(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 459 461 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **91108822.7**

(51) Int. Cl.5: **C23C 18/16**, C25D 5/02

(22) Date of filing: **29.05.91**

(30) Priority: **31.05.90 JP 142160/90**
01.06.90 JP 141611/90
04.06.90 JP 144547/90

(43) Date of publication of application:
04.12.91 Bulletin 91/49

(84) Designated Contracting States:
CH DE FR GB IT LI

(71) Applicant: **Toshiba Tungaloy Co., Ltd.**
7, Tsukagoshi 1-chome Saiwai-ku
Kawasaki-shi Kanagawa-ken(JP)

Applicant: **YAMATO PLATING CO., LTD.**
19-1, Higashitateishi 2-chome, Katsushika-ku
Tokyo(JP)

(72) Inventor: **Sato, Yoshiyuki, c/o Toshiba**
Tungaloy Co. Ltd.
7, Tsukagoshi 1-chome, Saiwai-ku
Kawasaki-shi, Kanagawa-ken(JP)
Inventor: **Kinashi, Daisuke, c/o Toshiba**
Tungaloy Co. Ltd.
7, Tsukagoshi 1-chome, Saiwai-ku
Kawasaki-shi, Kanagawa-ken(JP)
Inventor: **Shibuki, Kunio, c/o Toshiba**
Tungaloy Co. Ltd.
7, Tsukagoshi 1-chome, Saiwai-ku
Kawasaki-shi, Kanagawa-ken(JP)
Inventor: **Watanabe, Noriko, c/o Yamato**
Plating Co. Ltd.
19-1, Higashitateishi 2-chome
Katsushika-ku, Tokyo(JP)
Inventor: **Watanabe, Akihiro, c/o Yamato**
Plating Co. Ltd.
19-1, Higashitateishi 2-chome
Katsushika-ku, Tokyo(JP)

(74) Representative: **Hansen, Bernd, Dr.**
Dipl.-Chem. et al
Hoffmann, Eitle & Partner Patent- und
Rechtsanwälte Arabellastrasse 4 Postfach
81 04 20
W-8000 München 81(DE)

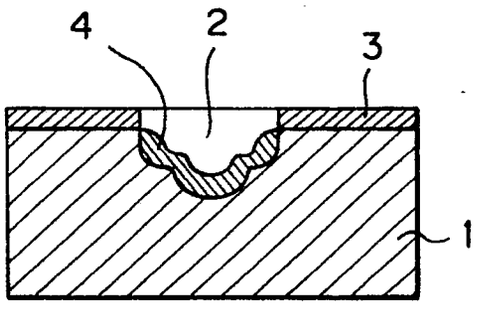
(54) Multi-colored product and process for producing the same.

(57) There are disclosed a multi-colored product which comprises a base material (1) and a film formed at a specific portion of one surface of the base material,

said film being a single layer film (4) or plural layered films (3,4) consisting essentially of at least one of copper (Cu), silver (Ag), gold (Au), platinum (Pt), iridium (Ir), osmium (Os), palladium (Pd), rhodium (Rh), ruthenium (Ru) and an alloy containing the above metal(s) and being formed on a heat-fused surface with concave-shaped surface (2) or line provided on the surface of said base material, and a process for producing the same.

EP 0 459 461 A1

FIG. 6



BACKGROUND OF THE INVENTION

This invention relates to a multi-colored product in which at least one kind of a film different in color and/or color tone from a base material is formed on at least one surface of the base material and a process for producing the same. More specifically, it relates to a multi-colored product used for decoration or ornamentation, display and carved seal such as ornament parts including watch cases, watch bands or belts, dials, brooches, cuff buttons, tiepins and lighters, sports goods including golf clubs, tools, flames of glasses or goods with various carved seal, and a process for producing the same.

The surface of base materials such as stainless steel, hard alloy and cermet have heretofore been subjected to mirror polishing and the product has been practically employed for ornamental parts exemplified by watch cases, bands or belts and dials. However, according to this method, ornaments become monotonous since it relies on the inherent color of the base material whereby ornamental value is restricted. Also, even when carving seal or letter is carried out by means of etching, etc., sharp and clear one cannot be obtained.

In order to solve the above problem, there have been attempted to provide many proposals relating to ornamental parts on which films showing plural kinds of color hues in combination of gold, silver and black according to the dry plating methods such as chemical vapor deposition method (CVD) and physical vapor deposition method (PVD); or the wet plating methods such as anodic oxidation treatment, electrolytic plating and non-electrolytic plating. Of these proposals, representative ones relating to multi-color ornamental parts are disclosed in Japanese Provisional Patent Publications No. 100682/1985, No. 157673/1986 and No. 75659/1989.

Of the proposals relating to multi-coloration of the above ornamental parts, in Japanese Provisional Patent Publication No. 100682/1983, there is disclosed the process for producing exterior parts for a watch in which a flame coating material comprising Al_2O_3 and TiO_2 is flame coated on the surface of an austenite type stainless steel with low carbon content with a thickness of 0.1 to 1 mm, then the surface is made mirror surface by lapping finishing and the remaining stainless steel portion is subjected to gold plating or TiN coating. However, this process involves the problems that the exterior parts for a watch produced by this process causes strain between the stainless steel and the flame coated film due to heat and cool during flame coating and fine cracks cause on the surface of the flame coated film so that aesthetic value becomes low, that shape of design or pattern is restricted since fine line design or pattern cannot be formed by masking and flame coating, and that a film of gold easily peel off in the case of gold plating.

Also, in Japanese Provisional Patent Publication No. 157673/1986, there is disclosed the process for producing multi-color hard film in which a hard color layer is formed on the surface of a base material by ion plating method, then optional parts of the hard color layer are masked and subjected to ion plating to form a layer with a color different from said hard color layer. However, in the multi-color film product obtained by the method, there involves the problems that it is difficult to form fine pattern or design, and even when noble metal such as Au or Pt is formed as a film, they easily peel off whereby the process cannot be practically used.

Further, in Japanese Provisional Patent Publication No. 75659/1989, there is disclosed the multi-coloration process of a metal surface in which a colored film is formed on the surface of a fundamental metal by ion plating method, then a part of the film is removed by laser working to develop the metal. However, the multi-colored product obtained by the above method has problems that a material of the film or color thereof is restricted, formation of fine pattern or design by a noble metal is difficult particularly when a film of a noble metal such as Au or Pt is to be formed, and adhesiveness to the base material is bad and easily peeled off so that it cannot be practically used.

SUMMARY OF THE INVENTION

The present invention has solved the above problems and an object thereof is to provide a multi-colored product having practical value in which plural colors are formed with a surface portion of a noble metal color formed by a film of a noble metal such as Au or Pt and copper series metal with good adhesiveness on at least whole or a part of one surface of the base material, and a surface portion of a film-(s) different in color and/or color tone from the noble metal color whereby enabling fine pattern or design, letter and mark as well as heightening adhesiveness of the film, and a process for producing the same.

The present inventors have investigated to form a fine pattern with a noble metal film with plural colors by coating a film of a noble metal such as Au, Ag, Pt on the surface of a base material with good adhesiveness and other film different in color and/or color tone from the noble metal film, and as the results, they have found that a film of a noble metal formed by the wet plating method, which is formed after

removing the surface portion of a base material by locally irradiating a laser beam to the surface of the base material, shows markedly excellent adhesiveness to the base material and it easily peel off formed on other than the base material processed by the laser beam. The present invention has accomplished by the above findings.

That is, the multi-colored product of the present invention comprises a base material and a film formed at a specific portion of one surface of the base material, and said film being a single layer film or plural layered films consisting essentially of at least one of copper (Cu), silver (Ag), gold (Au), platinum (Pt), iridium (Ir), osmium (Os), palladium (Pd), rhodium (Rh), ruthenium (Ru) and an alloy containing the above metal(s) and being formed on a heat-fused surface with concave-shaped surface or line provided on the surface of said base material.

As one of the preferred embodiments (first embodiment) of the present invention, the product comprises a base material at least one surface of which being a multi-colored surface constituted by (i) a first film surface and a second film surface which is different in color and/or tone from the first film surface, or (ii) the first film surface, the second film surface and a surface of the base material, and said second film being a single layer film or plural layered films consisting essentially of at least one of Cu, Ag, Au, Pt, Ir, Os, Pd, Rh, Ru and an alloy containing the above metal(s) and being formed on a heat-fused surface with a concave-shaped surface or line provided on the surface of said base material.

As the other preferred embodiments (second embodiment) of the present invention, the product comprises a base material at least one surface of which being a multi-colored surface constituted by (i) a first film surface and a second film surface which is different in color and/or tone from the first film surface, or (ii) the first film surface, the second film surface and a surface of the base material,

said first film being a single layer film or plural layered films consisting essentially of at least one of a metal; an alloy; a carbide, nitride, carboxide or oxynitride of a metal of group 4a (titanium (Ti), zirconium (Zr) and hafnium (Hf)), 5a (vanadium (V), niobium (Nb) and tantalum (Ta)) or 6a (chromium (Cr), molybdenum (Mo) and tungsten (W)) of the periodic table; an oxide, carbide or nitride of aluminum (Al) or silicon (Si); mutual solid solution of the above; and hard carbon, and

said second film being a single layer film or plural layered films consisting essentially of at least one of Cu, Ag, Au, Pt, Ir, Os, Pd, Rh, Ru and an alloy containing the above metal(s).

Also, the process for producing the product of the present invention comprises the steps of

(a) providing on the surface of a base material a temporarily-provided film composed of a substance having low affinity to a film to be provided at the later stage;

(b) irradiating on the surface of said temporarily-provided film by a laser beam to melt and remove said temporarily-provided film and the surface of the base material of said portion whereby forming heat-fused surface with a concave-shaped surface or line on the surface of the base material;

(c) forming the film consisting essentially of at least one of Cu, Ag, Au, Pt, Ir, Os, Pd, Rh, Ru and an alloy containing the above metal(s);

(d) removing the film formed in the above step (c) remained on said temporarily-provided film; and

(e) removing said temporarily-provided film.

As one of the preferred embodiments (first embodiment) of the present invention, the process for producing the product comprises the steps of:

(a) forming a first film on one surface or part of a base material by the dry plating method or wet plating method;

(b) irradiating a laser beam on the surface of the first film to locally remove said first film and finely remove the surface of the base material of the portion corresponding to the first film whereby to form a concave-shaped surface or line on the base material;

(c) forming a second film consisting essentially of at least one of Cu, Ag, Au, Pt, Ir, Os, Pd, Rh, Ru and an alloy containing the above metal(s) with a single layer or plural layers; and

(d) processing the product to remain said second film only on the concave-shaped surface or line formed in the step (b) whereby to form a surface portion of the first film which is different in color and/or tone from those of the second film formed in the step (c) and a surface portion of the second film.

As the other preferred embodiments (second embodiment) of the present invention, the process for producing the product comprises the steps of:

(a) forming a first film consisting essentially of at least one of a metal; an alloy; a carbide, nitride, carboxide or oxynitride of a metal of group 4a, 5a or 6a of the periodic table; an oxide, carbide or nitride of aluminum (Al) or silicon (Si); mutual solid solution of the above materials; and hard carbon, with a single layer or plural layers;

(b) irradiating a laser beam on the surface of the first film to partially remove said first film;

(c) forming a second film consisting essentially of at least one of Cu, Ag, Au, Pt, Ir, Os, Pd, Rh, Ru and

an alloy containing the above metal(s) with a single layer or plural layers by the wet plating method; and (d) removing the second film formed other than the portion at which the first film is removed in the step (b).

BRIEF DESCRIPTION OF THE DRAWINGS

Fig.s 1 to 5 are sectional views showing representative shapes of concave-shaped surface or concave-shaped line of the surface of the base material in the product according to the present invention wherein reference numeral 1 is a base material and 2 is a concave-shaped surface or concave-shaped line; Fig. 6 is a sectional view showing the representative product of the present invention wherein reference numeral 1 is a base material, 2 is a concave-shaped surface or concave-shaped line, 3 is a first film and 4 is a second film; Fig. 7 is a perspective view of a slow-away chip with letter inscription obtained in Example 4; Fig. 8 shows one example the process of the present invention (second embodiment) with sectional views wherein reference numeral 1 is a base material, 2 is a surface on which multi-colored surface is to be formed, 3 is a first film and 4 is a second film; Fig. 9 is a perspective view of a tool obtained in Example 11; and Fig. 10 shows one example of the process of the present invention with sectional views wherein reference numeral 1 is a base material, 2 is a surface on which multi-colored surface is to be formed, 3 is a temporarily-provided film and 4 is a film.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

A base material to be used for the multi-colored product in the present invention is not particularly limited and may include, for example, a material to be used for a watch case, watch bands or belts, dials, brooches, cuff buttons, tiepins and lighters, sports goods such as golf clubs, tools, flames of glasses and tool parts, including metal materials such as mild steel, nickel, stainless steel, high speed steel, Cr-Al-Ni alloy, brass and bronze; inorganic materials such as glass, ceramics and artificial sapphire; complexes of an inorganic material and metal such as cermet and hard alloy; and complexes of an inorganic material and organic material such as fiber reinforced polymer (FRP). Of these, preferred are stainless steel, heat-resistant alloy, high speed steel, hard alloy, Cr-Al-Ni alloy, cermet, brass, bronze, Al alloy and ceramics, and particularly preferred are stainless steel, cermet and hard alloy since they provide exquisite contrast to the color and/or tone of the film. In view of use, those which are suitable for materials for ornament parts, tool and inscription are preferred.

The concave-shaped surface or concave-shaped line which is heat-fused surface to be locally provided on the surface of the base material may vary depending on design or figure for desired ornament or display. More specifically, it comprises with a width of at least 0.1 μm and a depth of at least 0.5 μm, and for creating beautiful line or shape, a width of at least 0.5 μm and a depth of at least 1 μm are particularly preferred. The shape of the concave-shaped surface or concave-shaped line may include, for example, the shape with steps as shown in Fig.s 1 and 2, circular shape as shown in Fig. 3, rectangular shape as shown in Fig. 4, and V-letter shape as shown in Fig. 5. Of these, the shape with steps is particularly preferred for creation of beautiful line and shape, and enhancing adhesion strength of the film to the base material. The shape with steps may include the shape with one step as shown in Fig. 1 or the shape with plural number of steps as exemplified by Fig. 2 depending on the width of the concave-shaped surface or concave-shaped line. The depth of the concave-shaped surface or line is preferred when it becomes at least 1 μm deeper than the standard value which is the minimum value (maximum depth of the surface of the base material) occurred from surface roughness of the base material, particularly preferably 3 to 100 μm deeper than the standard value because of adhesion strength of the film to the substrate and used amount of the film. In other expression or words, the concave-shaped surface or concave-shaped line is heat-fused surface or line formed by melting and removing the base material with heat.

As the materials to be used for forming the film consisting essentially of at least one of Cu, Ag, Au, Pt, Ir, Os, Pd, Rh, Ru and an alloy containing the above metal(s) (second films of the first and second embodiments), there may include Cu, Ag, Au, Pt, Ir, Os, Pd, Rh and Ru, and alloys mainly composed of these metals. Examples of such alloys may include Au-Ag alloy, Au-Ni alloy, Au-Ni-In alloy, Au-Cu alloy, Au-Cu-Cd alloy, Pt-Rh alloy, Cu-Zn alloy and Cu-Sn alloy.

Of these, employing at least one of Cu, Ag, Au, Pt and alloys containing the above metals is particularly preferred because of the beauties and fastness. Also, when Au, Pt and alloys containing these metals are employed, these materials are firstly adhered on the base material firmly only when the process of the present invention is used.

One kind of these may be used as a single layer film or else plural number of or layered films different

in color and/or tone from each other or from the base material may be formed by effecting formation of the film with plural number of times. In this case, part of films may be formed by using a metal such as Ti according to the dry plating method.

The thickness of the film is not particularly limited, but preferably 0.01 to 20 μm in order to develop a color possessed by the material for the film and not causing internal peel off, more preferably 0.1 to 5 μm because of color tone, gloss and production cost. If it is too thick, the raw material is spoiled or external power is much required for cutting border portion when removing a portion of the film formed on a temporarily-provided film as described below. It is particularly preferred to form the film in the state of lower than the base material surface. More specifically, when observed by the sectional view of the product, it is preferred to form the film, for example, in the concave-shaped surface or concave-shaped line of the surface of the base material as shown in Fig. 6, wherein reference numeral 1 is the base material, 2 is the concave-shaped surface or concave-shaped line, 3 is the first film and 4 is the second film. In other word, when observed by the sectional view of the product, it is preferred to form the film lower than the second film mentioned below.

In the second embodiment of the present invention, the above (second) film is generally formed on the surface of the base material (heat-fused portion of the base material), but it may be formed on the surface of the first film remained on the base material.

In the preferred embodiments of the present invention (first and second embodiments), the first film may be formed with a single layer film or plural layered films on the surface of the substrate. The material to be used for forming the first film is not particularly limited so long as it is different in color and/or tone from those of the second film, and in view of adhesiveness to the base material and beauty of gloss, there may be mentioned, for example, metals such as titanium (Ti), zirconium (Zr), hafnium (Hf), vanadium (V), niobium (Nb), tantalum (Ta), chromium (Cr), molybdenum (Mo), tungsten (W), cobalt (Co), nickel (Ni), zinc (Zn) and tin (Sn); alloys containing at least one of the above metals such as Ti-Zr alloy, Ti-Al alloy, Ti-Ni alloy, Ti-Cr alloy and Ti-V alloy; a carbide, nitride, oxide, boride or silicate of a metal belonging to group 4a, 5a or 6a of the periodic table such as TiC, ZrC, HfC, NbC, TaC, Cr_3C_2, MoC, WC, W_2C, TiN, ZrN, HfN, VN, NbN and TaN; carboxide or oxynitride of the above metals such as Ti(C, O), Ti(C, N), Ti(N, O), Ti(C, N, O), (Ti, Zr)C and (Ti, Zr) (C, O); oxide, carbide or nitride of Al or Si (transition metals) such as Al_2O_3, SiO_2, SiC, AlN and Si_3N_4; mutual solid solutions thereof; or hard carbon including diamond-like carbon. Of these, at least one of Ti, Zr, Cr or an alloy containing these metals or a compound thereof; a carbide, nitride, carboxide and oxynitride (particularly TiC and TiN); and mutual solid solutions thereof are particularly preferred.

Also, metals used for the second film as mentioned above or alloys containing at least one of these may be used as the first film so long as it is different from the second film actually used and provides different color and/or tone.

In the description, an alloy containing a specific metal is not particularly limited so long as the alloy has low affinity to the second film in either of the two-component system alloy or multiple-component system alloy.

One kind of them may be used as a single layer film or the film may be formed by using two kinds or more as a plural layered film or partially making plural layered structure so that the film itself may have two or more colors.

The thickness of the first film may be optionally selected depending on the object thereof, but preferably 10 μm or less, more preferably 1 μm or less, further preferably 0.1 to 0.5 μm, particularly preferably 0.2 to 0.4 μm.

This first film may be used as the temporarily-provided film mentioned in the process for producing the product.

These first and second films comprise a single layer film or plural layered film, and of these, the plural layered film can be made laminated layer of two kinds or more formed in parallel on the surface of the base material or two kinds or more layers formed perpendicularly on the surface of the base material.

When the color and/or tone of the base material is different from either of the first or second films, an effect as the third color hue may be provided to the base material by exposing part of the base material as such.

In the present invention, the film of a noble metal or the second film may be formed on a metal or alloy film (as a subbing layer) which is at least one selected from nickel (Ni), cobalt (Co), chromium (Cr), zinc (Zn), cadmium (Cd), aluminum (Al), tin (Sn) and lead (Pb), which is formed on the base material or the first film.

The multi-colored product can be produced by applying the dry plating method represented by the physical vapor deposition method or chemical vapor deposition method such as ion plating, sputtering,

electron beam deposition, which are conventionally carried out; or the wet plating method represented by electrolytic plating, non-electrolytic plating and anodic oxidation treatment, but for forming a figure with beautiful and fine pattern, it is preferred to employ the process of the present invention as mentioned below (see Fig. 8 and Fig. 10).

(a) Formation of a first film or a temporarily-provided film

First, on the surface of the base material to be multicolored, a first film or a temporarily-provided film is formed. If necessary, pre-treatment such as polishing, lapping or washing may be provided on the surface thereof.

The temporarily-provided film is removed after formation of the film of the present invention by an acid treatment or other method. Thus, the material of the temporarily-provided film should be selected from materials which are capable of forming a film and easily removable such as a metal and an alloy which are other than those used for formation of the film of the present invention. Selected are those having less affinity to the materials for forming the multi-colored film so as to easily remove the multi-colored film formed on the temporarily-provided film. That is, Ti, Zr, Cr, Ti-Zr alloy, Ti-Al alloy, Ti-Ni alloy and Ti-V alloy are preferred, provided that a metal or an alloy which is different from that actually used for the base material should be used. When adhesiveness to the base material is poor, other subbing layer such as a layer of Ni is preferably provided.

As the method for forming the first film or the temporarily-provided film, optional dry plating method such as ion plating, vacuum vapor deposition, electron beam deposition, metal spraying, sputtering and CVD; and wet plating method such as anodic oxidation treatment, electrolytic plating and non-electrolytic plating depending on the material of the film composition and the method can be selected depending on the same, but generally the wet plating method is preferred. Formation of the film may be carried out on the whole surface of the base material or may be carried out only on part thereof, for example, only on part necessary for forming multi-colored surface.

The thickness of the temporarily-provided film may be optionally selected depending on the object, but preferably 10 μm or less, more preferably 1 μm or less, further preferably 0.1 to 0.5 μm.

(b) Laser beam treatment

After formation of the first film or the temporarily-provided film as mentioned above, said film is locally removed by the laser beam treatment and the base material corresponding to said film portion is also preferably removed by melting with a depth of at least 0.5 μm. That is, the laser beam is irradiated only to the portion on which a film (including a second film) is to be coated at the later stage with a shape of a design, pattern, letter, mark or symbol to remove by melting the first film, or the temporarily-provided film and the base material (only the surface portion) at the said portion whereby the base material is exposed.

As the laser, there may be exemplified by a gas laser such as Ne-He, argon and CO_2; a solid laser such as ruby, YAG (yttrium-aluminum-galium) and glass; and a semiconductor laser such as GaAs (galium-arseinic), but YAG laser is preferred since continuous oscillation can be easily carried out at room temperature and controllability at the low irradiation energy region is good. The irradiation conditions are different depending on the material and film thickness of the first film or temporarily-provided film, and irradiation may be carried out by controlling the irradiation energy so as to form a heat-fused surface by melting the film and the surface of the base material with heat.

The width of destroying the first film or removing the temporarily-provided film and the surface of the base material with heat according to the laser irradiation varies depending on the object and it can be set optionally within the range of 0.1 μm or more, but for the use of an appearance of multi-colored surface, it is preferred in the range of 0.1 to 2 mm.

(c) Formation of a film (including a second film)

After washing the surface in which the laser beam irradiation is carried out with water or an organic solvent, a film consisting essentially of at least one of Cu, Ag, Au, Pt, Ir, Os, Pd, Rh, Ru and an alloy containing the above metal(s) is formed. Formation of the film can be carried out by the conventional wet plating method such as anodic oxidation treatment, electrolytic plating and non-electrolytic plating.

In the step of the laser beam irradiation, the groove formed by the laser beam generally reaches to the surface of the base material penetrating the first film or temporarily-provided film, and in some case, it penetrates into the base material with a depth of at least 0.5 μm. And thus, at the portion of the latter case,

the film is formed by penetrating into the base material with the depth of the groove. In the film formed, a film formed on the heat-fused surface is preferably formed at the portion lower than the surface of the base material. That is, at this portion, the film is preferably formed at the inside of the concave-shaped surface or concave-shaped line. Also, the groove reaches only in the first film and not reaches to the base film, and thus the main part of the second film may be sometimes formed on the first film remained at the bottom of the groove. This can be made depending on the object by optionally controlling the laser beam irradiation, and is included in the present invention so long as it does not deviate the summary of the present invention.

(d) Removal of the film (or the second film) on the first film or temporarily-provided film

According to the findings by the present inventors', the film (or the second film) thus formed on the base material or the groove formed by the laser beam treatment is excellent in adhesiveness to the base material and firmly adhered to the same. To the contrary, the film (or the second film) formed on the temporarily-provided film (or the first film) shows peel-off property to the film (or the second film).

Thus, the next step after forming the film (or the second film) of the present invention is to peel off or remove the film (or the second film) at the portion formed on the temporarily-provided film (or the first film) by optional methods such as washing with water, an alcohol, a ketone or a mixed solvent of these or rubbing with a cloth or a leather. The material of the film (or the second film) removed can be recovered and utilized again.

The above explanation relates to the case where two-colored surface using the first film and the second film each of which is a single film or layer is formed on the base material. By multi-coloring the first film with optional and conventionally known method or by effecting the laser beam irradiation and formation of the second film with plural times and changing the material to be used for formation of the second film to those different in color and/or tone, a product having multi-colored surface with three or more colors can be formed.

(e) Removal of the temporarily-provided film

When the temporarily-provided film is formed as shown in Fig. 10, then the metal or alloy used as the temporarily-provided film is removed. Removal thereof can be carried out by selecting the conditions which do not impair the film of the present invention depending on the material of the temporarily-provided film such as an acid treatment.

In the second embodiment of the process for producing the product according to the present invention, the step (a) can be processed while it may vary depending on the material of the base material and that of the first film. It is preferred to use the ion plating, sputtering or plasma CVD method since these methods can be carried out at a relatively low temperature so that there is a little effect to the base material, adhesion between the base material and the first film is excellent, attachment of the first film is good and a minute amount of film thickness can be easily controlled. Also, the laser used in the step (b) may be used as those mentioned above, and of these, the solid laser is preferred since melting and removal at fine portion of the surface of the base material are easy, and YAG is particularly preferred since adjustment of a pulse width and control of low energy irradiation are easy. Further, formation of the second film in the step (c) can be carried out by electrolytic plating or non-electrolytic plating, but electrolytic plating is preferred in order to adhere densely with good adhesiveness to the concave-shaped surface or concave-shaped line of the base material in which fine portion is melted and removed. As the post-treatment as the step (c), washing and drying are carried out, and at the washing procedure, almost all the second film attached on the surface of the first film are removed and recovered. When the second film is remained on the surface of the first film, the first film can be removed by rubbing the film with a cloth, leather or paper.

The above steps (a), (b) and (c) can be carried out by effecting each step of (a), (b) and (c) with one time. However, when the first film or the second film is made plural layered film, particularly when the first film is made plural layered film to produce a product having at least one surface with colors and/or tones of three or more, it is preferred to carry out the whole steps (a), (b) and (c) or a part thereof repeatedly. Also, when the color of the base material is used for multi-coloring by locally exposing it, or not laminating on part of the film, it is preferred, if necessary, to partially use masking which has conventionally carried out.

According to the present invention, multi-colored surface containing fine design, pattern, letter, mark and/or symbol can be formed by the first film and the second film or the base material and the film. After previously forming the first film, by irradiating the laser beam, a portion of the first film, at which the second film is to be formed, is destroyed and adhesiveness of the second film then formed to the base material can be enhanced. Also, according to irradiation of the laser beam, a portion of the temporarily-provided film at

which the film is to be formed is destroyed as well as the base material at the said portion is fused and removed to an optional depth whereby adhesiveness of the formed film to the base material can be enhanced.

More specifically, in the multi-colored product of the present invention (second embodiment), by forming the second film in the concave-shaped surface or concave-shaped line provided locally on the surface of the base material, adhesiveness between the base material and the second film is enhanced. Also, in the case where Au or platinum group metal is used as the second film, peel off between the first film and the second film easily occurs and adhesiveness of the second film to the concave-shaped surface or concave-shaped line of the surface of the base material is good. Thus, on the surface of the product, beautiful and fine design, pattern, letter, mark and/or symbol are formed.

Further, the process for producing the multi-colored product of the present invention is easy in post-treatment particularly when Au or platinum group metal is used as the second film since the second film is scarcely laminated on the surface of the first film at the step (c).

According to the present invention, a multi-colored surface which is rich in ornamental property and fastness, and a product having such a surface can be easily formed. The multi-colored surface obtained according to the present invention retains inherent color tone possessed by the material itself and is capable of expressing fine design, pattern, letter, mark and/or symbol.

Thus, the present invention is extremely useful for formation of multi-colored pattern or display of letters of ornament parts such as watch cases, watch bands or belts, dials, brooches, cuff buttons, tiepins, lighters and glasses, sports goods such as golf clubs; improvement in aesthetic effect of tools such as cutting tools and wear-resistant tools; and display of product name, trade mark, company seal and quality of the product in various products or their carved seals.

EXAMPLES

In the following, the present invention will be explained by referring to Examples and Comparative examples. Reference numerals mentioned in Examples are numerals of each portion used in Fig.s 8 and 10 for explaining the processes of the present invention. The present invention is not limited by these Examples.

Example 1

SUS 304 base material which is mirror-surfaced by polishing and lapping was processed by the hollow cathode discharging (HCD) method which has conventionally been carried out to form a film of Ti on the surface of the base material as the first film. Then, a laser beam was irradiated from the film surface of Ti by using YAG laser processor LAY-603 special type (trade name, manufactured by K.K. Toshiba) to form designed lines with a width of 0.5 μm to 1 mm. This laser irradiation was carried out with a power density of 200 kw/cm^2 and a puls width of 0.7 ms, and it was confirmed that the surface of the base material had been fused and/or removed. Next, the base material on which designed lines had been processed was washed with water and an organic solvent, and then gold plating treatment which has been conventionally carried out was carried out by using potassium aurous cyanide. After this gold plating treatment, washing and drying were carried out to obtain the present product 1. When the sectional view of the present product 1 was observed by the metal microscope, a gold film as the second film with a film thickness of 3 μm was formed in the concave-shaped surface and concave-shaped line with a width of 0.5 μm to 1 mm and a depth from the surface of the base material to the inside of the same of 10 μm at the surface of the base material, and at the other surface of the base material, the film of Ti was formed with a thickness of 0.3 μm. Thus, the film surface showed two-colored beautiful color since gold colored-designed line due to the film of gold was clearly embossed in the metallic luster of the Ti film.

Comparative example 1

As a comparison, the surface of the base material which is the same one as mentioned above was locally masked and a mixed film of Al_2O_3-TiO_2 was formed by metal spraying method. Then, after removing the masking on the surface of the base material, the same gold plating treatment as mentioned above was applied to, and the coated film surface was subjected to lapping treatment to obtain comparative product 1. The comparative product 1 comprises an Al_2O_3-TiO_2 film thickness of about 500 μm and a gold film thickness of 3 μm, and fine cracks were present at the Al_2O_3-TiO_2 film surface whereby gloss of the surface was poor and its aesthetic value was low.

When the adhesive strengths of the base material and the gold film of the present product 1 and the comparative product 1 thus obtained were examined by adhering a cellophane tape on the surface of the gold film and then tearing the tape off, almost all the gold film of the comparative product 1 peel off by one cellophane tape adhesion. To the contrary, the gold film of the present product 1 did not peel off even when cellophane tape adhesion and tearing off were repeated five times.

Example 2

In the same manner as in the present product 1 of Example 1, surface treatments were applied to on the surface of SUS 304 base material by ion plating or sputtering, laser beam irradiation and electrolytic plating whereby the present products 2 to 5 in which the surface position of the first film and the surface portion of the second film were formed were produced. The thus obtained present products 2 to 5 were examined as in Example 1 to obtain the results shown in Table 1. Also, when peel off resistant test of the second film by the cellophane tape adhesion was carried out with respect to the present products 2 to 5, all the present products 2 to 5 endured five times of repeated tests. Further, the concave-shaped surface and concave-shaped line of the surface of the base material were measured as a depth from the sectional surface of the base material and the results (depths) are also shown in Table 1. The present product 5 was produced by masking the peripheral portions of the surface to be treated before the treatment and formed a design from the metallic color of the base material and a color of the film.

Table 1

	Second film			First film		Color of the treated surface
	Material	Film thickness	Depth from the surface of the base material	Material	Film thickness	
Present product 2	Au	3 μm	15 μm	Zr	0.3 μm	Two colors of metallic color of Zr and gold color
Present product 3	Pt	0.5 μm	5 μm	TiN	2 μm	Two colors of yellowish brown color of TiN and Pt
Present product 4	Ag	1 μm	5 μm	Ti(C, O)	3 μm	Two colors of black color of Ti(C, O) and Ag
Present product 5	Au	5 μm	10 μm	Ti(C, O)	5 μm	Three colors of black, gold and color of base material

Example 3

By using WC-18 % by weight Ni-1 % by weight Cr hard alloy as a base material, and after subjecting the base material to mirror-surface lapping, a half of the mirror surface was masked and a film of Ti(C, O)

was formed by the ion plating. Then, the first masking was removed and the film surface of Ti(C, O) was masked, a film of Ti was formed by the ion plating. Thereafter, the masking was removed, and designed line with a width of 20 μm to 1 mm was formed by a laser on the film surface of Ti(C, O) and the film surface of Ti. Next, in the same manner as in Example 1, gold plating treatment, washing and drying were carried out to emboss the designed line with gold color in the metallic luster surface of Ti and black colored surface of Ti(C, O) to obtain the present product 6.

When the thus prepared present product 6 was examined in the same manner as in Example 1, the gold film with a thickness of 3 μm, Ti film with a thickness of 1 μm and Ti(C, O) film with a thickness of 2 μm were formed, and the surface of the base material at the portion under the gold film was concave-shaped toward inside of the base material with a depth of 5 to 30 μm. When the adhesion strength of the gold film of the present product 6 was examined by the peel off resistant test using a cellophane tape, no peel off occurred even after five times of repetition.

Example 4

A film of TiC was formed on the surface of a base material with slow away chip TNMN 220408 shape for cutting tool with a material corresponding to P20 of JIS standard by CVD treatment which has been conventionally carried out, and then letters of "TUNGALOY" in Japanese character as shown in Fig. 7 were formed by a line with a width of 0.5 μm to 0.1 mm by irradiating a laser beam on the surface of TiC film, wherein 1 is the base material, 3 is the first film and 4 is the second film. Then, Cu-Zn film treatment according to electrolytic plating, washing and drying were carried out to obtain the present product 7. In this present product 7, letters of "TUNGALOY" in Japanese character comprising Cu-Zn having a brass color were clearly carved in gray-blackish color TiC film and it was beautiful. Also, when the sectional surface of the present product 7 was examined in the same manner as in Example 1, the base material in which Cu-Zn film was formed became concave-shaped with a depth of 10 μm from the surface of the base material in which TiC film was formed, and comprised Cu-Zn film with a thickness of 5 μm and TiC film with a thickness of 2 μm. Further, when the adhesion strength of the Cu-Zn film of the present product 7 was examined by the peel off resistant test using a cellophane tape, no peel off occurred even after five times of repetition.

Example 5

Titanium film 3 was formed on the surface 2 in which multi-colored surface is to be formed of the plate-shaped base material 1 comprising SUS 304 the surface of which had been mirror surfaced according to polishing and lapping of the surface, by subjecting to the ion plating according to the conventional hollow cathode discharging (HCD method) method. Then, on said film, YAG laser was irradiated and scanned with 30 W and 12 A whereby the laser beam was irradiated to striped shape with a line width of 1 mm to melt and remove the film at the said portion.

The surface in which the film 3 was remained on the surface 2 with pattern state thus obtained was washed with water and acetone, and subjected to gold plating by the conventional method using potassium aurous cyanide to obtain a film 4 of gold. This film 4 was joined to the base material 1 at the portion in which the laser beam irradiation had been previously carried out and thinly joined to 3 at the portion other than the above. By washing with water, the portion of the film 4 joined to the film 3 peel off and removed from the film 3, followed by washing and drying to obtain the present product 8 having two colored surface of silver white and gold colors.

When the two colored surface thus obtained was observed by a metal microscope, a thickness of the film 3 was 0.3 μm and a thickness of the film 4 was 2 μm.

Comparative example 2

On one surface of the base material which is the same with that used in Example 5 was locally masked and a mixed film 3 of Al_2O_3-TiO_2 was formed by metal spraying method. Then, after partially removing the masking on the surface of the base material, the same gold plating treatment 4 as mentioned in Example 5 was applied to, and the coated film surface was polished to obtain comparative product 2 having two-colored surface.

When the surface of the comparative product 2 was examined by the metal microscope, a thickness of the film 3 was about 500 μm and a thickness the film 4 was 2 μm.

When appearance and peel off test of the film were carried out with regard to both products obtained in

Example 5 and Comparative example 2. The results are shown in Table 2. As can be seen from Table 2, it can be understood that the product of Example 5 is superior to that of Comparative example 2 in appearance and adhesiveness of the film.

Table 2

	Appearance	Peel off test*
Example 5	Titanium film surface showed metallic luster due to lapping surface of the substrate and showed beautiful color coupled with designed line with gold color.	No peel off after five times repetition
Comparative example 2	Fine cracks occurred at the Al_2O_3-TiO_2 film portion and gloss of the surface was poor and aesthetic value was low.	Gold film peel off at the first test

(Note) * A cellophane tape was adhered on the surface of the multi-colored surface and was strongly teared off, and the procedure was repeated five times to observe whether the gold film peel off or not.

Examples 6 to 9

In the same manner as in Example 5 except for changing the material of the film, two-colored surfaces having film materials and thicknesses as shown in Table 3 were formed on the surface of the base material comprising SUS 304 by subjecting to formation of the film 3 according to the ion plating, laser beam irradiation and formation of the film 4 according to plating. The colors thereof are shown in Table 3, each of which showed beautiful appearance and excellent in adhesiveness of the film 3 to the base material.

Table 3

	First film		Second film		Appearance
	Material	Thickness (μm)	Material	Thickness (μm)	
Example 6	TiN	0.5	Pt	0.5	Gold/Silver white
Example 7	TiC	0.3	Ag	1	Black/Silver white
Example 8	TiC	0.3	Au	1	Black/Gold
Example 9	Zr	0.3	Au	3	Metallic luster/Gold

Example 10

A disc of hard alloy comprising 80 % by weight of WC, 18 % by weight of Ni and 2 % by weight of Cr was used as the base material. After this base material was subjected to mirror surface lapping, part thereof

was masked and a film 3 of Ti(C, O) was formed by the ion plating. Then, after masking the Ti(C, O) film surface reversely, a film 3' of titanium was formed by the ion plating. To the disc plate surface having different color was drawn parallel line-shaped pattern with a width of 1 mm by a laser beam irradiation. To the material was subjected to gold plating in the same manner as in Example 5, followed by peel off and removal, washing and drying to obtain a film 4.

Thus, a product having three-colored surface with high aesthetic value wherein metallic luster of titanium and gold color due to gold are drawn on the black color ground of Ti(C, O) can be obtained.

Example 11

To a base material of slow away chip SNGN 120412 shape for cutting tool which is P30 with JIS standard was formed a film B of TiC by the chemical deposition method. To this material was printed by a laser beam irradiation letters of "TUNGALOY" in Japanese character as shown in Fig. 9 followed by Cu-Zn plating. Then, peel off and removal, washing and drying were carried out to obtain the tool to which letters were carved.

This tool is as shown in Fig. 9, letters of "TUNGALOY" in Japanese character comprising Cu-Zn having a brass color were clearly embossed in black colored TiC film and it has high aesthetic effects.

Example 12

Titanium film 3 with a thickness of 0.3 μm was formed as a temporarily-provided film on the surface 2 in which multi-colored surface is to be formed of the plate-shaped base material 1 comprising SUS 304 the surface of which had been mirror surfaced according to polishing and lapping of the surface, by subjecting to the ion plating according to the conventional hollow cathode discharging (HCD method) method. Then, on said film, YAG laser was irradiated and scanned with a pulse width of 2.0 ms and a power density of 400 kW/cm^2 whereby the laser beam was irradiated to striped shape with a line width of 1 mm to melt and remove the film at the said portion and part of the base material at the said portion whereby a heat-fused surface with a depth of 30 μm was formed.

The surface in which the temporarily-provided film 3 was remained on the surface 2 with pattern state thus obtained was washed with water and acetone, and subjected to gold plating by the conventional method using potassium aurous cyanide to obtain a film 4 of gold with a thickness of 2 μm. This film 4 was joined to the base material 1 at the portion in which the laser beam irradiation had been previously carried out and thinly joined to 3 at the portion other than the above. By washing with water, the portion of the film 4 joined to the film 3 peel off and removed from the film 3, followed by washing and drying. Then, the film 4 remained partially on the film 3 was wiped off and removed with a cloth.

Next, the titanium film was removed by dipping the material in a hydrofluoric acid solution whereby the gold film was remained. Then, the material was washed with water and alcohol to obtain the product of the present invention.

According to the above steps, the product of the present invention having two-colored surface of metallic luster and gold color was obtained.

When the two-colored surface thus obtained was observed by a metal microscope, a thickness of the film was 15 μm. Also, on the surface of the product was adhered a cellophane tape and the tape strongly teared off to observe the film peel off or not. This procedure was repeated five times but no peel off was observed.

Example 13

By using the same base material as in Example 12, Ni plating with a thickness of 2 μm was carried out on the surface of the base material according to the conventionally known electrolytic plating method, and then Cr plating was subjected on the surface of the Ni film so as to become the film thickness of 2 μm. Then, from the surface side of the film, a laser with a pulse width of 1.7 ms and a power density of 600 kW/cm^2 was irradiated and scanned to form groove with a depth of 20 μm whereby the film at the said portion and the base material of the same were fused and removed to form a heat-fused surface on the surface of the base material. Next, in the same manner as in Example 1, a gold plating layer with a thickness of 1 μm was formed, and then washing, drying and wiping with a cloth were carried out.

Thereafter, Cr and Ni films were removed by hydrochloric acid and a commercially available releasant for Ni film whereby the product of the present invention in which the gold film was formed on the surface of the base material was obtained.

Comparative example 3

As a comparison, by using the same base material as in Examples 12 and 13, gold plating was carried out on the surface of the base material so as to become the film thickness of 2 μm to obtain the product for comparison.

With regard to the products obtained in Examples 12 and 13 and Comparative example 3, adhesive strengths between the gold film and the base material were each examined by scratching the surface with a wire brush. As the results, in the product of Comparative example 3, the gold film peel off at the first trial. However, in the products of Examples 2 and 3 of the present invention, the gold films did not peel off even after three times of trial and the states were that scratched lines were merely added.

Claims

1. A multi-colored product which comprises a base material and a film formed at a specific portion of one surface of the base material,

   and said film being a single layer film or plural layered films consisting essentially of at least one of copper (Cu), silver (Ag), gold (Au), platinum (Pt), iridium (Ir), osmium (Os), palladium (Pd), rhodium (Rh), ruthenium (Ru) and an alloy containing the above metal(s) and being formed on a heat-fused surface with concave-shaped surface or line provided on the surface of said base material.

2. The product according to Claim 1, wherein said heat-fused surface is formed at a depth of 0.5 μm from the surface of said base material.

3. A multi-colored product which comprises a base material at least one surface of which being a multi-colored surface constituted by (i) a first film surface and a second film surface which is different in color and/or tone from the first film surface, or (ii) the first film surface, the second film surface and a surface of the base material,

   and said second film being a single layer film or plural layered films consisting essentially of at least one of copper (Cu), silver (Ag), gold (Au), platinum (Pt), iridium (Ir), osmium (Os), palladium (Pd), rhodium (Rh), ruthenium (Ru) and an alloy containing the above metal(s) and being formed on a heat-fused surface with a concave-shaped surface or concave-shaped line provided on the surface of said base material.

4. The product according to Claim 3, wherein said second film has a film thickness of 0.05 to 20 μm.

5. The product according to Claim 3, wherein said first film is a single layer film or plural layered films consisting essentially of at least one of a metal; an alloy; a carbide, nitride, carboxide or oxynitride of a metal of group 4a (titanium (Ti), zirconium (Zr) and hafnium (Hf)), 5a (vanadium (V), niobium (Nb) and tantalum (Ta)) or 6a (chromium (Cr), molybdenum (Mo) and tungsten (W)) of the periodic table; an oxide, carbide or nitride of aluminum (Al) or silicon (Si); mutual solid solution of the above; and hard carbon

6. The product according to Claim 4, wherein said concave-shaped surface or concave-shaped line is a width of at least 0.1 μm and a depth of at least 0.5 μm.

7. A multi-colored product which comprises a base material at least one surface of which being a multi-colored surface constituted by (i) a first film surface and a second film surface which is different in color and/or tone from the first film surface, or (ii) the first film surface, the second film surface and a surface of the base material,

   said first film being a single layer film or plural layered films consisting essentially of at least one of a metal; an alloy; a carbide, nitride, carboxide or oxynitride of a metal of group 4a (titanium (Ti), zirconium (Zr) and hafnium (Hf)), 5a (vanadium (V), niobium (Nb) and tantalum (Ta)) or 6a (chromium (Cr), molybdenum (Mo) and tungsten (W)) of the periodic table; an oxide, carbide or nitride of aluminum (Al) or silicon (Si); mutual solid solution of the above; and hard carbon, and

   said second film being a single layer film or plural layered films consisting essentially of at least one of copper (Cu), silver (Ag), gold (Au), platinum (Pt), iridium (Ir), osmium (Os), palladium (Pd), rhodium (Rh), ruthenium (Ru) and an alloy containing the above metal(s).

8. The product according to Claim 7, wherein said heat-fused surface is formed at a depth of 0.5 μm from the surface of said base material.

9. A process for producing a multi-colored product which comprises the steps of
(a) providing on the surface of a base material a temporarily-provided film composed of a substance having low affinity to a film to be provided at the later stage;
(b) irradiating on the surface of said temporarily-provided film by a laser beam to melt and remove said temporarily-provided film and the surface of the base material of said portion whereby forming heat-fused surface with a concave-shaped surface or line on the surface of the base material;
(c) forming the film consisting essentially of at least one of copper (Cu), silver (Ag), gold (Au), platinum (Pt), iridium (Ir), osmium (Os), palladium (Pd), rhodium (Rh), ruthenium (Ru) and an alloy containing the above metal(s);
(d) removing the film formed in the above step (c) remained on said temporarily-provided film; and
(e) removing said temporarily-provided film.

10. A process for producing a multi-colored product which comprises the steps of:
(a) forming a first film on one surface or part of a base material by the dry plating method or wet plating method;
(b) irradiating a laser beam on the surface of the first film to locally remove said first film and finely remove the surface of the base material of the portion corresponding to the first film whereby to form a concave-shaped surface or line on the base material;
(c) forming a second film consisting essentially of at least one of copper (Cu), silver (Ag), gold (Au), platinum (Pt), iridium (Ir), osmium (Os), palladium (Pd), rhodium (Rh), ruthenium (Ru) and an alloy containing the above metal(s) with a single layer or plural layers; and
(d) processing the product to remain said second film only on the concave-shaped surface or line formed in the step (b) whereby to form a surface portion of the first film which is different in color and/or tone from those of the second film formed in the step (c) and a surface portion of the second film.

11. A process for producing a multi-colored product which comprises the steps of:
(a) forming a first film consisting essentially of at least one of a metal; an alloy; a carbide, nitride, carboxide or oxynitride of a metal of group 4a (titanium (Ti), zirconium (Zr) and hafnium (Hf)), 5a (vanadium (V), niobium (Nb) and tantalum (Ta)) or 6a (chromium (Cr), molybdenum (Mo) and tungsten (W)) of the periodic table; an oxide, carbide or nitride of aluminum (Al) or silicon (Si); mutual solid solution of the above materials; and hard carbon, with a single layer or plural layers;
(b) irradiating a laser beam on the surface of the first film to partially remove said first film;
(c) forming a second film consisting essentially of at least one of copper (Cu), silver (Ag), gold (Au), platinum (Pt), iridium (Ir), osmium (Os), palladium (Pd), rhodium (Rh), ruthenium (Ru) and an alloy containing the above metal(s) with a single layer or plural layers by the wet plating method; and
(d) removing the second film formed other than the portion at which the first film is removed in the step (b).

FIG. 1

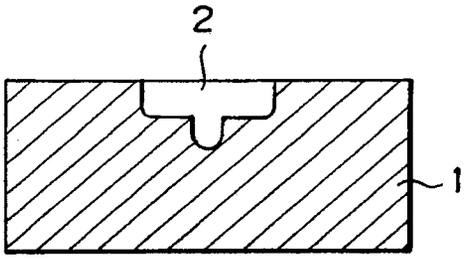


FIG. 2

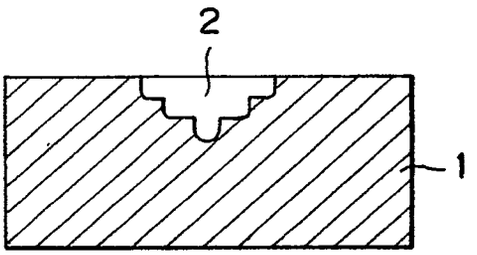


FIG. 3

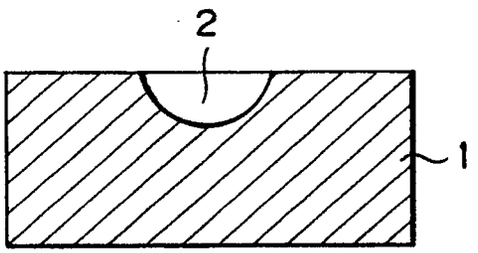


FIG. 4

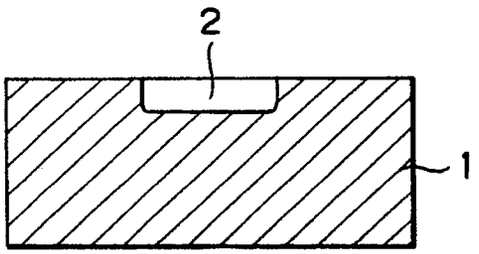


FIG.5

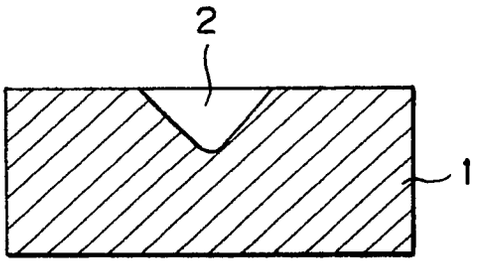


FIG.6

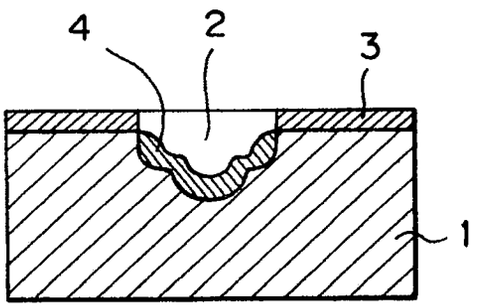


FIG.7

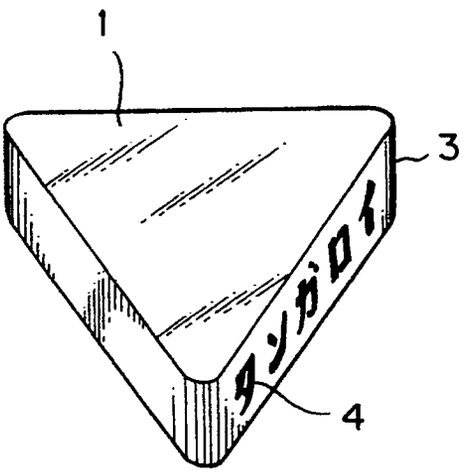


FIG. 8

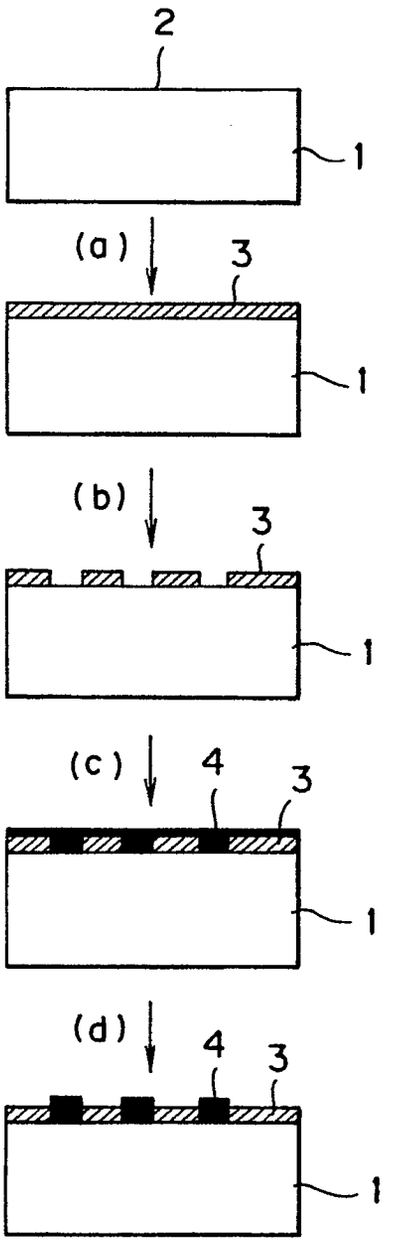


FIG.9

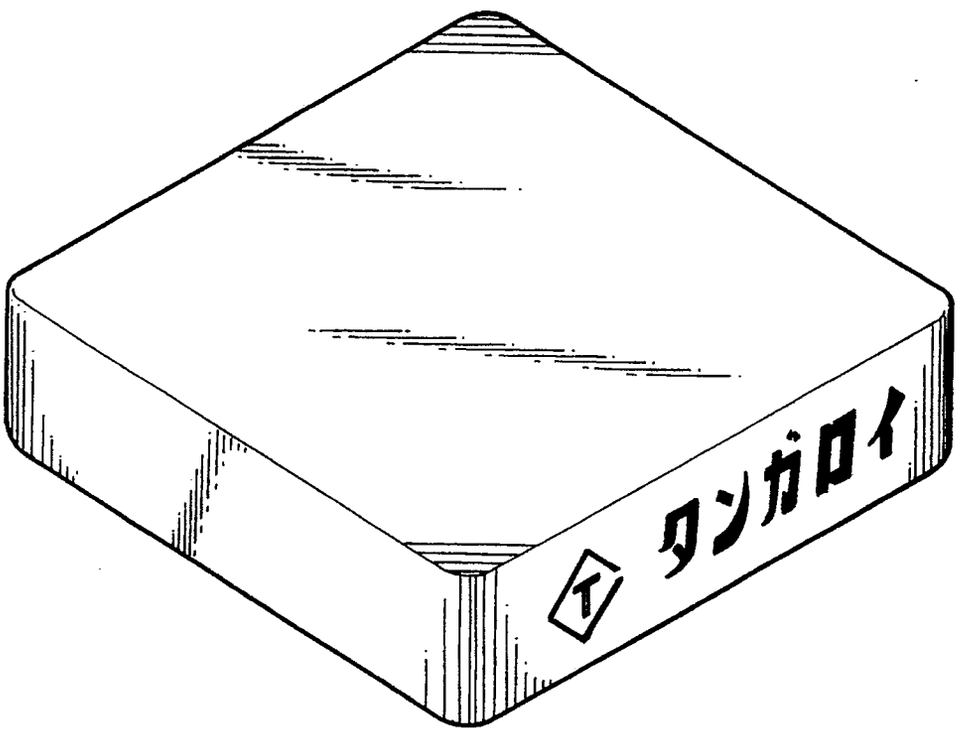
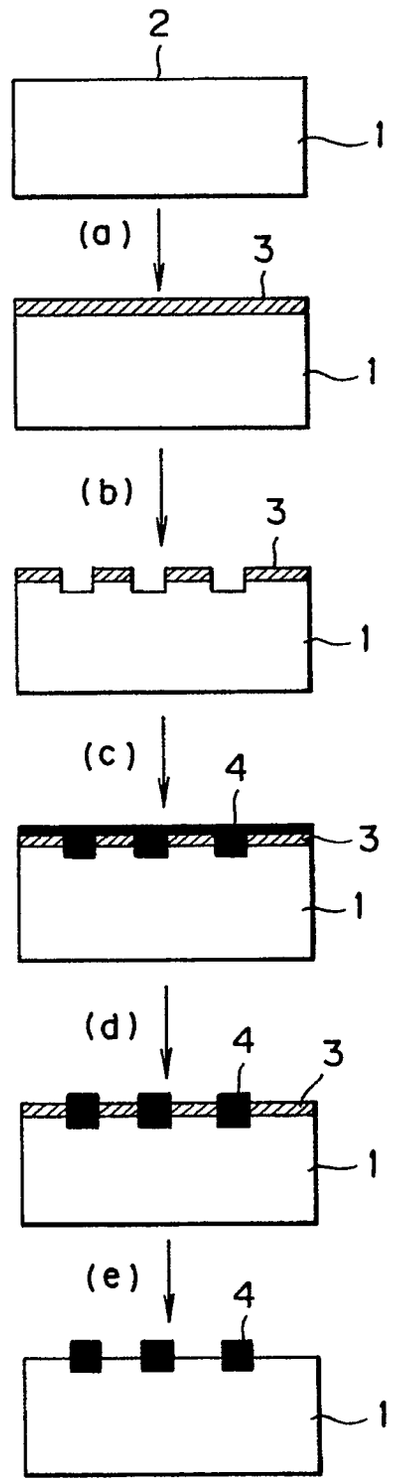


FIG. 10



European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 10 8822

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	EP-A-0 260 514 (GENERAL ELECTRIC CO.) * Column 2, lines 30-53; column 3, line 33 - column 5, line 5 * – – –	1	C 23 C 18/16 C 25 D 5/02
Y	WORLD PATENTS INDEX (LATEST), week 49, accession no. 87-345698, Derwent Publications Ltd, London, GB; & JP-A-62 250 161 (MITSUBISHI DENKI K.K.) 31-10-1987 * The whole document * – – –	1	
P,X	GB-A-2 227 756 (CITIZEN WATCH CO.) * Page 3, line 8 - page 8, line 18 *	7	
P,A		1,3,5	
	– – –		
D,A	WORLD PATENTS INDEX (LATEST), week 46, accession no. 89-334975, Derwent Publications Ltd, London, GB; & JP-A-1 075 659 (KOWA ENGINEERING K.K.) 22-03-1989 * The whole document * – – –	1,3,5,7, 9-11	
A	US-A-4 645 734 (M. TAKADA et al.) * Column 2, line 3 - column 5, line 5 * – – –	1	
A	APPLIED PHYSICS LETTERS, vol. 35, no. 9, 1st November 1979, pages 651-653; R.J. VON GUTFELD et al.: "Laser enhanced electroplating and maskless pattern generation" * The whole document * – – – – –	1	TECHNICAL FIELDS SEARCHED (Int. Cl.5) C 23 C C 25 D B 44 C

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	29 August 91	DOOLAN G.J.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same catagory
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention

E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons

&: member of the same patent family, corresponding document