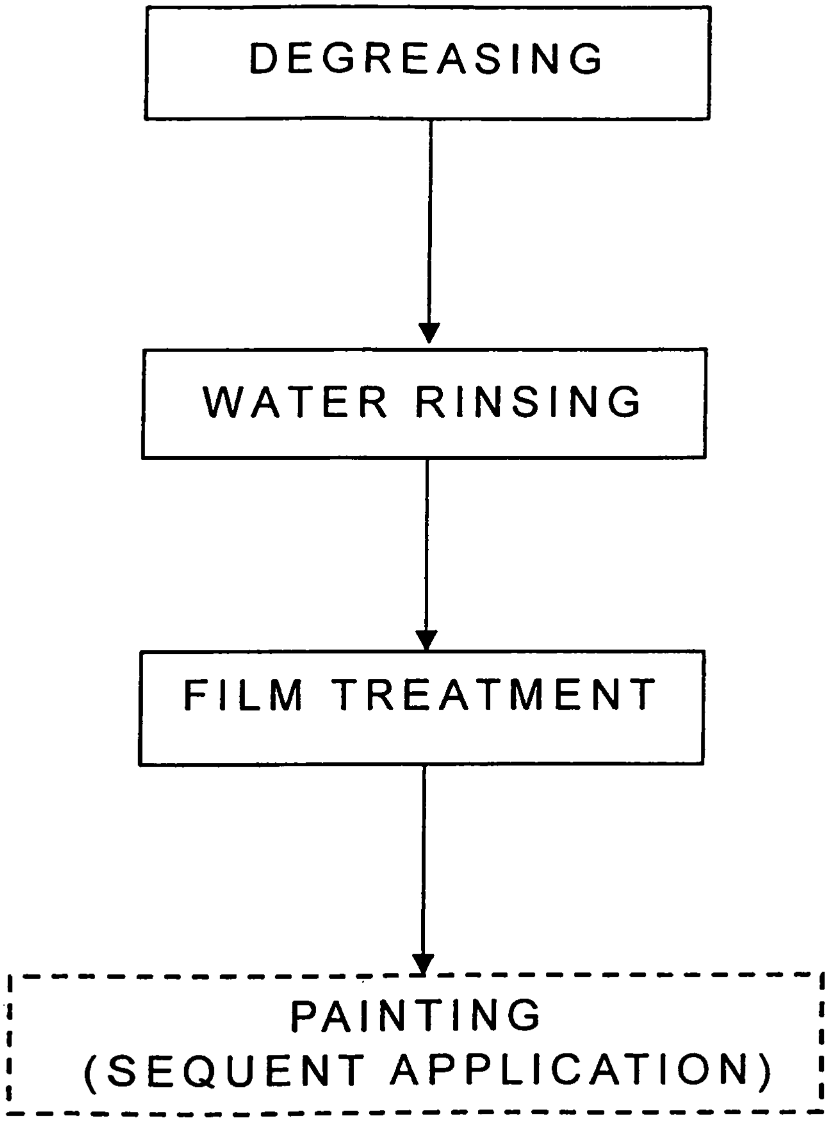
DEGREASING
WATER RINSING
FILM TREATMENT
PAINTING
(SEQUENT APPLICATION)

FIG. 2

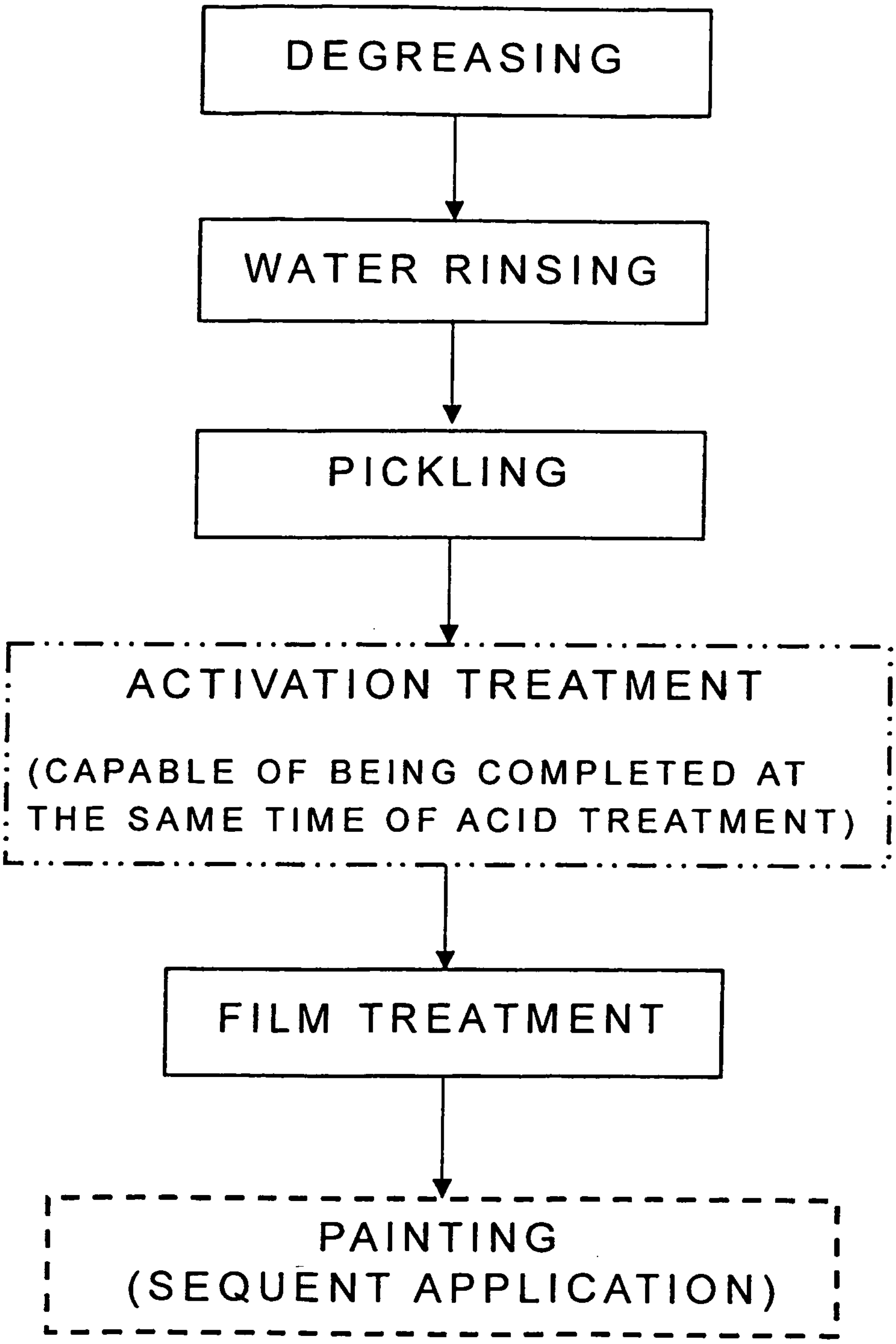
DEGREASING
WATER RINSING
PICKLING
ACTIVATION TREATMENT
(CAPABLE OF BEING COMPLETED AT THE SAME TIME OF ACID TREATMENT)
FILM TREATMENT
PAINTING
(SEQUENT APPLICATION)

FIG. 3

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- EP 0358338 A2 **[0004]**
- JP 57023057 A **[0005]**
- JP 02034790 A **[0006]**