



(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
21.07.2004 Bulletin 2004/30

(51) Int Cl.7: **C23C 18/12**

(21) Application number: **03001023.5**

(22) Date of filing: **17.01.2003**

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IT LI LU MC NL PT SE SI SK TR
 Designated Extension States:
AL LT LV MK RO

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

(57) A method of non-chromate pretreatment for metal alloys includes steps of degreasing, water rinsing and film treatment. The film treatment is to have the alloy surface coated with coating liquid which will carry out film coating reaction to the alloy surface and bond with the alloy surface to form a film thereon. In the process of the film treatment, it is impossible to produce industrial waste water containing heavy metallic ion, able to reduce environmental pollution to the minimum.

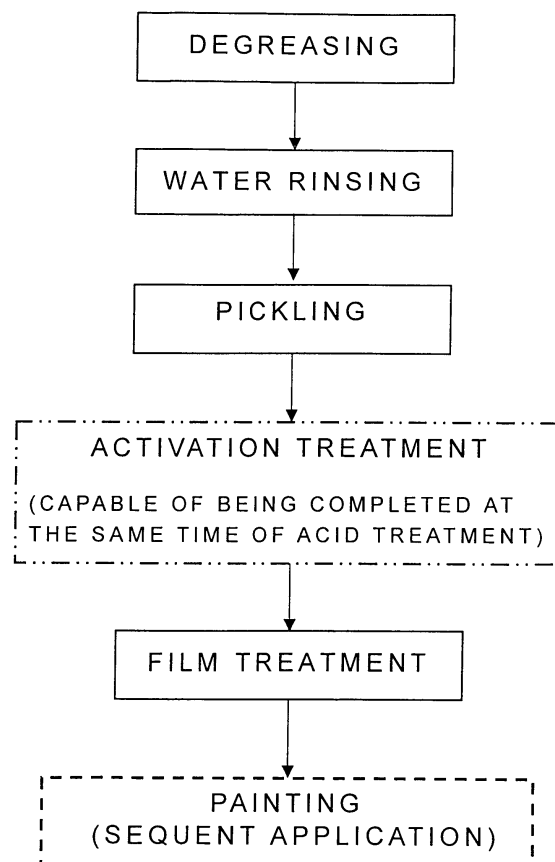


FIG. 3

Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] This invention relates to a method of non-chromate pretreatment for metal 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.

SUMMARY OF THE INVENTION

[0004] 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.

[0005] 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.

[0006] The main feature of the invention is a treating process including degreasing, water rinsing and film treatment. 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-butyl dimethylchlorosilane, 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.

[0007] A second feature of the invention is a method of non-chromate pretreatment for such alloys as aluminum alloy, titanium alloy, zinc alloy or copper alloy.

[0008] A third feature of 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

[0009] 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 in the present invention; 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

[0010] One preferred embodiment of a method of non-chromate pretreatment for metal alloys, inclusive of aluminum alloy, titanium alloy, zinc alloy or copper alloy, in the present invention, 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 0.5~1μm. 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-tetrahydroxy-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.

[0011] Another 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 haloalkanoic 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 hydroxyalkanoic acid;

when R is alkenyl, the organic acid is hydroxyalkenoic acid;

when R is aryl, the organic acid is aryl alcoholic acid; and,

when R is alkynyl, the organic acid is hydroxyalkynoic acid.

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 (R₁O), (R₂O)-(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 haloalkylphosphoric acid;

when R is hydrogen, the organic is phosphoric acid; and,

when R is alkynyl, the organic is dialkyne phosphoric acid.

phoric 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.

[0012] In addition, the modes of the film treatment in the steps of the two preferred embodiments 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 0.5~1μm, 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.

[0013] 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 performing well in quality.

[0014] 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.

[0015] As can be noted from the above description, the method of non-chromate pretreatment for metal 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 conductivity.

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.

[0016] 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 spirit and scope of the invention.

Claims

1. A method of non-chromate pretreatment for metal alloys comprising:

(1). 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:

(2). A second step of water rinsing: said alloy surface finished in the first step is rinsed with

water to make it clean;

(3). A third 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 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-butyltrimethoxysilane, vinyltrichlorosilane, γ -mercaptopropyl-trimethoxysilane, diphenyldichlorosilane, hexamethyldisilane, vinyltrisilane, zirconiumpropoxide, ethylsilicate, 1,1,2,2-tetrahydroxyethyl-1-triethoxysilane, titanium(IV)propoxide, titanium(IV)isopropoxide, titanium(IV)butoxide, titanium(IV)sec-butoxide, or titanium(IV)tert-butoxide.

2. The method of non-chromate pretreatment for metal alloys as claimed in Claim 1, wherein said metal is an aluminum alloy, a titanium alloy, a zinc alloy or a copper alloy.

3. The method of non-chromate pretreatment for metal alloys as claimed in Claim 1, wherein if said metal is a magnesium alloy, the steps of treating its surface include degreasing, water rinsing, acid pretreatment and film treatment; a mixed solution of organic-inorganic acid is applied to carry out acid pretreatment 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 subsequent film treatment.

4. The method of non-chromate pretreatment for metal alloys as claimed in Claim 1 or 3, wherein 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.

5. The method of non-chromate pretreatment for metal alloy as claimed in Claim 3, wherein 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 solu-

tion 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 alkanonic 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 (R₁O), (R₂O)-(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 di-
alkyne phosphoric acid.

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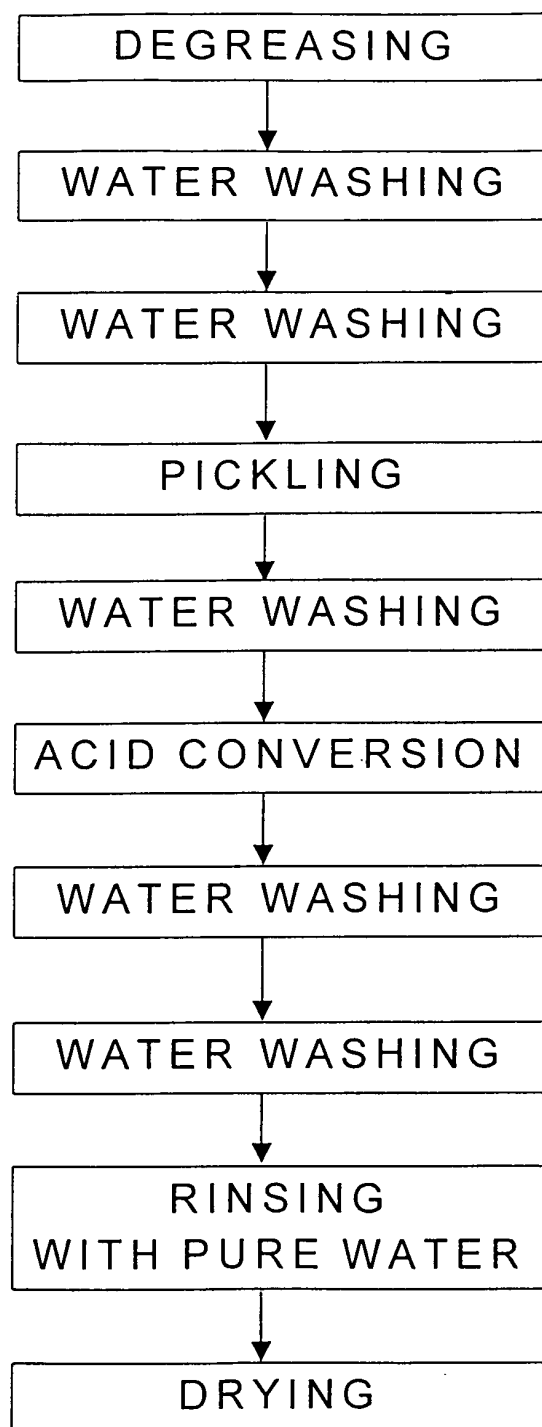


FIG. 1
(PRIOR ART)

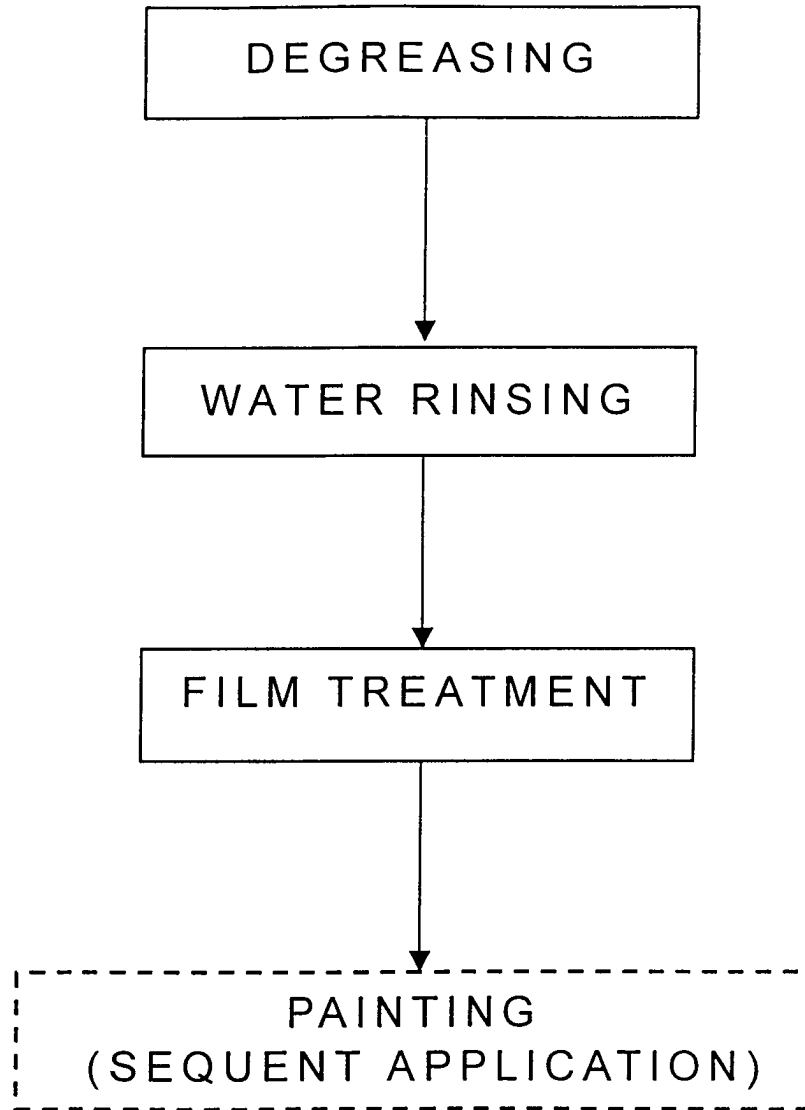


FIG. 2

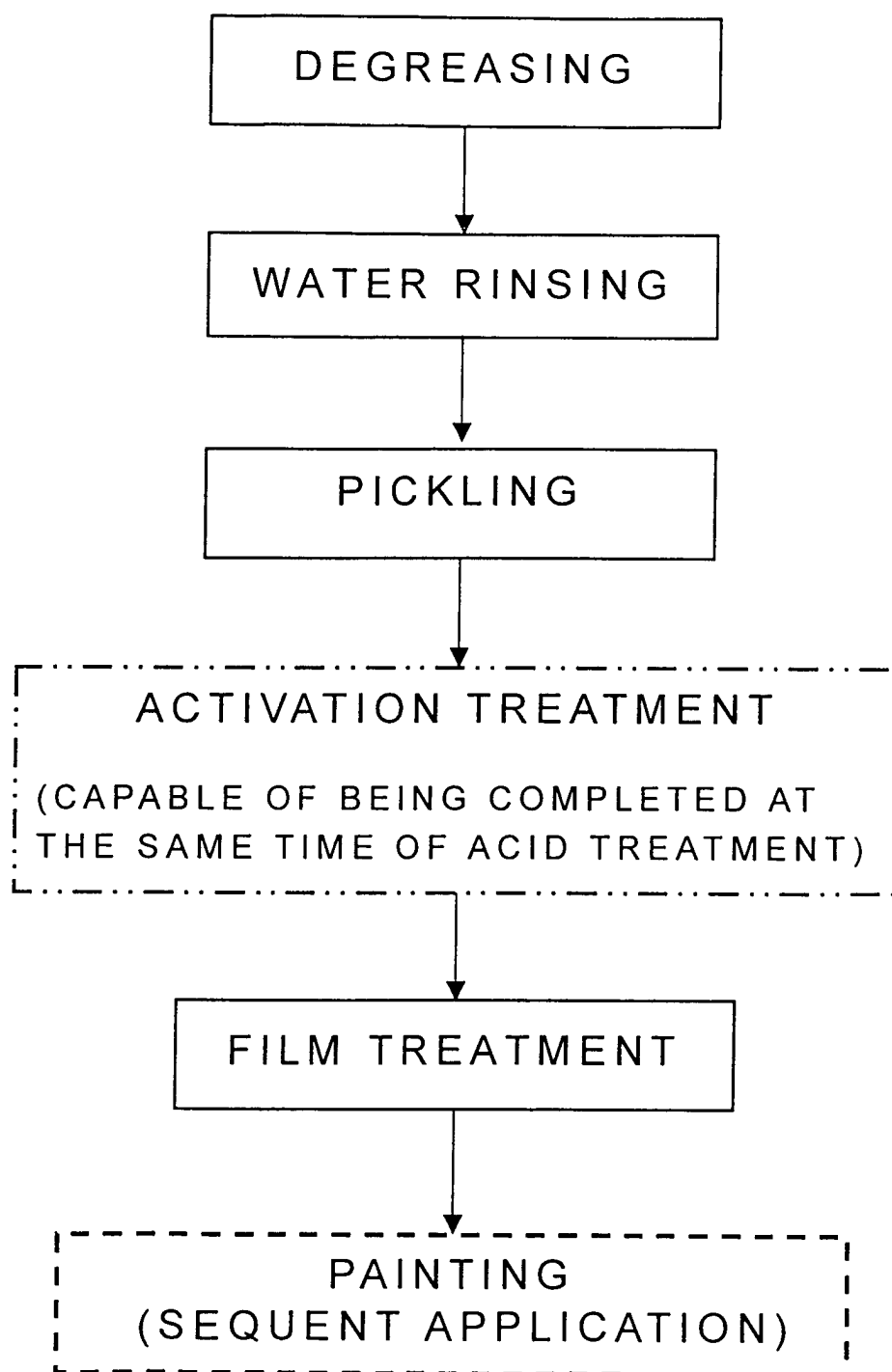


FIG. 3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 03 00 1023

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**ANNEX TO THE EUROPEAN SEARCH REPORT
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