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RESIN-COVERED METALLIC PLATE AND METHOD OF MANUFACTURING THE SAME

BACKGROUND OF THE INVENTION

The present invention relates to a resin-covered metallic plate and a method of manufacturing the same, and a capacitor container using the same.

Heretofore, resin-covered metallic plates such as an aluminum plate covered with a layer of a thermoplastic resin are used in various fields because they have excellent corrosion resistance, electrical insulating quality, designability, etc. For example, an aluminum electrolytic capacitor has a capacitor element impregnated with an electrolyte and housed in a cylindrical container formed by drawing an aluminum plate. The container is sealed with e.g. rubber and having its outer periphery covered by a heat-shrinkable tube of a vinyl chloride resin or an olefin-type resin for electrical insulation and indication.

In recent years, compactness of electronic parts is sought, and for aluminum electrolytic capacitors, too, there is a tendency toward compactness. Further, development of chip type electrolytic capacitors which have no lead wires for surface mounting is progressing. With such aluminum electrolytic capacitors, there is a



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problem that since the container is small, covering by a heat-shrinkable tube is extremely difficult, so that the capacitor element housed in the container contacts the inner surface of the container, thus making it impossible to achieve insulating properties.

For the purpose of solving this problem, it has been proposed to cover the surface of a metallic plate such as an aluminum plate with an insulating resin, and form the resin-covered plate into a container or cap by drawing or ironing to achieve insulating properties while omitting the covering step by a heat-shrinkable tube (Japanese patent publication 1-175222 and utility model publication 3-79974).

As a technique for covering the surface of an aluminum plate with an insulating resin into a resin-covered plate, there are two methods, one is to coat an epoxy resin, vinyl chloride resin or polyester resin to the surface of an aluminum plate, and the other is to laminate a resin layer on the surface of an aluminum plate.

But with resin-covered metallic plates on which is formed a covering layer by such known methods, there is a shortcoming that peeling can occur at the interface between the aluminum plate and the covering layer in the secondary working step such as drawing or ironing.

An object of this invention is to provide a resin-covered metallic plate which is superior in adhesion (bond

properties or bond strength), in which at the interface between the aluminum plate and the thermoplastic resin covering layer, ply separation, breakage or cracks of the thermoplastic resin covering layer do not occur, ply separation hardly occur with time, and which can be manufactured efficiently.

According to the present invention, there is provided a resin-covered metallic plate comprising a metallic plate, a chemical conversion treated layer formed on the metallic plate, a layer of a silane coupling agent formed on the surface of the chemical conversion treated layer, and a covering layer of a thermoplastic resin formed on the layer of a silane coupling agent.

The provision of the chemical conversion treated layer improves the corrosion resistance of the metallic plate and the adhesion between the metallic plate and the thermoplastic resin covering layer.

Since the layer of a silane coupling agent is disposed, the organic functional groups in the silane coupling agent react with the thermoplastic resin, so that the metallic plate and the thermoplastic resin covering layer are strongly bonded together through the silane coupling agent. Thus, it is possible to prevent ply separation between them, damage to the covering layer, etc.

Hereinbelow, this invention will be described in detail.

With the resin-covered metallic plate according to this invention, a chemical conversion treated layer is formed on a metallic plate, a layer of a silane coupling agent (hereinafter referred to as "silane coupling agent layer") is formed on the surface of the chemical conversion treated layer, and a covering layer of a thermoplastic resin (hereinafter referred to as "thermoplastic resin covering layer") is formed on the layer.

The metallic plate refers to a plate of a metal such as iron, various stainless steel, copper, copper alloy, aluminum, aluminum alloy, tin alloy, steel, nickel and zinc. Among them, an aluminum plate is preferable.

Aluminum forming the aluminum plate may be pure Al or an Al alloy. Specifically, pure Al, JIS 1000-family alloys such as JIS A 1050, A 1100 and A 1200, JIS 3000-family alloys of Al-Mn family such as JIS A 3003 and A 3004, and JIS 5000-family alloys of Al-Mg family can be cited. But aluminum is not limited to those cited above as examples.

Preferably, the aluminum plate has a thickness of 0.1-0.5 mm and more preferably 0.2-0.5 mm.

The chemical conversion treated layer serves to improve the corrosion resistance and adhesion of the metallic plate. As the chemical conversion treated layer for the aluminum thin plate, the following can be cited:

- (a) layer obtained by chemical conversion treatment with phosphate chromate,
- (b) layer comprising an organic thermoplastic resin covering layer and chrome,
- (c) layer containing zirconium by chemical conversion treatment,
- (d) layer containing titanium by chemical conversion treatment,
- (e) layer obtained by anodizing treatment,

The thickness of the chemical conversion treated layer is not specifically limited but is preferably 1-3000 Å (0.1-300 nm). If the thickness is less than 50 Å (5 nm), when the resin-covered metallic plate is subjected to drawing, the covering resin may peel or otherwise the workability will be inferior. If over 3000 Å (300 nm), formation of the layer may be difficult.

Also, if the chemical conversion treated layer is an anodized layer, the thickness is preferably 500-20000 Å (0.05-2 μm), and more preferably 1000-20000 Å (0.1-2 μm). In the case of other layers, 50-3000 Å (5-300 nm) is preferable. If the thickness of the anodized layer is less than 0.1 μm, adhesion would not be improved. On the other hand, if over 2 μm, long-time anodizing is necessary and thus the productivity would be inferior. The thickness of the anodized layer can be adjusted to a value within the above range by adjusting the treating

conditions, particularly exciting conditions and time.

As the anodized layer, anodized aluminum layer treated with an electrolyte containing at least phosphoric acid may be used, such as an anodized aluminum layer using phosphoric acid as an electrolyte, an anodized aluminum layer using phosphoric acid and sulfuric acid as an electrolyte, an anodized aluminum layer using phosphoric acid and oxalic acid as an electrolyte, and anodized aluminum layer using phosphoric acid and chromic acid as an electrolyte. Among them, anodizing with phosphoric acid is most preferable.

Besides the above, it is also possible to use a method in which after anodized aluminum phosphate has been formed, it is layer-laminated after electrolytic treatment in a bath of a silane coupling agent, a method in which after anodized aluminum phosphate has been formed, it is layer-laminated after electrolytic treatment in an epoxy emulsion bath, a method in which after anodized aluminum phosphate has been formed, it is layer-laminated after electrolytic treatment in a mixed bath of a silane coupling agent and an epoxy emulsion, and a method in which after the above electrolytic treatment, it is layer-laminated after silane coupling treatment or epoxy emulsion coating.

By forming an anodized layer on the surface of the aluminum plate, it is possible to improve adhesion (bond

properties or bond strength) at the interface between the aluminum plate and the thermoplastic resin covering layer.

For the treatment of the metallic surface, instead of forming a chemical conversion treated layer, single-layer plating, multiple-layer plating or alloy plating, or immersed chromic acid treatment or chromium phosphate treatment may be applied. Also, by electrolytic chromic acid treatment, it is possible to form a single-layer layer comprising a chrome hydrated oxide or a double-layer layer comprising a metallic chrome layer (lower layer) and a chrome hydrated oxide layer (upper layer) on the surface of the metallic plate. If a single-layer layer is formed, the chrome content is preferably about 3-30 mg/m². If a double-layer layer is formed, the chrome content of the lower layer is preferably about 2-200 mg/m² and that of the upper layer is preferably about 5-30 mg/m².

The silane coupling agent layer is formed by applying a silane coupling agent to the metallic plate or the chemical conversion treated layer and drying it. This layer functions to improve the bond strength between the metallic plate and the thermoplastic resin covering layer.

The silane coupling agent is an organic silicon compound having two or more different reactive groups. One of the two reactive groups is a group that chemically bonds to inorganic materials such as glass or metal. The

other is a reactive group that chemically bonds to organic materials such as synthetic resins. The reactive group that bonds to an inorganic material, a metallic plate or chemical conversion treated layer is not specifically limited but a methoxy group, ethoxy group, silanol group, etc. can be cited. On the other hand, as the reactive group that chemically bonds to organic materials, an epoxy group, amino group, vinyl group, methacrylic group, mercapto group, etc. can be cited. As representative silane coupling agents, γ -glycydoxypropyl triethoxysilane, γ -aminopropyl triethoxy silane, 3-methacryloxypropyl trimethoxy silane, etc. can be cited.

The aluminum plate and the silane coupling agent firmly bond together by forming an Al-O-Si bond. Also, the thermoplastic resin and the silane coupling agent firmly bond together because organic functional groups in the silane coupling agent react with the thermoplastic resin. Thus, the aluminum plate and the thermoplastic resin covering layer are firmly bonded together at the interface through the silane coupling agent.

As examples of the silane coupling agent that can be used, vinyltrimethoxy silane, chloropropyl trimethoxy silane, 3-glycydoxy propyltrimethoxy silane, 3-methacryloxypropyl trimethoxy silane, 3-aminopropyl triethoxy silane, N-2-aminoethyl-3-aminopropyl trimethoxy silane, 3-mercaptopropyl trimethoxy silane, 3-(N-

styrylmethyl-2-aminoethylamino)propyltrimethoxy silane hydrochloride, ureidoaminopropylethoxy silane, etc. can be cited.

The layer of the silane coupling agent layer is preferably formed by applying a silane coupling agent on the metallic plate or the chemical conversion treated layer by $0.01\text{--}1000\text{ mg/m}^2$, more preferably $0.5\text{--}500\text{ mg/m}^2$. If the amount of the silane coupling agent is less than 0.01 mg/m^2 , the adhesion (bonding property) of the interface may be insufficient. If over 1000 mg/m^2 , bond strength would reach saturation, so that increase in the bond strength will not be proportional to the amount applied. Also, since the silane coupling agent tends to aggregate, it becomes difficult to apply the agent evenly.

When applying a silane coupling agent on a metallic plate or anodized layer, in order to increase wettability on its surface, the silane coupling agent is preferably applied uniformly by diluting it with alcohol or water to uniformly dissolve or disperse it to lower the surface tension. As a method of lowering the surface tension, an organic compound such as an organic solvent or a surfactant may be added.

If an aqueous solution of the silane coupling agent is applied to the surface of a metallic plate or a chemical conversion treated layer, its concentration of is not specifically limited, but the content of the

silane coupling agent is preferably 0.01-10 parts by weight relative to 100 parts by weight of water. If less than 0.01 part by weight, the bonding function may not be sufficient. If over 10 parts by weight, the silane coupling agent becomes likely to agglomerate, so that it may not sufficiently perform the bonding function.

Also, an aqueous solution of the silane coupling agent is preferably adjusted so that the contact angle when applied to the surface of the metallic plate or the chemical conversion treated layer will be 55° or under. The magnitude of this contact angle is determined by the surface tension between the metallic plate and the aqueous solution of the silane coupling agent, and the surface tension can be easily adjusted by the kinds and added amounts of organic solvents and surfactants added to the aqueous solution of silane coupling agent. As the organic solvents, ethanol, isopropanol, etc. may be used. As the surfactants, anionic surfactants, cationic surfactants, ampholytic surfactants, nonionic surfactants, etc. may be used. For these organic solvents and surfactants, those which do not impair stability of the silane coupling agent should be selected and added by suitable amounts.

If the contact angle is over than 55°, the surface tension between the metallic plate and the aqueous solution of the silane coupling agent would be too large to form a uniform layer on the surface of the metallic

plate, so that the adhesive function will not be performed sufficiently.

To the aqueous solution of the coupling agent, besides the organic solvents and surfactants, thickeners, antiseptic agents, etc. may be added of such kinds and in such amounts that the contact angle will be maintained at 55° or under. The contact angle may be measured by a so-called droplet method in which the contact angle of a droplet of the aqueous solution of the silane coupling agent that adhered to the surface of the metallic plate is measured with various measuring devices.

The aqueous solution of the silane coupling agent may be applied to the surface of the metallic plate by an ordinary method such as a dip method, spray method, roll-coat method, gravure-roll method, reverse-roll method, air-knife method, kiss-roll method, spray-coat method, bar-coat method, dipping method, gravure-roll method, reverse-roll method, and air-knife-roll method.

To the silane coupling agent, various organic or inorganic additives may be added such as viscosity adjusting agents, defoamers, colorants such as pigments and dyes, stabilizers and solvents for adjusting dissolving properties.

After applying an aqueous solution of the silane coupling agent, solvents and the like are preferably volatilised and scattered by drying. When drying,

temperature is preferably raised at a rate of 50 °C /s or under. If over 50 °C /s, the aqueous solution of the silane coupling agent applied tends to be modified, so that the adhesion function of the layer formed by the aqueous solution of the silane coupling agent may lower. Temperature rise is preferably at a rate of 5-50 °C /s within the range of from room temperature to 150 °C .

The layer formed by applying and drying the aqueous solution of the silane coupling agent has the Si content of preferably 5-15 atomic % when its surface is measured by an X-ray electron spectroscopy (hereinafter referred to as "ESCA method"). If the Si element content is lower than 5 atomic %, the adhesive function of the aqueous solution of the silane coupling agent is not sufficiently obtained. Also, even if over 15 atomic %, it will not improve any further.

Also, the ESCA method is a method of analyzing the surface of a solid by electron spectroscopy, in which soft X-rays are shed on the surface of a solid specimen such as a metal, ceramic, inorganic compound, high-molecular material, and photoelectrons released from the surface of the solid specimen are detected by a static type energy analyzer to analyse the kinds of elements, state of oxidation and bond, etc. on the surface of the solid specimen. In the ESCA method, ordinary measuring conditions may be used without limitation. For example,

as a X-ray source, $MgK\alpha$, $AlK\alpha$, etc may be used. The output may be set at 15 kv x 33 mA and the degree of vacuum set at 5×10^{-8} Torr.

On the layer of the silane coupling agent, a covering layer of a thermoplastic resin is formed. This thermoplastic resin covering layer improves electric insulating properties and chemical resistance, etc. of the resin-covered metallic plate to provide a printing surface for identification.

For the thermoplastic resin covering layer, a layer of a thermoplastic resin may be used. As the thermoplastic resin, a polyester resin or a polyamide resin may be used. As the polyester resin, a polyester resin such as polyethylene terephthalate, polybutylene terephthalate, poly-1,4-cyclohexadimethylene terephthalate, or their copolymer; a copolymer of such a polyester resin and a polyolefin resin such as polyethylene or polypropylene, ethylene-vinyl acetate copolymer, ethylene-vinyl alcohol copolymer, and a copolymer of ethylene and an acrylic acid derivative; or a mixture of these polyester resins may be used.

As the polyamide resin, polyamide 6, polyamide 11, polyamide 12, polyamide 66, polyamide 610, polyamide 612, polyamide 46, their copolymeric polyamide, mixed polyamide, an aromatic polyamide such as polymethaxylyleneadipamide containing 90 mole % or over of structural units produced

in polycondensation reaction of methaxylylenediamine and adipic acid, amorphous polyamide, polyamide-family elastomer, shock-resistant polyamide, or a mixture of these polyamide resins may be used.

Among them, in view of heat resistance, particularly heat resistance in the solder re-flow step, a polyamide resin or polyester resin having a melting point of 180 °C or over can be used favorably in manufacturing a container for a capacitor from a resin-covered plate.

The method of forming the thermoplastic resin covering layer is not particularly limited, but it can be formed by a known method such as extrusion method using a coat-hanger die, T-die, I-die or inflation die, or calendering. The thermoplastic resin covering layer may be non-oriented or biaxially oriented.

The thermoplastic resin covering layer formed beforehand may be laminated on the silane coupling agent layer. Also, a thermoplastic resin may be laminated on the silane coupling agent layer while extruding it in a layer-like shape from an extruder equipped with a base of a T die, I die, etc.

To the thermoplastic resin, various kinds of resin additives may be added as required before forming a layer. As resin additives, colorants such as dyes and pigments, lubricants, blocking preventive agents, heat stabilizers, antistatic agents, light stabilizers, rust

preventives, ultraviolet absorbers, shock resistance improvers, antioxidants, antistatic agents, etc. can be cited. These resin additives may be blended by such an amount as not to have any bad effect on the thermoplastic resin covering layer. Further, in order to improve adhesion, surface treatment such as corona treatment or flame treatment may be applied.

The thermoplastic resin covering layer preferably has a thickness of 5-200 μm , more preferably 5-100 μm , most preferably 10-50 μm . If less than 5 μm , pin holes tend to develop and thus it becomes difficult to improve corrosion resistance and electric insulating properties of the aluminum plate. Also, it becomes extremely difficult to laminate the thermoplastic resin covering layer on the metallic plate. On the other hand, if over 200 μm , it is too thick, so that cracks tend to develop during drawing or ironing. Also, this is economically not favorable.

As a method of forming or laminating the thermoplastic resin covering layer on the silane coupling agent layer, a continuous method or a batch method may be used.

In the continuous method, firstly, the silane coupling agent is applied to the metallic plate or the chemical conversion treated layer. Next, it is heated to a temperature of 250-350 $^{\circ}\text{C}$ to scatter the liquid content in the silane coupling agent. And immediately, a

thermoplastic resin is laminated by extruding it in a layer shape by an extruder equipped with a base of a T or I die, or a thermoplastic resin layer that has already been formed into layer is pressed and laminated by a nip roller heated to the melting point of the thermoplastic resin or under. After lamination, it is immediately cooled by air or water cooling.

) If the temperature during lamination is lower than 250 °C, adhesion between the aluminum plate and the covering layer of a thermoplastic resin may be insufficient. If higher than 350 °C, heat deterioration of the covering layer will proceed, so that the covering layer may get damaged or cracks develop during drawing or ironing.

) On the other hand, in the batch method, a metallic plate formed with a silane coupling agent layer is heated to a temperature from the melting point to 350 °C, preferably to 200-350 °C, then the thermoplastic resin is laminated while extruding in a layer shape with an extruder equipped with a base of a T or I die, or a thermoplastic resin layer that has already been formed into layer is pressed and laminated by a nip roller heated to the melting point of the thermoplastic resin or under. After lamination, it is immediately cooled by air or water cooling.

If it is lower than the melting point of the

thermoplastic resin, the thermoplastic resin covering layer may not sufficiently adhere, and it may peel when the resin-covered metallic plate is worked. Also the thermoplastic resin covering layer of the resin-covered metallic plate becomes too hard to achieve a good workability. On the other hand, if higher than 350 °C, the metal in the resin-covered metallic plate will become too soft, so that its strength drops markedly and recesses or the like tend to develop. Also, the thermoplastic resin covering layer may deteriorate. The abovementioned melting point refers to a peak temperature of the crystalline melting temperature when temperature is raised at a rate of 10 °C /minute by a differential scanning calorimeter (DSC).

For the resin-covered metallic plate according to this invention, the Vickers hardness of the thermoplastic resin covering layer forming the resin-covered metallic plate as measured from its outer surface is preferably within the range of 25-55. If less than 25, the resin-covered metallic plate would be too soft to achieve a required workability. On the other hand, if over 55, the resin-covered metallic plate would be too hard. The "Vickers hardness" refers to a hardness measured under JIS Z 2244 "Vickers hardness test method".

Next, the method of manufacturing the resin-covered metallic plate according to this invention is

specifically described in several examples.

As a first example, a resin-covered metallic plate is manufactured by forming an anodized layer of 0.05-2 μ m thick on the surface of an aluminum plate, applying a silane coupling agent on the anodized layer at the rate of 0.5-500 mg/m², and laminating a covering layer of a thermoplastic resin having a thickness of 5-200 μ m on the layer of the silane coupling agent at a temperature of 250-350 °C .

As a second example, a resin-covered metallic plate is manufactured by forming a chemical conversion treated layer on one side of an aluminum plate having a thickness of 0.1-0.5 mm, applying a silane coupling agent on the layer at a rate of 0.01-1000 mg/m², heating the aluminum plate on which are laminated the chemical conversion treated layer and a silane coupling agent layer at a temperature of 200-350 °C , and laminating and pressing a thermoplastic resin layer having a thickness of 5-200 μ m onto the layer of the silane coupling agent so that the Vickers hardness of the surface of the covering layer of a thermoplastic resin will be 25-60.

Further as a third example, a resin-covered metallic plate is manufactured by blending a silane coupling agent by 0.01-10 parts by weight relative to 100 parts by weight of water, applying the aqueous solution of the silane coupling agent, which has been adjusted such

that the contact angle when applied to the surface of a metallic plate will be 55° or under, to the surface of the metallic plate, drying at the temperature rising speed of 50 °C /s or under to form a layer, heating the layer within the temperature range of from the melting point of the thermoplastic resin to 350 °C , and laminating a thermoplastic resin covering layer on the surface of the layer.

If the resin-covered metallic plate according to this invention is worked by drawing, cracks are less liable to develop in the thermoplastic resin covering layer. Also, since the thermoplastic resin covering layer will not easily peel off the metallic plate, the resin-covered metallic plate can be advantageously used as the material for a container formed through secondary forming steps such as bending, drawing and ironing. Also, since the resin-covered metallic plate will not easily peel off the metallic plate even if heated after working by various methods, a container manufactured from this resin-covered metallic plate can withstand heating.

Also, since this resin-covered metallic plate is superior in workability such as drawing, it can be advantageously used for the manufacture of containers for aluminum electrolytic capacitors. Also, if the Vickers hardness of the resin-covered surface is 25-60, even if containers contact each other during pressing, recesses

hardly develop in the top or side surfaces. Also, the pressure resistance increases and graceful printing for identification can be applied on the top of the containers.

Further, besides as wall surface materials of a building, partitioning plate materials, design materials, and materials for manufacturing various cans, this resin-covered metallic plate can be used advantageously as material for containers for capacitors. In manufacturing such containers for capacitors, since the solder re-flow step is required, a resin-covered metallic plate on which is laminated a thermoplastic resin covering layer having excellent heat resistance should be preferably used. Also, it is preferable to work such that the thermoplastic resin covering layer will face outside. As a container for a capacitor, a container for an electrolytic capacitor, an electrolytic capacitor cap, etc. can be cited.

[Examples]

Hereinbelow, the present invention is further described with reference to Examples. But the present invention is not limited to these Examples. The resin-covered metallic plates obtained in the Examples were evaluated by the following method.

(1) Drawability: Resin-covered metallic plates obtained in Examples were fed into a progressive drawing machine, and with the covering layer of a thermoplastic resin on the outer side of containers, 100 cylindrical containers

of 10 mm dia. x 20 mm high (drawing rate: 20%) were manufactured. The interface between the aluminum plate surface and the covering layer was visually observed, and those in which no ply separation was observed at the interface were indicated as good articles and in terms of good article rate (%) or "○".

(2) Caulkability: 100 cylindrical containers of 10 mm dia. x 20 mm were manufactured, and a disk-shaped caulking こま having a thickness of 3 mm (with a section having a radius R of 1.5 mm) was pressed against them while rotating them at 100 rpm to perform caulking so that the diameter would be 7.5 mm (diameter change rate = 25%). The interface between the aluminum plate surface and the covering layer was visually observed, and those in which no ply separation was observed at the interface were indicated as good articles in terms of good article rate (%) or "○".

(3) Change with time: After the 100 containers that had been subjected to the evaluation test for caulkability were left for 10 days at room temperature, the interface between the aluminum plate surface and the covering layer was visually observed, and those in which no ply separation was observed at the interface were indicated as good articles in terms of good article rate (%).

[Experiment Example 1]

(Test Examples 1-5)

<Manufacture of the resin-covered metallic plate>

Both sides of an aluminum plate (JIS A 1050 H22) 0.3 mm thick were anodized with a 20% phosphoric acid solution to form an anodized aluminum layer shown in Table 1. Next, a silane coupling agent shown in Table 1 was applied to the anodized layer at the rate of 50 mg/m², and the applied surface was heated to 280 °C. On the heated surface, a separately manufactured layer of polyamide 6 (melting point: 223 °C) having a thickness of 15 μm was laminated by pressurizing with a pair of pressure rollers to obtain a resin-covered metallic plate. For the obtained plates, evaluation tests were carried out for the test items (1) to (3). The test results are shown in Table 1.

(Test Examples 6 and 7)

In the example described in Test Example 1, instead of anodizing with a 20% phosphoric acid solution, phosphate chromate treatment (chrome content: 10 mg/m², Test Example 6) or anodizing with an oxalic acid (Test Example 7) was carried out to form layers. For the resin-covered metallic plates obtained, evaluation tests were conducted for the same items. The test results are shown in Table 1.

(Results)

From Table 1, the following is apparent.

(1) With layers anodized with a phosphoric acid, for ones

in which a layer having a thickness of 0.05-2 μ m was formed, drawability and caulkability were excellent, no ply separation was observed at the interface in each step, and no change with time (deterioration) was observed (see Test Examples 2, 4 and 5).

(2) In contrast, for ones in which layer of less than 0.1 μ m thick was formed (see Test Example 1), even though layer anodized with a phosphoric acid was formed, in the caulking step, ply separation was observed at the interface, and marked change with time was observed.

(3) Also, for ones in which a layer anodized with phosphate chromate was formed, although there was no problem with drawing, it was inferior in caulkability and marked change with time was observed (see Test Example 6).

(4) Further, for one in which layer anodized with an oxalic acid was formed, it is inferior both in caulkability and change with time (see Test Example 7).

(5) For one in which a silane coupling agent was not applied even though a layer anodized with a phosphoric acid was formed, it was inferior in caulkability and marked change with time (deterioration) was observed (see Test Example 3).

(Test Examples 8-12)

Both sides of an aluminum plate (JIS A 1050 H22) 0.3 mm thick were anodized with a 20% phosphoric acid solution to form an anodized layer having a thickness of

0.6 μ m. To the layer, a silane coupling agent having functional groups shown in Table 2 was applied at a rate of 20 mg/m², and the applied surface was heated to 280 °C. On the heated surface, a separately manufactured layer of polyamide 6 (melting point: 223 °C) having a thickness of 15 μ m was laminated by pressurizing with a pair of pressure rollers to obtain a resin-covered metallic plate. For the obtained plates, evaluation tests were carried out for the same items. The test results are shown in Table 2.

(Results)

From Table 2, the following is apparent.

(1) For ones in which a silane coupling agent was applied, it was superior both in drawability and caulability, no ply separation was observed at the interface in each step, and no change with time (deterioration) was observed (see Test Examples 8-12).

(Test Examples 13-15)

Both sides of an aluminum plate (JIS A 1050 H22) 0.3 mm thick were anodized with a 20% phosphoric acid solution to form an anodized layer having a thickness of 0.5 μ m. To this layer, a silane coupling agent having ureide groups was applied at a rate of 20 mg/m², and the applied surface was heated to 250 °C. On the heated surface, a layer of 15 μ m thick separately manufactured from a resin shown in Table 3 was laminated by

pressurizing with a pair of pressure rollers to obtain a resin-covered metallic plate. For the obtained plates, evaluation tests were carried out. The test results are shown in Table 3.

(Results)

From Table 3, the following is apparent.

(1) In the case in which the covering layer of the aluminum plate was of a polyester resin or a polyamide resin, drawability and caulkability were excellent, no ply separation at the interface was observed in each step, and no change with time (deterioration) was observed (see Test Examples 13 and 14).

(2) In contrast, in the case in which the covering layer is of polypropylene, in the drawing step, ply separation was observed at the interface, and it was inferior in drawability (see Test Example 15).

(Test Examples 16-19)

Except that anodizing was done in the following manner, resin-covered metallic plates were obtained as in Test Example 13. For the resin-covered metallic plates obtained, evaluation tests were conducted. The test results are shown in Table 5.

(Anodizing method)

The anodizing treatment was carried out by use of the electrolytes No. 1-4 shown in Fig. 4.

The organic acid used for electrolyte No. 4 is

selected from dicarboxylic acids (maleic acid, malonic acid), aromatic sulfonic acids (sulfosalicylic acid, sulfophthaleic acid), carboxylic acid sulfonate (sulfomaleic acid), amine sulfonate (sulfamic acid), etc.

The conditions for treatment were as follows:
concentration of phosphoric acid: 0.1-500 g/l,
concentration of sulfuric acid, oxalic acid or chromic acid: 0.1-500 g/l, voltage: 1-100 VAC or 1-100 VDC, or both applied, time: 1-60 minutes, layer thickness: 50 Å to 50 μ m, content of phosphoric acid anion: 1-5000 ppm.

Further, as other conditions, the following conditions were used.

- Other condition No. 1: After formation of aluminum layer anodized with phosphoric acid, AC or DC electrolysis (with the substrate as the cathode) in a bath of silane coupling agent, and layer is laminated.

- Other condition No. 2: After formation of aluminum layer anodized with phosphoric acid, AC or DC electrolysis (with the substrate as the cathode) in an epoxy emulsion bath, and layer is laminated.

- Other condition No. 3: After formation of aluminum layer anodized with phosphoric acid, AC or DC electrolysis (with the substrate as the cathode) in a mixed bath of a silane coupling agent and an epoxy emulsion, and layer is laminated.

- Other condition No. 4: After electrolysis in the other

conditions No. 1-3, silane coupling treatment or epoxy emulsion coating, and layer is laminated.

[Experiment Example 2]

Next, Test Examples subjected to other evaluations are shown. Evaluation methods used in the following Test Examples 20-33 are shown.

(a) Vickers hardness: For resin-covered surfaces of aluminum thin plates of the resin-covered metallic plates prepared, the Vickers hardness was measured under JIS Z2244 "Vickers hardness testing method". The load applied during hardness measurement was 0.9807 N.

(b) Workability: For the resin-covered metallic plates prepared, seven-stage drawing was carried out using a progressive drawing machine to manufacture cylindrical containers of 10 mm dia. x 20 mm high (drawing rate: 20%) with the resin-covered layer as the outer side of the container, and the peel state between layers was observed visually. For those in which no ply separation was observed were indicated as "○" and those in which ply separation was observed were indicated as "×".

(c) Recess properties: Specimen containers were prepared in which in the cylindrical containers of 10 mm dia. x 20 mm high, elements for capacitors were filled and the containers were caulked with mouth-sealing rubber. With 100 pieces of these specimen containers put in a paper container of 200 mm x 200 mm x 200 mm, vibration was

applied in a longitudinal direction for one hour at the vibrating speed of 10 cm/second. After one hour, the specimen containers were taken out and the appearance of the top portions was observed. Those in which recesses were observed at the bottom or side walls of the specimen containers were indicated as "×" and those in which recesses were not observed were indicated as "○".

(d) General evaluation: Those which showed passable quality for all the evaluation items (a)-(c) were judged good "○" and those which were not passable even in one item were judged bad "×".

[Test Example 20]

After the surface of an aluminum plate (JIS A 1100) having a thickness of 0.3 mm had been etched for 30 seconds with a 10% sodium hydroxide aqueous solution at 50 °C, neutralizing was carried out with a 10% nitric acid aqueous solution and it was washed with water for 10 seconds. Then, on one side of this aluminum plate, layer anodized with phosphoric acid chromate ($\text{Cr} = 20 \text{ mg/m}^2$) was formed. On the layer, γ -aminopropyltriethoxy silane as a coupling agent was applied at a rate of 50 mg/m^2 , and after drying, the aluminum plate was heated to a temperature of 210 °C, and a polyamide 6 layer having a thickness of $15 \mu\text{m}$ was pressed onto the surface to which was applied the coupling agent to obtain a polyamide resin-covered metallic plate. The obtained metallic

plates were evaluated for the above items. The test results are shown in Table 6.

[Test Example 21]

Except that in the Test Example 20, the layer was changed to a 1000 Å -thick layer formed by anodizing with an oxalic acid, γ -glycidoxy propyltriethoxy silane was used as the coupling agent, and the aluminum plate temperature was 250 °C , a polyamide resin-covered metallic plate was obtained in the same manner as in the Test Example 20. The obtained polyamide resin-covered metallic plate was evaluated in the same manner. The results are shown in Table 6.

[Test Example 22]

Except that the layer used in Test Example 21 was changed to a layer formed by anodizing with a phosphoric acid, a polyamide resin-covered metallic plate was obtained in the same manner as in the Test Example 21. The obtained polyamide resin-covered metallic plate was evaluated in the same manner. The results are shown in Table 6.

[Test Example 23]

Except that the layer used in Test Example 21 was changed to a layer formed by anodizing with a phosphate chromate, a polyamide resin-covered metallic plate was obtained in the same manner as in the Test Example 21. The obtained polyamide resin-covered metallic plate was

evaluated in the same evaluation method. The results are shown in Table 6.

[Test Example 24]

Except that as the coupling agent, γ - aminopropyltriethoxy silane was used, a polyamide resin-covered metallic plate was obtained in the same procedure as in the Test Example 23. The obtained metallic plates were evaluated in the same method. The results are shown in Table 6.

[Test Example 25]

Except that no coupling agent was applied, a polyamide resin-covered metallic plate was obtained in the same procedure as in the Test Example 20. The obtained polyamide resin-covered metallic plate was evaluated in the same method. The results are shown in Table 7.

[Test Example 26]

Except that as the coupling agent, γ - methacryloxypropyltriethoxy silane was used, and the aluminum plate temperature was changed to 380 °C, a polyamide resin-covered metallic plate was obtained in the same procedure as in the Test Example 20. The obtained metallic plate was evaluated in the same method. The results are shown in Table 7.

[Test Example 27]

Except that the aluminum plate temperature was

changed to 380 °C , a polyamide resin-covered metallic plate was obtained in the same procedure as in the Test Example 23. The obtained metallic plate was evaluated in the same method. The results are shown in Table 7.

[Test Example 28]

Except that the aluminum plate temperature was changed to 200 °C , a polyamide resin-covered metallic plate was obtained in the same procedure as in the Test Example 24. The obtained metallic plate was evaluated in the same method. The results are shown in Table 7.

(Results)

From Tables 6 and 7, the following is apparent.

(1) Resin-covered metallic plates in which a chemical conversion treated layer is provided on the surface of an aluminum plate, a layer of a silane coupling agent is provided thereon, the aluminum plate is heated to 200-350 °C to laminate and press a resin layer so that the hardness of the resin-covered surface of the aluminum plate is within the range of 25-60 in Vickers hardness are superior in the adhesion between the aluminum plate and the covering layer. Thus the covering layer will not peel off, and even if the containers contact each other, recesses hardly form in the wall surfaces (see Test Examples 20-24).

(2) In contrast, ones in which even though a chemical conversion treated layer is formed on the surface of the

aluminum plate, no layer of a coupling agent is provided and a resin layer is covered and pressed, the covering layer may peel during pressing (see Test Example 25).

(3) Also, for ones in which even though a chemical conversion treated layer is formed on the surface of the aluminum thin plate and a layer of a silane coupling agent is provided thereon, but a resin layer is covered and pressed with the temperature of the aluminum plate above 350 °C, the Vickers hardness of the surface of the resin-covered metallic plate will be less than 25, so that recesses are liable to be formed if the containers contact each other (see Test Examples 26-27).

(4) Also, for ones in which even though a chemical conversion treated layer is provided on the surface of the aluminum plate, and a layer of a silane coupling agent is provided thereon, and a resin layer is pressed with the temperature of the aluminum plate at 200 °C, the hardness of the resin-covered surface of the resin-covered metallic plate exceeds 60 in Vickers hardness, the aluminum plate as the substrate may break during pressing (Test Example 28).

[Test Example 29]

Except that the amount of the coupling agent was changed to 100 mg/m² and the temperature of the aluminum plate was changed to 290 °C, a polyamide resin-covered metallic plate was obtained in the same procedure as in

the Test Example 20. The obtained metallic plate was evaluated in the same method. The results are shown in Table 8.

[Test Example 30]

Except that the amount of the coupling agent was changed to 500 mg/m² and the temperature of the aluminum plate was changed to 290 °C, a polyamide resin-covered metallic plate was obtained in the same procedure as in the Test Example 23. The obtained metallic plate was evaluated in the same evaluation method as in Test Example 23. The results are shown in Table 8.

[Test Example 31]

Except that the amount of the coupling agent was changed to 1000 mg/m², a polyamide resin-covered metallic plate was obtained in the same procedure as in the Test Example 30. The obtained polyamide resin-covered metallic plate was evaluated in the same method. The results are shown in Table 8.

[Test Example 32]

Except that the amount of the coupling agent was changed to 0.005 mg/m², a polyamide resin-covered metallic plate was obtained in the same procedure as in the Test Example 29. The obtained polyamide resin-covered metallic plate was evaluated in the same method. The results are shown in Table 8.

[Test Example 33]

Except that the amount of the coupling agent was changed to 1300 mg/m², a polyamide resin-covered metallic plate was obtained in the same procedure as in the Test Example 31. The obtained polyamide resin-covered metallic plate was evaluated in the same method. The results are shown in Table 8.

(Results)

From Table 8, the following is apparent.

(1) Ones in which a layer is provided on the surface of the aluminum plate, and a layer of a silane coupling agent is provided thereon with the amount of the silane coupling agent within the range of 0.01-1000 mg/m² are superior in press workability. Thus, even if containers contact each other, recesses hardly form in the wall surfaces (see Test Examples 29-31).

(2) In contrast, ones in which the amount of the silane coupling agent was as small as 0.005 mg/m², adhesion between the aluminum thin plate and the covering layer was inferior, so that the covering layer peeled during pressing (see Test Example 32).

(3) Also, for ones in which the amount of the silane coupling agent was as large as 1300 mg/m², stability of the coupling agent was so bad that it was impossible to apply it uniformly on the surface of the aluminum plate (see Test Example 33).

[Experiment Example 3]

Next, Test Examples evaluated for other evaluation items are shown. Evaluation methods used in the following Test Examples 34-52 are shown below. The silane coupling agent aqueous solution was evaluated by the methods described in the following (1) and (2). Also, the resin-covered plates was evaluated by methods described in the following (3)-(6).

(1) Measurement of contact angle: At temperature of 23 °C and humidity of 50%, an aqueous solution of a silane coupling agent was dripped on the surfaces of prepared metallic plates by a required amount, and its contact angle was measured using a contact angle meter (CA-A made by Kyowa Kaimen Kagaku).

(2) Evaluation of wettability: Prepared metallic plates were cut to A4 size, and an aqueous solution of a silane coupling agent was applied to their surfaces using a bar coater at a rate of 10 g/m², and the state of the layer was visually observed. For the results, those formed with uniform layer with no repelling were judged "○" and those in which layer was spotty were judged "×".

(3) Measurement of Si element content: In the step of preparing resin-covered plates, after an aqueous solution of a silane coupling agent was applied to the surface of metallic plates and dried to form a layer, the Si element content (atomic %) on the surface of the layer was measured by the ESCA method (X-ray source: MgK α , output:

15 kv x 33 mA, degree of vacuum: 5×10^{-8} Torr).

(4) Evaluation of workability: Resin-covered plates were subjected to seven-stage drawing by use of a progressive drawing machine to manufacture cylindrical containers 10 mm in outer diameter and 20 mm high with the surface on which was laminated a thermoplastic resin layer on the outer side of the container. It was checked visually whether or not the thermoplastic resin layer had peeled off the metallic plate. For those in which no peeling was observed at all were indicated as "○" and those in in which peeling was observed were indicated as "×".

(5) Evaluation of adhesion after working: The cylindrical container prepared for the evaluation of workability was put in a hot-air drying oven at 270 °C and left for one minute. Thereafter, the cylindrical containers were taken out of the hot-air drying oven, and it was checked visually whether or not the thermoplastic resin layer laminated on the outer side of the container had peeled off. For those in which no peeling was observed at all were indicated as "○" and those in which peeling was observed were indicated as "×".

(6) General evaluation: Those judged good both in workability and adhesion after working were judged ○ in the general evaluation, and those judged bad in one or either of them were judged × in the general evaluation.

[Test Examples 34-45]

<Preparation of aqueous solution of silane coupling agent>

A silane coupling agent and a non-ionic surfactant (effective component: polyoxyethylenealkylether, clouding point: 42.1 °C) were blended into 100 g of water by the amounts shown in Table 9 to prepare four kinds of aqueous solutions of silane coupling agent.

<Preparation of metallic plates>

Three kinds of metallic plates, i.e. a stainless plate (SUS430-2B) 0.3 mm thick, an aluminum plate 0.3 mm thick, anodized with a phosphate chromate (alloy number: A1100P H24, chrome content in hydrated chrome oxide: 20 mg/m²), and an electrolytic chromic acid-treated steel plate 0.3 mm thick (metallic chrome content in the lower layer: 100 mg/m², chrome content in hydrated chrome oxide in the upper layer: 18 mg/m²) were prepared.

<Evaluation of aqueous solution of silane coupling agent>

The four kinds of aqueous solutions of silane coupling agent shown in Table 9 were dripped onto the surfaces of the three kinds of metallic plates to conduct measurement of the contact angle. Further, the four kinds of aqueous solutions of silane coupling agent shown in Table 9 were applied to the surfaces of the three kinds of metallic plates to evaluate wettability. The results are shown in Table 10.

From Tables 9 and 10, the following is apparent.

(i) As result of measurements of the contact angle, for

any metallic plate, the contact angle of aqueous solutions of silane coupling agent I to III was 55° or under (Test Examples 34-36, 38-40 and 42-44). In contrast, the contact angle of silane coupling agent aqueous solution IV was greater than 55° (Test Examples 37, 41 and 45). This is because the amount of non-ionic surfactant in silane coupling agent aqueous solution IV was insufficient.

(ii) Also, as a result of evaluation of wettability, uniform layer was formed on the surface of any of the metallic plates on which were applied aqueous solutions I to III of silane coupling agent, and wettability was good (Test Examples 34-36, 38-40 and 42-44). In contrast, no uniform layer was formed on the surface of any of the metallic plates on which were applied silane coupling agent aqueous solution IV. Film was spotty and wettability was inferior (Test Examples 37, 41 and 45). This is because the contact angle of silane coupling agent aqueous solution IV was greater than 55°.

[Test Example 46]

An aluminum plate (the same as prepared in Test Example 38) was continuously fed in a long strip. A silane coupling agent aqueous solution was prepared by blending 0.1 g of a silane coupling agent (γ - aminopropyltriethoxy silane) and 0.4 g of a nonionic surfactant (the same as used in Test Example 34) into 100 g of water and adjusting the contact angle when applied to

the surface of the aluminum plate to 50° was applied to the surface of the aluminum plate by 10 g/m², and dried at the temperature rising speed of 5 °C /s to form a layer. Then, the layer was heated at 250 °C , and to the surface of this layer, a polyamide 6 layer having a melting point of 220 °C and a thickness of 20 um was laminated to prepare a resin-covered plate. In the step of preparing this resin-covered plate, measurement of Si element content was carried out, and for the resin-covered plate, evaluation of workability and adhesion after working and total evaluation were conducted. The results are shown in Table 11.

[Test Examples 47-52]

Except that the kind and amount of silane coupling agents, the temperature raising speed in drying after application of a silane coupling agent aqueous solution (layer heating temperature), and the kind of thermoplastic resin layer was changed to those described in Table 11, resin-covered plates were prepared in the same manner as in Test Example 46. In the steps of preparing these resin-covered plates, measurement was conducted in the same manner as in Example 46. For the resin-covered plates, evaluation tests were conducted in the same manner as in Example 46. The results are shown in Table 11.

From Tables 10 and 11, the following is apparent.

(iii) For the resin-covered plates prepared so that any of the amount of the silane coupling agent, contact angle of the silane coupling agent aqueous solution, temperature raising speed during drying after application of the silane coupling agent aqueous solution, and heating temperature of the layer would be within the predetermined ranges, the Si element content on the surface of the resin layer was within the range of 5-15 atomic %, and workability and adhesion after working were excellent (see Test Examples 46-48).

(iv) For the resin-covered plates prepared using a silane coupling agent aqueous solution of which the content of a silane coupling agent was less than 0.01 parts by weight, the Si element content on the surface of the resin layer was less than 5 atomic %, and adhesion after working was inferior (see Test Example 49).

(v) For the resin-covered plates prepared with the temperature raising speed during drying after application of a silane coupling agent lower than 50 °C/s, the Si element content on the surface of the resin layer was less than 5 atomic %, and adhesion after working was inferior (see Test Example 50).

(vi) For the resin-covered plates prepared with the heating temperature of the layer lower than the melting point of the thermoplastic resin (220°C), workability was inferior and the polyamide 6 layer peeled during working.

In this case, since evaluation of adhesion after working was impossible, it was not carried out (see Test Example 51).

(vii) For the resin-covered plates prepared with the heating temperature of the layer higher than 350 °C, workability was inferior and cracks developed in the polyethylene terephthalate layer. Also, adhesion after working was inferior (see Test Example 52).

The present invention offers the following effects and has a large value for industrial application.

1. The resin-covered metallic plate according to the present invention formed with a layer anodized with a phosphoric acid having a thickness of 0.05-2 μ m as an anodized layer is superior in the adhesion (bonding property or bond strength) at the interface between the aluminum plate surface and the covering layer. Even when drawing or ironing is carried out, damage or cracks of the thermoplastic resin covering layer will not develop, and it hardly deteriorates with time, and ply separation will not develop.

2. The resin-covered metallic plate according to the present invention having a silane coupling agent disposed between the layer anodized with a phosphoric acid and the resin layer has a good adhesion (bonding property or bond strength) at the interface between the aluminum plate surface and the covering layer. Even when drawing or

ironing is carried out, damage or cracks of the thermoplastic resin covering layer will not develop, and it hardly deteriorates with time, and ply separation hardly develops.

3. With the manufacturing method according to the present invention, there is no need to re-melt the thermoplastic resin covering layer by heating after drawing or ironing, as in the methods described in Japanese patent publications 1-66030 and 2-16043. Thus it is possible to efficiently manufacture a resin-covered metallic plate superior in the adhesion (adhesion or bond strength) at the interface between the aluminum plate surface and the covering layer.

4. With the manufacturing method of a resin-covered metallic plate according to the present invention, it is possible to obtain a resin-covered metallic plate which is superior in the press workability such as drawing, and in which the covering layer hardly peels during working.

5. With the manufacturing method of a resin-covered metallic plate according to the present invention, since one side of the aluminum plate is covered by a resin layer, it allows to apply graceful printing thereon for identification.

6. With the manufacturing method of a resin-covered metallic plate according to the present invention, since the Vickers hardness of the resin-covered surface of the

aluminum plate is within the range of 25-60, it is superior in press workability, and even if the containers obtained by working contact each other, recesses are hardly formed in wall surfaces.

7. The container for aluminum electrolytic capacitors according to the present invention needs no step of covering with a heat-shrinkable tube as before. Thus the manufacturing steps are simple.

8. If the resin-covered metallic plate according to the present invention is prepared by applying an aqueous solution of a specific silane coupling agent on the surface of the metallic plate to form a layer, drying it at a specific temperature-raising speed, and laminating a thermoplastic resin layer while heating the layer at a specific temperature, cracks hardly develop in the thermoplastic resin layer if the resin-covered metallic plate is worked by ironing, and also the thermoplastic resin layer will not easily peel off the metallic plate.

9. If the resin-covered metallic plate is prepared by applying an aqueous solution of a specific silane coupling agent on the surface of the metallic plate to form a layer, drying it at a specific temperature-raising speed, and laminating a thermoplastic resin layer while heating the layer at a specific temperature, the thermoplastic resin layer will not easily peel off the metallic plate even if the resin-covered metallic plate is

subjected to heat treatment after working by various methods.

10. If the resin-covered metallic plate is prepared by laminating a thermoplastic resin layer by heating the layer formed on the surface of the metallic plate within the temperature range of from the melting point of the thermoplastic resin layer to 350 °C , the strength of the metallic plate will not lower, and the themoplastic resin layer will not deteriorate.

11. If the resin-covered metallic plateis prepared by laminating a thermoplastic resin layer by heating the layer formed on the surface of the metallic plate within the temperature range of from the melting point of the thermoplastic resin layer to 350 °C , economical disadvantages produced during conventional high-temperature heat treatment can be eliminated.

12. With the manufacturing method of a resin-covered metallic plate according to the present invention, it is possible to manufacture a resin-covered metallic plate that provides the abovesaid effects.

13. Since the container for a capacitor according to the present invention has the resin-covered metallic plate prepared by drawing or ironing, even if heat treatment is applied after it has been made into an end product, the thermoplastic resin layer forming the container will not easily peel off the metallic plate. Thus it has a high

commercial value.

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TABLE 1

Test example	Experiment example 1						
	1 (Ex.)	2 (Ex.)	3 (Comp.ex)	4 (Ex.)	5 (Ex.)	6 (Comp.ex)	7 (Comp.ex)
Chemical conversion treated layer	A	A	A	A	A	B	C
Thickness of layer (μm)	0.05	0.1	0.6	0.1	1.8	0.3	0.5
Coupling agent	100	100	100	100	100	100	100
Drawability (%)	D	E	Nil	D	E	E	F
Caulkability (%)	80	100	40	100	100	60	0
Change with time	40	100	0	100	100	0	0

A : anodized with phosphoric acid
 B : treated with phosphate chromate
 C : anodized with oxalic acid
 D : 3-aminopropyltriethoxysilane
 E : 3-glycidopropyltrimethoxysilane
 F : N-2-aminoethyl-3-aminopropyltrimethoxysilane

TABLE 2

Test example	Experiment example 1				
	8 (Ex.)	9 (Ex.)	10 (Ex.)	11 (Ex.)	12 (Ex.)
Chemical conversion treated layer	treated with phosphoric acid				
Thickness of layer (μm)	0.6	0.6	0.6	0.6	0.6
Coupling agent	D	F	E	G	H
Drawability (%)	○	○	○	○	○
Caulkability (%)	○	○	○	○	○
Change with time	100	100	100	100	100

D : 3-aminopropyltriethoxysilane
 E : 3-glycidopropyltrimethoxysilane
 F : N-2-aminoethyl-3-aminopropyltrimethoxysilane
 G : 3-methacryloxypropyltrimethoxysilane
 H : ureidoaminopropyltriethoxysilane

TABLE 3

	Experiment example 1		
Test example	1 3 (Ex.)	1 4 (Ex.)	1 5 (Comp. ex)
Chemical conversion treated layer	treated with phosphoric acid		
Thickness of layer (μm)	0.5	0.5	0.5
Resin covering layer	polyester	polyamide 6	polypropylene
Drawability (%)	○	○	×
Caulkability (%)	○	○	not done
Change with time	○	○	not done

TABLE 4

Electrolyte No.	Kind of electrolyte	Concentration (g/l)	Voltage (v)	Time (min)	Layer thickness (μm)	Content of phosphoric acid anion (ppm)
1	phosphoric acid	1 5 0	3 0 0 vDC	1 0	3	1 0 0 0
	sulfuric acid	1 0 0				
2	phosphoric acid	3 0 0	4 0 vDC	5	1	2 0 0 0
	oxalic acid	3 0				
3	phosphoric acid	5 0	2 0 vAC	2 0	1 0	2 0 0
	chromic acid	1 0				
4	organic acid	1 0 0	3 0 vAC	1	1	5 0 0
	phosphoric acid	2 0 0				

TABLE 5

	Test example	Electrolyte No.	Other condition No.	Drawability	Caulkability	Change with time
Experiment example 1	16 (Ex.)	1	1	○	○	○
	17 (Ex.)	2	2	○	○	○
	18 (Ex.)	3	3	○	○	○
	19 (Ex.)	4	4	○	○	○
	6 (Comp. ex)	—	—	○	△	×
	7 (Comp. ex)	—	—	○	×	×

TABLE 6

	Experiment example 2				
Test example	2 0 (Ex.)	2 1 (Ex.)	2 2 (Ex.)	2 3 (Ex.)	2 4 (Ex.)
Treating method for forming layer	Q	R	S	Q	Q
Silan coupling agent	I	J	I	J	I
Thermoplastic resin layer	polyamide 6	polyamide 6	polyamide 6	polyamide 6	polyamide 6
Al plate temperature (°C)	210	250	250	250	250
Vickers hardness	45	40	42	40	52
Press workability	○	○	○	○	○
Recess workability	○	○	○	○	○
Total evaluation	○	○	○	○	○

I : γ -glycidopropyltriethoxysilaneJ : γ -aminopropyltriethoxysilane

Q : treated with phosphate chromate

R : anodized with oxalic acid

S : anodized with phosphoric acid

TABLE 7

Test example	Experiment example 2			
	2 5 (Comp. ex)	2 6 (Comp. ex)	2 7 (Comp. ex)	2 8 (Comp. ex)
Treating method for forming layer	Q	Q	Q	Q
Silan coupling agent	Nil	K	I	J
Thermoplastic resin layer	polyamide 6	polyamide 6	polyamide 6	polyamide 6
Al plate temperature (°C)	210	380	380	200
Vickers hardness	45	15	15	63
Press workability	×	○	○	Al broken
Recess workability	not done	×	×	not done
Total evaluation	×	×	×	×

I : γ -glycidopropyltriethoxysilaneJ : γ -aminopropyltriethoxysilane

K : 3-methacryloxypropyltrimethoxysilane

Q : treated with phosphate chromate

TABLE 8

	Experiment example 2				
Test example	2 9 (Ex.)	3 0 (Ex.)	3 1 (Ex.)	3 2 (Comp. ex)	3 3 (Comp. ex)
Treating method for forming layer	Q	Q	Q	Q	Q
Silan coupling agent	J	I	I	J	I
Amount of silan coupling agent (mg/m ²)	100	500	1000	0.005	1300
Thermoplastic resin layer	polyamide 6	polyamide 6	polyamide 6	polyamide 6	polyamide 6
Vickers hardness	35	35	40	30	46
Press workability	○	○	○	× (layer peeled)	not done
Recess workability	○	○	○	not done	not done
Total evaluation	○	○	○	×	×

I : γ -glycidopropyltriethoxysilaneJ : γ -aminopropyltriethoxysilane

Q : treated with phosphate chromate

TABLE 9

Aqueous solution of silane coupling agent	Kind of silane coupling agent	Amount of anionic surfactant (g)
	Amount (g/100g of water)	
I	γ -glycidoxypropyltriethoxysilane	0.5
	5.0	
II	γ -aminopropylethoxysilane	0.5
	5.0	
III	γ -aminopropylethoxysilane	0.2
	5.0	
IV	γ -aminopropylethoxysilane	0.01
	5.0	

TABLE 10

	Test example	Kind of metallic plate	Aqueous solution of silane coupling agent	Contact angel (degree)	Wettability
Experiment example 3	34 (Ex.)	Stainless plate (SUS430-2B)	I	53	○
	35 (Ex.)		II	43	○
	36 (Ex.)		III	52	○
	37 (Comp. ex)		IV	58	×
	38 (Ex.)	phosphate chromate aluminum plate	I	50	○
	39 (Ex.)		II	40	○
	40 (Ex.)		III	50	○
	41 (Comp. ex)		IV	57	×
	42 (Ex.)	steel plate treated with electrolytic chromic acid	I	51	○
	43 (Ex.)		II	41	○
	44 (Ex.)		III	48	○
	45 (Comp. ex)		IV	56	×

TABLE 11

Test example	Kind of silane coupling agent		Temp. rising speed (°C/s)	Heating temp. of layer(°C)	Thermoplastic resin covering layer	Content of Si (atomic %)	Workability		Total evaluation
	amount (g/100g of water)						Adhesion after working		
46 (Ex.)	γ -aminopropylethoxysilane		5	250	polyamide 6	7.34	○	○	○
	0.1						○		
47 (Ex.)	γ -aminopropylethoxysilane		20	330	polyamide 6	10.52	○	○	○
	2.0						○		
48 (Ex.)	γ -glycidopropyltriethoxysilane		5	280	PET	9.15	○	○	○
	0.1						○		
49 (Comp. ex)	γ -aminopropylethoxysilane		40	250	polyamide 6	4.10	○	×	×
	0.009						×		
50 (Comp. ex)	γ -aminopropylethoxysilane		53	280	polyamide 6	4.14	○	×	×
	0.5						×		
51 (Comp. ex)	γ -aminopropylethoxysilane		5	200	polyamide 6	12.12	×	not done	×
	3.0						×		
52 (Comp. ex)	γ -aminopropylethoxysilane		45	380	PET	8.35	×	×	×
	1.0						×		

Experiment example 3

Experiment example 3

What is claimed is:

1. A resin-covered metallic plate comprising a metallic plate, a chemical conversion treated layer formed on said metallic plate, a layer of a silane coupling agent formed on the surface of said chemical conversion treated layer, and a covering layer of a thermoplastic resin formed on said layer of a silane coupling agent.

2. The resin-covered metallic plate as claimed in claim 1 wherein said chemical conversion treated layer is selected from the group consisting of a layer treated with phosphate chromate, a layer comprising an organic resin layer and chrome, a chemical conversion treated layer containing zirconium, a chemical conversion treated layer containing titanium, and an anodic oxidation-treated layer.

3. The resin-covered metallic plate as claimed in claim 1 or 2 wherein said covering layer of a thermoplastic resin is a layer comprising a resin selected from the group consisting of a polyester resin and a polyamide resin.

4. The resin-covered metallic plate as claimed in claim 1 wherein said metallic plate is an aluminum plate,

said chemical conversion treated layer is an anodic oxidation layer having a thickness of 0.05-2 μ m, and said covering layer of a thermoplastic resin has a thickness of 5-200 μ m.

5. The resin-covered metallic plate as claimed in claim 4 wherein said anodic oxidation layer is a layer anodized with an electrolyte containing at least phosphoric acid.

6. The method of manufacturing a resin-covered metallic plate comprising steps of forming an anodic oxidation layer having a thickness of 0.05-2 μ m on the surface of an aluminum plate, applying a silane coupling agent to said anodic oxidation layer at the rate of 0.5-500 mg/m² to form a layer, and forming a covering layer of a thermoplastic resin having a thickness of 5-200 μ m on the layer of a silane coupling agent by melting at a temperature of 250-350 °C .

7. The resin-covered metallic plate as claimed in claim 1 wherein said metallic plate is an aluminum plate having a thickness of 0.1-0.5 mm, said layer of a silane coupling agent is formed by applying a silane coupling agent at a rate of 0.01-1000 mg/m², said covering layer of a thermoplastic resin has a thickness of 5-200 μ m , and

the surface of said covering layer of a thermoplastic resin has a Vickers hardness of 25-60.

8. A method of manufacturing a resin-covered metallic plate comprising the steps of forming a chemical conversion treated layer on one side of an aluminum plate having a thickness of 0.1-0.5 mm, applying a silane coupling agent at a rate of 0.01-1000 mg/m² on said layer to form a layer, heating said aluminum plate on which are laminated said chemical conversion treated layer and the layer of a silane coupling agent at a temperature of 200-350 °C, and covering and pressing a thermoplastic resin layer having a thickness of 5-200 μ m on said layer of a silane coupling agent, whereby the Vickers hardness of the surface of said thermoplastic resin layer is within the range of 25-60.

9. The resin-covered metallic plate as claimed in claim 1 wherein said layer of a silane coupling agent is formed by applying an aqueous solution of a silane coupling agent to the surface of a metallic plate, said aqueous solution being prepared by blending a silane coupling agent with 100 parts by weight of water at the rate of 0.01-10 parts by weight so that the contact angle when applied to the surface of said metallic plate will be 55° or under, and drying at a temperature-raising speed

of 50 °C /s or under, and said covering layer of a thermoplastic resin is laminated on the surface of said silane coupling agent layer which has been heated at a temperature of from its melting point to 350 °C .

10. The resin-covered metallic plate as claimed in claim 1 wherein said layer of a silane coupling agent has a Si element content of 5-15 atomic % when its surface is measured by an X-ray electric spectroscopy.

11. A method of manufacturing a resin-covered metallic plate comprising the steps of applying an aqueous solution of a silane coupling agent to the surface of a metallic plate, said aqueous solution being prepared by blending a silane coupling agent with 100 parts by weight of water at the rate of 0.01-10 parts by weight so that the contact angle when applied to the surface of said metallic plate will be 55° or under, drying at a temperature-raising speed of 50 °C /s or under to form a layer, and laminating a covering layer of a thermoplastic resin on the surface of said layer by heating said layer at a temperature of from the melting point of the thermoplastic resin to 350 °C .

12. A container for a capacitor manufactured by drawing or ironing the resin-covered metallic plate

claimed in any of claims 1-5, 7, 9 and 10.

13. The container for a capacitor as claimed in claim 12 wherein said covering layer of a thermoplastic resin is on the outer side of the container.