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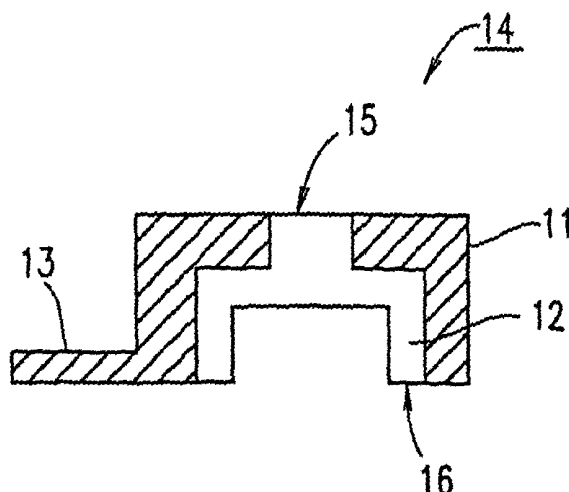
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(54) Title: METHOD FOR PRODUCING PLATED MOLDED PRODUCT



(57) Abstract: A method for producing a plated
molded product is provided, in which a surface of
a molded product having a thin portion obtained by
coinjection molding of resin is subjected to plating.
A surface of a molded product having a thin portion
obtained by high-speed injection molding of resin is
plated by the steps of: (a) forming a metal plating
layer on a surface of the molded product by electroless
plating; (b) forming a copper plating layer on a surface
of the electroless plating layer by electroplating; (c)
forming a nickel layer on a surface of the copper
plating layer by electroplating; and (d) forming a
chromium or chromium alloy layer on a surface of
the nickel layer by electroplating. Even for a molded
product having a thin portion obtained by high-speed
injection molding, a plating which resists removal
can be obtained. Further, even when a plating is
formed on a satin-finished surface, the plating can
reproduce the satin-finished surface.

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DESCRIPTION

METHOD FOR PRODUCING PLATED MOLDED PRODUCT

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TECHNICAL FIELD

The present invention relates to a method for producing a plated molded product having a thin portion. The present invention also relates to a method for plating
10 a surface of a coinjection molded product having a resin molded product and an elastic layer incorporated on a rear side thereof. Particularly, the present invention relates to a method for plating surfaces of electrical or electronic components (e.g., switches, and key tops for controlling
15 a personal computer), OA equipment (e.g., personal computers and telephones), and communication equipment (e.g., DVDs and MDs), and more particularly to a method for producing operation buttons (keys) for cellular phones.

20

BACKGROUND ART

For example, there is an increasing demand for reduction in thickness of folding-type (flap-type) cellular phones. For such cellular phones, operation buttons (keys)
25 attached thereto need to be as thin as possible.

Generally, operation buttons are molded from ABS resin (acrylonitrile · butadiene · styrene copolymer) which is easy to plate. However, ABS resin has poor adhesiveness
30 to the body of a cellular phone. Further, an operation button may have a portion which is not plated for decoration purposes. In this case, coinjection molding may be performed using resin other than ABS resin, such as PC

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(polycarbonate) resin. Further, a bright surface and a deluster surface (minute rough surface) may be provided on a surface of an operation button for decoration purposes.

5 Conventionally, when operation buttons for cellular phones are produced by inmolding, the resultant operation buttons exhibit a lack of sharpness and bright impression. To avoid this, the surface of a molded product is plated after coinjection molding as described above.

10

 When a thin coinjection molded product is produced, a molding method in which a cavity and a core are reversed is typically used other than commonly used methods.

15 Further, when a thin molded product is produced by coinjection molding, resin is conventionally injected into a cavity at a high injection speed. If the resin injection speed is slow, the resin does not enter the cavity and the thin molded product is not obtained. However, the fast
20 injection speed causes a problem that plating easily comes off the resultant molded product. The reason for this problem is considered to be that the surface of a molded product may lack the ability to anchor plating thereon depending on the flowability or orientation of resin in
25 molding.

 Specifically, according to conventional plating, a metal plating layer is formed on a surface of a molded product by electroless plating; a nickel layer is formed on a surface
30 of the electroless plating layer by electroplating; and a chromium or chromium alloy layer is formed on a surface of the nickel layer by electroplating. Such plating easily comes off in a cross-out adhesion test, a heat shock test,

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etc.

Therefore, it was considered that after the metal plating layer is formed by electroless plating, copper
5 plating is formed by electroplating. Conventional copper plating has a strong leveling effect, causing the following problem.

10 In conventional plating, even when a minute rough (e.g., satin finish) surface of an operation button has been created, such a rough surface is leveled by the plating to generate brightness and the roughness is lost. That is, the features of the surface of an electroformed cavity are destroyed.

15 Operation buttons for cellular phones may be provided with an elastic layer which is incorporated into a coinjection molded product in order to provide a cushion on a rear surface of the molded product. Further, a surface
20 of the coinjection molded product may be subjected to plating.

The plating of the surface of such a molded product is typically conducted by electroless plating, in which an
25 etching step, a washing step, a catalyst step, and an accelerator step are successively performed, followed by electroplating.

30 In the etching step, a molded product is immersed in a chromic acid mixture of chromic acid and sulfuric acid. However, in etching, the elastic layer tends to be easily dissolved in the chromic acid mixture. The dissolved components may agglomerate in the subsequent washing step

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etc. and are diffused in the further subsequent steps so that the small foreign particles are attached to a plated surface of the molded product, resulting in a defective product.

5

To avoid such a problem, it is considered that the concentration of the chromic acid mixture is lowered to a point that the elastic layer resists being dissolved. In this case, however, a plating layer plated on the molded product surface has poor adhesiveness.

10

Alternatively, it is considered that after only a molded product is subjected to plating, an elastic layer is adhered to a rear surface of the molded product. In this case, however, the yield is much lowered.

15

When a molded product (e.g., buttons or the like for cellular phones) is plated, the molded product is subjected to pretreatment (a chemical process), washing, nickel plating, washing, chromium plating, washing, and drying. In this case, chromium plating solution used employs a bath composition containing hexavalent chromium, and hexavalent chromium is ionized and deposited on a surface of a subject product by electrophoresis to form a metal chromium coating. Although hexavalent or trivalent ions or the like are not present in the metal chromium coating, there is a need to consider the adverse influence of the coating on the skin of a human. Moreover, after such products are discarded, metal chromium corrosion leads to a reduction to hexavalent chromium which remains in nature, causing a problem.

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To avoid this problem, conventionally, a treatment method employing trivalent chromium in chromium plating

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solution has been studied. However, it has been revealed from the beginning of such a study that a method employing trivalent chromium cannot provide sufficient coating formation and corrosion resistance as compared to conventional methods in which only hexavalent chromium is used to form metal coating.

Further, when operation buttons for cellular phones, which are coinjection molded products, are subjected to plating with a newly introduced trivalent chromium plating bath, if plating conditions are set within standard control values defined by the manufacturer, some problems arise so that the specification which a user desires cannot be well controlled, and changes in the standard control values and equipment are required.

For example, minute ridges and protrusions may be formed on a surface of a plated product. The cause is considered to be that dust entering the solution or impurities generated in electrolysis are captured in the plating coat. Further, the throwing power is poor. The cause is speculated to be that current cannot flow at a standard current density when a plated product has a very rough surface.

DISCLOSURE OF THE INVENTION

According to one aspect of the method for producing a plated molded product of the present invention, a surface of a molded product having a thin portion obtained by high-speed injection molding of resin is subjected to plating. The method comprises the steps of:

(a) forming a metal plating layer on a surface of

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the molded product by electroless plating;

(b) forming a copper plating layer on a surface of the electroless plating layer by electroplating;

(c) forming a nickel layer on a surface of the copper plating layer by electroplating; and

(d) forming a chromium or chromium alloy layer on a surface of the nickel layer by electroplating.

The "high-speed" of the high-speed injection molding means a level of speed at which the orientation of the butadiene molecules in ABS resin is changed. Specifically, the butadiene molecules are substantially circularly oriented at a conventional injection speed. At a speed greater than or equal to a predetermined speed, the butadiene molecules are elliptically oriented. Therefore, conventional plating easily comes off the surface of a molded product.

In one embodiment, the copper plating is conducted under the following conditions:

the molded product is immersed in a copper sulfate bath containing copper sulfate having a concentration of 70 to 90 g/l and sulfuric acid having a concentration of 170 to 210 g/l at 10 to 30°C and at a cathode current density of 1 to 4 A/dm².

In one embodiment, a bright surface and a rough surface are provided on the surface of the molded product.

The plated molded product of the present invention is produced by any of the above-described methods.

In one embodiment, the molded product is a button

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for operating a cellular phone.

In one embodiment, the metal plating layer formed by the electroless plating is a nickel layer, a copper layer,
5 or the like.

According to the present invention, even for a molded product having a thin portion obtained by high-speed injection molding, a plating which resists removal can be
10 obtained. Further, even when a plating is formed on a satin-finished surface, the plating can reproduce the satin-finished surface.

The function of the present invention is the
15 following.

After a metal plating layer, such as a nickel layer or a copper layer, is formed on the surface of a molded product by electroless plating, a copper plating layer is
20 formed on the surface of the electroless plating layer. Thereafter, a nickel layer and a chromium or chromium alloy layer is formed on the surface of the copper plating layer by electroplating. Therefore, even for a molded product having a thin portion, a metal plating layer can be securely
25 adhered to the underlying surface (the molded product) and resists in coming off. Further, the plating can reproduce the luster surface and the satin-finished surface of the molded product.

30 The ease of removal of plating on a molded product is measured under the following conditions.

A cross-out adhesion test: 1 mm by 1 mm cross-cut

Heat shock test: Repetition of cycles of 85°C · 1 hour and -35°C · 1 hour. The plating needs to be still intact after 6 cycles or more. Conventional plating are destroyed after 3 cycles.

According to another aspect of the method for producing a plated molded product of the present invention, a surface of a molded product obtained by integrally molding an elastic layer as a secondary molded product on at least a portion of a surface of a primary molded product is treated by plating. The method comprises the step of etching the surface of the molded product by immersing the molded product in a mixture of chromic acid and sulfuric acid, wherein the etching step is conducted under the following conditions:

- (a) the temperature of the mixture is 65 to 69°C;
- (b) the chromic acid concentration of the mixture is 370 g/l to 390 g/l; and
- (c) the sulfuric acid concentration of the mixture is 190 g/l to 230 g/l.

In one embodiment, the method further comprises a washing step, a catalyst step, and an accelerator step in this order after the etching step. The accelerator step comprises the steps of immersing the molded product in an acidic solution having a pH closer to the neutral than the pH of an acidic solution used in the catalyst step and causing the acidic solution to be in contact with activated charcoal so that impurities contained in the acidic solution were adsorbed, and thereafter washing the molded product.

In one embodiment, the washing step comprises the step of providing a nozzle on a bottom side of a water tank,

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the nozzle blowing minute air bubbles, and blowing the air bubbles toward the molded product.

5 In one embodiment, the elastic layer consists of thermoplastic polyurethane elastomer.

The plated molded product of the present invention is obtained by any of the above-described methods. The plated molded product is a button for a cellular phone.

10

According to the present invention, plating can be provided on the surface of a coinjection molded product comprising a resin molded product and an elastic layer integrally molded to the rear surface of the resin molded product without fine roughness.

15

The function of the present invention is the following.

20

By etching the coinjection molded product under optimum etching conditions, plating can be provided on the surface of the molded product with good adhesion while inhibiting dissolution of the elastic layer as much as possible. When the etching conditions are not sufficiently satisfied, the adhesion of the plating is insufficient, leading to less durability. When etching is excessively conducted, the elastic layer is dissolved, leading to degradation of the surface condition of the molded product. As a result, the incidence of defective products is increased.

25
30

According to another aspect of the method for producing a plated molded product of the present invention,

- 10 -

a surface of a molded product obtained by coinjection molding is treated by trivalent chromium plating. The method comprises the step of plating under the following conditions:

5 (a) the trivalent chromium concentration of a plating bath is 6 to 10 g/l;

(b) the amount of overall impurities in the plating bath is 60 ppm or less;

(c) bathing temperature is 40 to 50°C;

10 (d) the pH of the plating bath is 3.2 to 3.6;

(e) cathode current density is 3 to 5 A/dm²; and

(f) anode/cathode ratio is 1.5 to 2 : 1.

15 In one embodiment, the plating conditions further includes:

(g) rectifier: one that has an ability to rectify an amount of current which is three times or more as much as the total current amount; and

20 (h) filtering ability: the entire bathing solution is passed through a filter continuously seven times or more per hour.

In one embodiment, the molded product is a silver button for operating a cellular phone.

25

According to still another aspect of the method for producing a plated molded product of the present invention, a surface of a molded product obtained by coinjection molding is treated by trivalent chromium plating. The method comprises the step of plating under the following conditions:

30

(a) the trivalent chromium concentration of a plating bath is 5 to 10 g/l;

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(b) the amount of overall impurities in the plating bath is 60 ppm or less;

(c) bathing temperature is 53 to 63°C;

(d) the pH of the plating bath is 3.2 to 3.6

5 (e) cathode current density is 3 to 5 A/dm²; and

(f) anode/cathode ratio is 1.5 to 2 : 1.

In one embodiment, the plating conditions further includes:

10 (g) rectifier: one that has an ability to rectify an amount of current which is three times or more as much as the total current amount; and

(h) filtering ability: the entire bathing solution is passed through a filter continuously seven times or more
15 per hour.

In one embodiment, the molded product is a black button for operating a cellular phone.

20 Plated molded products are produced with any one of the above-described methods.

According to the present invention, a chemically converted coat having excellent resistance to corrosion can
25 be formed by surface treatment using a treatment solution without hexavalent chromium.

The function of the present invention is the following.

30

In the present invention, plating conditions are changed as follows with respect to the following items.

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(1) Surface ridges and protuberances (attached foreign matters, flaws)

Filtering performance in a plating bath is improved, and the impurity control value of the bath is changed, resulting in an improvement in the uniformity of particles in liquid (an improvement in filtering precision) and a reduction in attached foreign matters.

(2) Throwing power

The liquid concentration control range is adjusted, the liquid temperature standard value is reset, and the pH value is reset.

Specifically, the metal concentration of the bath is adjusted to be high as compared to conventional methods, thereby improving the throwing power. Further, the reaction rate is improved, thereby improving the throwing power. Furthermore, the pH is set to be higher, thereby increasing the reaction rate.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a cross-sectional view of an exemplary plated molded product obtained by a production method according to the present invention.

Figure 2 is a cross-sectional view of another exemplary plated molded product obtained by a production method according to the present invention.

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BEST MODE FOR CARRYING OUT THE INVENTION

(First Invention)

As shown in Figure 1, a thin molded product 14 according to the present invention comprises a thin portion 13 produced by coinjection molding. Further, the thin molded product 14 comprises a primary molded product 11 formed of ABS resin, and a secondary molded product 12 molded at an inner side of the primary molded product 11 by coinjection molding. The secondary molded product 12 can be formed of transparent resin, such as PC.

This dish-like injection-molded product 14 has a thin portion typically having a thickness of 0.35 mm or less and preferably 0.15-0.30 mm. The molded product can be molded by coinjection molding where a cavity and a core are reversed. Since the thin portion is provided, the injection speed is faster than conventional.

The thus-obtained molded product having the thin portion is subjected to plating to plate a surface of the molded product by the following steps.

(a) After washing the molded product, a metal plating layer is formed on the surface of the molded product by electroless nickel plating (chemical plating) or electroless copper plating (chemical plating).

The electroless plating can be conducted in the following manner.

Etching step: the molded product is immersed in an aqueous solution containing chromic anhydride and sulfuric

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acid at a predetermined temperature, followed by washing, and the surface of the molded product is roughened.

5 Catalyst (catalyzer) step: the molded product is immersed in an aqueous solution containing palladium chloride, stannous chloride and hydrochloric acid, followed by washing, so that palladium is absorbed to the surface of the molded product.

10 Accelerator step: the molded product is immersed in an aqueous hydrochloric acid solution, followed by washing, so that tin which has been absorbed along with palladium in the catalyst step is dissolved and detached with the hydrochloric acid solution.

15 Electroless nickel plating or electroless copper plating (chemical plating):

 the molded product is immersed in a mixture of nickel or copper, formalin, Rochelle salt, sodium hydroxide, water, 20 sodium hypophosphite, ammonia, etc., followed by washing, so that nickel (copper) is deposited on the palladium due to a reduction reaction of formalin and sodium hypophosphite.

25 Next, electroplating is conducted on the electroless plating layer in the following manner.

 In the present invention, after copper plating, nickel plating, and chromium plating or chromium alloy 30 plating is conducted.

 (b) A copper plating layer is formed on a surface of the electroless plating layer by electroplating.

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A thickness of the copper plating layer is typically 5 μm to 15 μm .

5 Conditions for copper plating may be the following.

 The molded product is immersed in copper sulfate bath having a copper sulfate concentration of 70-90 g/l and a sulfuric acid concentration of 170-210 g/l at 10-30°C
10 (more preferably 20°C), and plating is conducted at a cathode current density of 1-4 A/dm².

 Thus, in the present invention, non-leveling copper sulfate is employed. Since copper sulfate has an excellent
15 followingness, a portion of the original surface of the molded product subjected to blasting (grain) becomes ridges and protrusions of blast pattern (grains) as they are. Moreover, a flat portion (bright surface) can exhibit brightness impression as is conventionally obtained.

20

 (c) A nickel layer is formed on a surface of the copper plating layer by electroplating.

 The molded product is immersed in a mixture of nickel sulfate, nickel chloride, boric acid, and brightener, and
25 treated under predetermined conditions of voltage and current, followed by washing, whereby a nickel coat is formed on the surface of the molded product.

 (d) A chromium or chromium alloy layer is formed on
30 a surface of the nickel layer by electroplating.

 Thereafter, the molded product was washed and dried.

 In this manner, the molded product comprises

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portions (15, 16) of different resin materials. Therefore, a portion of the surface of the molded product may be transparent. Alternatively, the plating is scratched away from a portion of the surface of the molded product via which
5 the molded product is securely attached with an adhesive to a silicone rubber sheet of a cellular phone body, for example.

As described above, conventional copper sulfate for
10 decoration provides plating having a high leveling ability. Therefore, the blasted portion (grain) and smooth portion (bright surface) of the underlying layer are all caused to be bright-finished by the plating.

15 In contrast, according to the present invention, the non-leveling copper sulfate can provide plating having excellent followingness. Therefore, the coat layer can follow and maintain the ridge-and-protuberance pattern of the blasted portion (grain) of the underlying layer. The
20 smooth portion (bright surface) of the underlying layer is conventionally caused to have a brightness impression.

(Second Invention)

A molded product 24 according to the present
25 invention, such as operation buttons of a cellular phone, is obtained by coinjection molding as shown in Figure 2. The molded product 24 comprises a primary molded product 21 formed of a molded resin, and an elastic layer 22 as a secondary molded product which is molded on the rear side
30 of the primary molded product 21 by coinjection molding.

The primary molded product 21 can be made of ABS resin, polypropylene, vinyl chloride resin, polystyrene,

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polycarbonate, methacryl resin, polysulfone, polyester, polyacetal, polyamide, etc. ABS resin is particularly preferable.

5 The secondary molded product (elastic layer) 22 is made of rubber, elastomer, etc. The elastic layer 22 confers cushioning to operation buttons. The hardness of the elastic layer 22 is preferably 80 or more in Shore A, and particularly about 85 to 92. The elastic layer 22 can
10 confer button cushioning, leading to an improvement in the operability of the buttons, and can absorb the impact when an instrument, such as a cellular phone, is dropped, thereby preventing damage.

15 The elastic layer 22 can be particularly made of thermoplastic polyurethane elastomer. Thermoplastic polyurethane elastomer is commercially available.

20 A surface of the thus-obtained molded product 24 is subjected to the following plating treatment to provide a plating 23.

25 (A) The molded product is washed and the surface thereof is subjected to electroless nickel plating (chemical plating) or electroless copper plating (chemical plating) to form a metal plating layer.

The electroless plating can be conducted as follows.

30 A-1. Etching step

The molded product is immersed in a mixture (chromic acid mixture) of chromic anhydride and sulfuric acid at predetermined temperature for a predetermined time,

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followed by washing, so that the surface of the molded product is roughened.

For this step, preferable conditions are the following:

the temperature of the chromic acid mixture used is preferably 65 to 69°C, and more preferably 66 to 68°C.

The chromic acid concentration of the chromic acid mixture is preferably 370 g/l to 390 g/l. The sulfuric acid concentration thereof is preferably 190 g/l to 230 g/l. The processing time of the etching step is typically 8 to 12 minutes.

When the chromic acid concentration is excessively higher than the above-described range, the elastic layer 22 is disadvantageously melted and impurities are dissolved into the mixture. When the sulfuric acid concentration is excessively higher than the above-described range, a crystal is developed, inhibiting continuous production. The reason is considered to be that high sulfuric acid concentration causes the chromic acid in the chromic acid mixture to be saturated.

A preliminary etching step may be conducted before the above-described etching step. In this case, conditions for the etching are the following.

Preliminary etching step:

The temperature of the chromic acid mixture used is preferably 66 to 68°C.

The chromic acid concentration of the chromic acid

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mixture is preferably 135 g/l to 165 g/l. The sulfuric acid concentration is preferably 180 g/l to 220 g/l. The processing time of the etching step is typically 2 to 4 minutes.

5

A-2. Washing step

In order to remove the above-described chromic acid mixture from the surface of the molded product, washing step is conducted. The washing step can be conducted by showering the molded product with water. Further, after the washing, if necessary, neutralization is conducted and washing is then conducted again.

10

A-3. Catalyst (catalyzer) step

The above-described molded product is immersed in an aqueous solution of palladium chloride, stannous chloride, and hydrochloric acid, followed by washing, whereby palladium is absorbed to the surface of the molded product surface.

20

In the catalyst step, the immersion is conducted under the following conditions.

Temperature: 31 to 35°C

25

Concentration (catalyst): 53 to 67 g/l

Concentration (hydrochloric acid): 280 to 320 g/l

Concentration (chromium impurity): 150 ppm or less

30

The washing can be conducted by showering.

A-4. Accelerator step

The molded product is immersed in an aqueous solution of hydrochloric acid, followed by washing, whereby

- 20 -

tin which has been absorbed along with palladium in the catalyst step is dissolved and detached with the hydrochloric acid.

5 Preferable immersion conditions in the accelerator step are the following.

Temperature: 36 to 40°C

Impurity (tin): 100 ppm or less

10

 In this step, if the molded product is directly washed with water, the pH of the acidic solution used in the catalyst step (typically, pH 1) is rapidly reduced toward the neutral, so that impurities such as hydroxide
15 are generated and are likely to be attached to the surface of the molded product. To avoid this, preferably, the pH of the acidic solution is about 1.5 and the acidic solution is passed through activated charcoal so that the impurities are absorbed.

20

 For the washing step, a nozzle which blows out minute air bubbles is provided at the bottom of a water tank so that the elastic layer 22 is washed. The air bubbles strike the surface of the molded product (particularly, the elastic
25 layer 22) so that the impurities and residual drug attached on the surface of the molded product can be effectively removed.

 A-5. Electroless nickel plating or copper plating
30 (chemical plating)

 The molded product is immersed in a mixture of nickel or copper, formalin, Rochelle salt, sodium hydroxide, sodium hypophosphite, ammonia, water, etc.; followed by

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washing. As a result, nickel (copper) is deposited on palladium due to a reducing reaction of formalin and sodium hypophosphite.

5 Thereafter, electroplating is conducted on the electroless plating layer as follows.

 In the present invention, after the nickel or copper plating, nickel electroplating, chromium plating, chromium
10 alloy plating, gold plating, or other alloy plating are conducted.

 (Third Invention)

 Trivalent chromium plating is conducted on the
15 surface of the above-described molded product having a thin portion by the following steps.

 (A) The molded product is washed. A metal plating layer is formed on the surface of the molded product by
20 electroless nickel plating (chemical plating) or electroless copper plating.

 The electroless plating can be conducted as follows.

25 Etching step: the molded product is immersed in an aqueous solution containing chromic anhydride and sulfuric acid at a predetermined temperature, followed by washing, and the surface of the molded product is roughened.

30 Catalyst (catalyzer) step: the molded product is immersed in an aqueous solution containing palladium chloride, stannous chloride and hydrochloric acid, followed by washing, so that palladium is absorbed to the surface

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of the molded product.

Accelerator step: the molded product is immersed in an aqueous hydrochloric acid solution, followed by washing, so that tin which has been absorbed along with palladium in the catalyst step is dissolved and detached with the hydrochloric acid solution.

Electroless nickel plating or electroless copper plating (chemical plating):

the molded product is immersed in a mixture of nickel or copper, formalin, Rochelle salt, sodium hydroxide, sodium hypophosphite, ammonia, water, etc., followed by washing, so that nickel (copper) is deposited on the palladium due to a reduction reaction of formalin and sodium hypophosphite.

Next, electroplating is conducted on the electroless plating layer in the following manner.

In the present invention, after copper plating, nickel plating, and chromium plating or chromium alloy plating is conducted.

(B) A copper plating layer is formed on the surface of the electroless plating layer by electroplating.

A thickness of the copper plating layer is typically 5 μm to 15 μm .

Conditions for copper plating may be the following.

The molded product is immersed in copper sulfate

bath having a copper sulfate concentration of 70-90 g/l and a sulfuric acid concentration of 170-210 g/l at 10-30°C (more preferably 20°C), and plating is conducted at a cathode current density of 1-4 A/dm².

5

(C) A nickel layer is formed on a surface of the copper plating layer by electroplating.

The molded product is immersed in a mixture of nickel sulfate, nickel chloride, boric acid, and brightener, and treated under predetermined conditions of voltage and current, followed by washing, whereby a nickel coat is formed on the surface of the molded product.

In the washing after the plating, water is preferably given vibration by means of a particular device, so that liquid penetrating the gaps or the like between the primary and secondary molded products 1 and 2 of the coinjection molded product can be completely removed.

(D) A chromium or chromium alloy layer is formed on the surface of the nickel layer by electroplating.

In the present invention, trivalent chromium plating is conducted. The composition of a plating solution is, for example, chromium sulfate (trivalent), chromium acetate (trivalent), chromium nitrate (trivalent), chromium chloride (trivalent), or biphosphate chrome (trivalent) (see Japanese Laid-Open Publication No. 2000-54157).

In this case, conditions for silver color plating are the following.

(a) The trivalent chromium concentration of the

- 24 -

plating bath: 6 to 10 g/l (preferably 7 to 9 g/l)

(b) The amount of overall impurities in the plating bath: 60 ppm or less (preferably 35 ppm or less)

5

(c) Bathing temperature: 40 to 50°C (preferably 47 to 49°C)

(d) The pH of the plating bath: 3.2 to 3.6
10 (preferably 3.35 to 3.45)

(e) Cathode current density: 3 to 5 A/dm²
(preferably 3.5 to 4.5 A/dm²)

15 (f) Anode/cathode ratio: 1.5 to 2 : 1

(g) Rectifier: one that has an ability to rectify an amount of current which is three times or more as much as the total current amount.

20

(h) Filtering ability: the entire bathing solution is passed through a filter seven times or more per hour. This filtering is continuously conducted. Specifically, whereas the amount of the circulating bathing solution is
25 conventionally about two time per hour, that is 7 to 10 times per hour in the present invention. The filter used (filter cloth) preferably has a mesh size of 5 μm to 10 μm (conventionally about 50 to 100 μm).

30 Further, the above-described current is preferably always applied to the plating bath.

In order to obtain a black color molded product, the

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treatment conditions are changed only with respect to the following points.

5 (a') The trivalent chromium concentration of the plating bath: 6 to 10 g/l (preferably 6 to 9 g/l)

(c') Bathing temperature: 53 to 63°C (preferably 57 to 59°C)

10 (d') The pH of the plating bath: 3.2 to 3.6 (preferably 3.45 to 3.55)

15 Thus, the chromium concentration and the liquid temperature is increased by about 2%, the pH is decreased by about 0.2, and the filtering ability is increased by a factor of 2.5 or more with respect to the standard plating conditions recommended by the manufacturer, thereby making it possible to reduce impurities.

20 (Example 1)

A primary molded product made of ABS resin and a secondary molded product made of thermoplastic polyurethane elastomer were molded together by coinjection molding to obtain a molded button product for a cellular phone.

25

30 This molded product was etched under the following conditions. After the etching, the molded product was washed with water two times. Each washing water was passed through a membrane filter (#2), and residues adsorbed by the filter paper were visually observed and evaluated (its factor ranges from the worst, 50, to the best, 0). Further, the washed molded product was plated with a conventional method and the plating of the molded product was visually

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observed.

A. Object of the test

It is believed that in the above-described second
5 etching step (the A-1 step in the second invention), the
thermoplastic polyurethane elastomer was dissolved, and
solidified by the washing or the like, and the solidified
elastomer is dispersed in the subsequent steps, so that
defective products are produced. Whether the cause is the
10 chromic acid or the sulfuric acid of the chromic acid mixture
was studied.

B. Testing conditions

Chromic acid mixtures are prepared by combining the
15 three levels of chromic acid concentrations (350 to 410 g/l
in 30 g/l steps) and the three levels of sulfuric acid
concentration (180 to 240 g/l in 30 g/l steps).

C. Testing method

20 Each chromic acid mixture prepared above was poured
into a one-liter beaker. Six of the above-described molded
products were immersed in this mixture and subjected to
etching for eight minutes. This etching process was
repeated two times.

25

D. Method for Evaluation

The molded products etched in section C were washed
two times. Each washing water was passed through a membrane
filter (#2), and residues adsorbed by the filter paper were
30 visually observed and evaluated (its factor ranges from the
worst 50 to the best 0). Further, oil film attached to the
filter paper was visually observed.

E. Results

The results are shown in Table 1.

Table 1

No.	Etching Concentration		First Washing		Second Washing		Test Results of Plated Products					
	Chromic acid	Sulfuric acid	Residue	Oil film	Residue	Oil film	n=	p=	%	Size of bump	Area of bump	
1	410g/l	180g/l	50	Slight	3	None	40	23	58%	Big	Large	
2	380g/l	180g/l	50	Much	3	Much	48	45	94%	Big	Large	
3	350g/l	180g/l	40	Much	10	Much	80	80	100%	Big	Large	
4	410g/l	210g/l	20	Much	1	Slight	48	6	13%	Middle	Middle	
5	380g/l	210g/l	1	Slight	2	None	40	8	20%	Middle	Small	
6	350g/l	210g/l	5	Much	3	Slight	96	4	4%	Middle	Middle	
7	410g/l	240g/l	2	Slight	1	Slight	48	32	67%	Small	Middle	
8	380g/l	240g/l	1	None	1	Slight	48	27	56%	Middle	Middle	
9	350g/l	240g/l	1	None	1	None	48	34	71%	Middle	Middle	

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In Table 1, n represents the total number of tests, p represents the number of defective products, and % represents the percentage of defective products. The size and area of a bump was visually measured.

5

As is apparent from Table 1, the best result was obtained when the chromic acid concentration was 380 g/l and the sulfuric acid concentration was 210 g/l. In the test where the sulfuric acid concentration was 240 g/l, liquid crystal was developed in the vicinity of the liquid surface of the beaker, indicating that such a condition is not suitable for actual manufacture. The reason is considered to be that the high sulfuric acid concentration leads to saturation of chromic acid in the mixture.

15

(Example 2)

A molded product treated by nickel plating was subjected to trivalent chromium plating under the following conditions to obtain a silver button for a cellular phone.

20

(a) The trivalent chromium concentration of a plating bath: 9 g/l

25

(b) The amount of overall impurities in the plating bath: 35 ppm or less

30

(c) Bathing temperature: 48°C

(d) The pH of the plating bath: 3.4

(e) Cathode current density: 4.0 A/dm²

(f) Anode/cathode ratio: 1.5 : 1

- 30 -

(g) Rectifier: one that has an ability to rectify an amount of current which is three times as much as the total current amount.

5

(h) Filtering ability: the entire bathing solution is passed through a filter continuously seven times or more per hour.

10

As a result, a silver button for a cellular phone having good throwing power and without roughness was obtained.

(Example 3)

15

A molded product treated by nickel plating was subjected to trivalent chromium plating under the following conditions to obtain a black button for a cellular phone.

20

(a) The trivalent chromium concentration of a plating bath: 9 g/l

(b) The amount of overall impurities in the plating bath: 35 ppm or less

25

(c) Bathing temperature: 58°C

(d) The pH of the plating bath: 3.5

(e) Cathode current density: 4.0 A/dm²

30

(f) Anode/cathode ratio: 1.5 to 1

(g) Rectifier: one that has an ability to rectify

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an amount of current which is three times as much as the total current amount.

(h) Filtering ability: the entire bathing solution is passed through a filter continuously seven times or more per hour.

As a result, a black button for a cellular phone having good throwing power and without roughness was obtained.

(Comparative Example 1)

A molded product treated by nickel plating was subjected to trivalent chromium plating under the following conditions to obtain a silver button for a cellular phone.

(a) The trivalent chromium concentration of a plating bath: 5 g/l

(b) The amount of overall impurities in the plating bath: 600 ppm

(c) Bathing temperature: 40°C

(d) The pH of the plating bath: 3.2

(e) Cathode current density: 7.0 A/dm²

(f) Anode/cathode ratio: 1.5 to 1

(g) Rectifier: one that has an ability to rectify an amount of current which is one times as much as the total current amount.

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(h) Filtering ability: the entire bathing solution is passed through a filter continuously two times per hour.

5 As a result, a silver button for a cellular phone having poor throwing power and without roughness was obtained.

(Comparative Example 2)

10 A molded product treated by nickel plating was subjected to trivalent chromium plating under the following conditions to obtain a black button for a cellular phone.

15 (a) The trivalent chromium concentration of a plating bath: 8 g/l

(b) The amount of overall impurities in the plating bath: 640 ppm or less)

20 (c) Bathing temperature: 50°C

(d) The pH of the plating bath: 3.4

25 (e) Cathode current density: 7.0 A/dm²

(f) Anode/cathode ratio: 1.5 to 1

30 (g) Rectifier: one that has an ability to rectify an amount of current which is two times as much as the total current amount.

(h) Filtering ability: the entire bathing solution is passed through a filter continuously two times per hour.

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As a result, a black button for a cellular phone having poor throwing power and without roughness was obtained.

5

The judgment of surface roughness was conducted as follows: attached foreign matters, flaws, etc. were visually observed from a distance of 30 cm or more, and a product having a foreign matter having a size of 0.2 mm or more was judged as a reject.

10

The judgment of throwing power was conducted as follows: whether or not the plating is uniform and the presence or absence of discoloration, tarnishing, etc. were visually observed, and a product having discoloration, tarnishing, etc. was judged as a reject.

15

INDUSTRIAL APPLICABILITY

According to the first invention, even for a molded product having a thin portion obtained by high-speed injection molding, a plating which resists removal can be obtained. Further, even when a plating is formed on a satin-finished surface, the plating can reproduce the satin-finished surface.

20

25

According to the second invention, a plating having good adhesion can be provided on a coinjection molded product by etching the surface of the molded product while the elastic layer is prevented from being dissolved as much as possible. Therefore, it is possible to prevent the development of bumps on the surface of the molded product, thereby reducing the incidence of defective products.

30

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According to the third invention, a metal coating having excellent corrosion resistance can be provided by surface treatment using a treatment solution which does not
5 contain hexavalent chromium. Further, the chromium concentration and the liquid temperature is increased by about 2%, the pH is decreased by about 0.2, and the filtering ability is increased by a factor of 2.5 or more with respect
10 to the standard plating conditions recommended by the manufacturer, thereby making it possible to reduce impurities.

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CLAIMS

1. A method for producing a plated molded product, wherein a surface of a molded product having a thin portion obtained by high-speed injection molding of resin is subjected to plating, the method comprising the steps of:

(a) forming a metal plating layer on a surface of the molded product by electroless plating;

(b) forming a copper plating layer on a surface of the electroless plating layer by electroplating;

(c) forming a nickel layer on a surface of the copper plating layer by electroplating; and

(d) forming a chromium or chromium alloy layer on a surface of the nickel layer by electroplating.

2. A method according to claim 1, wherein the copper plating is conducted under the following conditions:

the molded product is immersed in a copper sulfate bath containing copper sulfate having a concentration of 70 to 90 g/l and sulfuric acid having a concentration of 170 to 210 g/l at 10 to 30°C and at a cathode current density of 1 to 4 A/dm².

3. A method according to claim 1, wherein a bright surface and a rough surface are provided on the surface of the molded product.

4. A plated molded product produced by a method according to claim 1.

5. A plated molded product according to claim 4, wherein the molded product is a button for operating a cellular phone.

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6. A method for producing a plated molded product, wherein a surface of a molded product having a thin portion obtained by rapid coinjection molding of resin is subjected to plating, the method comprising the steps of:

- (a) forming a metal plating layer on a surface of the molded product by electroless plating;
- (b) forming a copper plating layer on a surface of the electroless plating layer by electroplating;
- 10 (c) forming a nickel layer on a surface of the copper plating layer by electroplating; and
- (d) forming a chromium or chromium alloy layer on a surface of the nickel layer by electroplating.

15 7. A method for producing a plated molded product, wherein a surface of a molded product obtained by integrally molding an elastic layer as a secondary molded product on at least a portion of a surface of a primary molded product is treated by plating, the method comprising the step of etching the surface of the molded product by immersing the molded product in a mixture of chromic acid and sulfuric acid, wherein the etching step is conducted under the following conditions:

- (a) the temperature of the mixture is 65 to 69°C;
- (b) the chromic acid concentration of the mixture is 370 g/l to 390 g/l; and
- 25 (c) the sulfuric acid concentration of the mixture is 190 g/l to 230 g/l.

8. A method according to claim 7, further comprising a washing step, a catalyst step, and an accelerator step in this order after the etching step, wherein

30 the accelerator step comprises the steps of immersing the molded product in an acidic solution having

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a pH closer to the neutral than the pH of an acidic solution used in the catalyst step and causing the acidic solution to be in contact with activated charcoal so that impurities contained in the acidic solution were adsorbed, and
5 thereafter washing the molded product.

9. A method according to claim 8, wherein the washing step comprises the step of providing a nozzle on a bottom side of a water tank, the nozzle blowing minute air bubbles, and
10 blowing the air bubbles toward the molded product.

10. A method according to claim 7, wherein the elastic layer consists of thermoplastic polyurethane elastomer.

15 11. A plated molded product obtained by a method according to claim 7.

12. A plated molded product according to claim 11, wherein the plated molded product is a button for a cellular phone.
20

13. A method for producing a plated molded product, wherein a surface of a molded product obtained by coinjection molding is treated by trivalent chromium plating, the method comprising the step of plating under the following
25 conditions:

(a) the trivalent chromium concentration of a plating bath is 6 to 10 g/l;

(b) the amount of overall impurities in the plating bath is 60 ppm or less;

30 (c) bathing temperature is 40 to 50°C;

(d) the pH of the plating bath is 3.2 to 3.6;

(e) cathode current density is 3 to 5 A/dm²; and

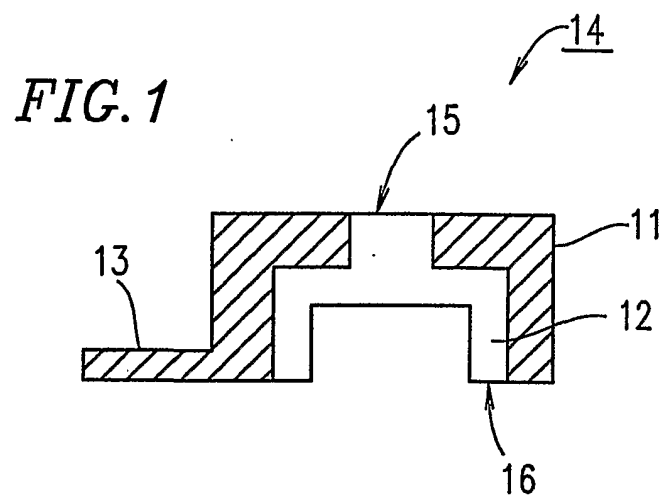
(f) anode/cathode ratio is 1.5 to 2 : 1.

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14. A method for producing a plated molded product, wherein
a surface of a molded product obtained by coinjection molding
is treated by trivalent chromium plating, the method
5 comprising the step of plating under the following
conditions:

- (a) the trivalent chromium concentration of a
plating bath is 5 to 10 g/l;
- (b) the amount of overall impurities in the plating
10 bath is 60 ppm or less;
- (c) bathing temperature is 53 to 63°C;
- (d) the pH of the plating bath is 3.2 to 3.6
- (e) cathode current density is 3 to 5 A/dm²; and
- (f) anode/cathode ratio is 1.5 to 2 : 1.

1/1

*FIG. 2*