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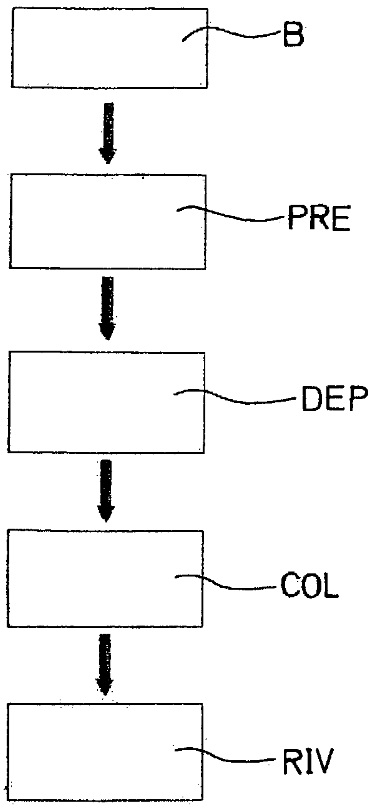
(54) Title: METHOD FOR THE PROTECTION/SELECTIVE COLOURING OF AN ENDPRODUCT



(57) Abstract: A method for the protection and selective colouring of an end-product comprises the following phases: preparing an end-product; pretreating the end-product to prepare its surface for a coating treatment; coating the end-product with one or more thin layers; colouring the most external layer of the coating by the formation of an outer surface protective oxide.

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METHOD FOR THE PROTECTION/SELECTIVE COLOURING OF AN END-PRODUCT

The present invention relates to a method for the protection/selective colouring of an end-product.

In particular, the invention relates to a method for the protection/selective colouring of an end-product made of steel and stainless steel, cast iron, copper and copper alloys, nickel and nickel alloys, magnesium and/or magnesium alloys, aluminum and/or aluminum alloys, cobalt and cobalt alloys, zinc and zinc alloys, composite materials with a metallic matrix, polymers and composite materials with a polymeric matrix, glass, ceramic, wood, leather, cellulose yarns, fabrics and materials.

In the last few years, the production of end-products having particular characteristics relating to mechanical or structural resistance combined with physico-chemical resistance against aggressive substances and the environment and sometimes combined with exterior characteristics, has been specifically oriented towards complex techniques for covering the materials forming the end-product.

Whatever its nature, the coating is directed at providing a barrier against external attack. It must therefore be uniform, well-adhering and free of porosity. One of the problems associated with these materials or fields of application is, in fact, linked to the poor resistance of the material to the environment in which the end-product is used.

The purpose of the coating is to overcome these drawbacks by protecting the end-product.

Following the coating treatment, it is frequently necessary to provide for the colouring of the end-product thus obtained.

A general objective of the present invention is consequently to provide a method for the protection/selective colouring of an end-product.

A particular objective of the present invention is to provide a method for the protection/selective colouring of an end-product made of one or more of the following materials: steel, stainless steel, cast iron, copper, copper alloys, nickel, nickel alloys, magnesium and/or magnesium alloys, aluminum and/or aluminum alloys, cobalt, cobalt alloys, zinc, zinc alloys, composite materials with a metallic matrix, polymers and composite materials with a polymeric matrix, glass, ceramic, wood, leather, cellulose yarns, fabrics and materials.

Another objective of the present invention is to provide an end-product made of one or more of the following materials: steel, stainless steel, cast iron, copper, copper alloys, nickel, nickel alloys, magnesium and/or magnesium alloys, aluminum and/or aluminum alloys, cobalt, cobalt alloys, zinc, zinc alloys, composite materials with a metallic matrix, polymers and composite materials with a polymeric matrix, glass, ceramic, wood, leather, cellulose yarns, fabrics and materials, coated with thin uniform layers, well-adhering, free of porosity and such as to be able to be coloured without being damaged.

These and other objectives of the present invention are achieved by a method for the protection/selective colouring of an end-product according to claim 1.

Further characteristics of the invention are object of the dependent claims.

The method for the protection/selective colouring of an end-product, according to the present invention comprises the following phases: preparing an end-product; pretreating the end-product to prepare its surface for a coating treatment; coating the end-product with one or more thin layers; colouring the most external layer of the coating by the formation of an outer surface protective oxide; possibly protecting the coloured layer by the application of a transparent layer.

The characteristics and advantages of a method for the protection/selective colouring of an end-product according to the present invention will appear more evident from the following illustrative and non-limiting description, referring to the enclosed schematic drawings in which:

figure 1 schematically represents the phases of the method according to the invention;

figure 2 schematically represents a structure of the coating of the end-product according to the present invention;

figures 3a, 3b schematically represent the structure of the coating of the end-product according to the present invention, made of a light alloy (Mg or Al);

figure 4 schematically represents the phases of the coating method of an end-product according to the invention made of a light alloy;

figure 5 schematically represents the pretreatment phases of the end-product made of a magnesium alloy or aluminum alloy;

figures 6a and 6b schematically represent an apparatus for the deposition and a colouring apparatus destined for a tape or yarn;

figure 7 schematically represents the phases of a physical vapour deposition (PVD) process of coating layers according to the invention;

figure 8 illustrates the light interference phenomenon;

figure 9 illustrates table 1 providing a thermal colour scale example (titanium);

figure 10 schematically illustrates an anodic colouring electrochemical cell;

figure 11 illustrates table 2 providing an example of an electrochemical colour scale (titanium, niobium, tantalum).

With reference to the figures, these describe a method for the protection/selective colouring of an end-product comprising the following phases:

- preparing an end-product or base B, or LL;
- pretreating PRE said end-product B or LL for preparing its surface for a coating treatment;
- optionally applying a barrier layer SB which also acts as an adhesion layer for the metallic layer;
- coating said end-product with one or more thin layers DEP;
- colouring said thin layer by the formation of an outer surface protective oxide;

- possibly protecting the coloured layer with a transparent protective layer (RIV).

In particular, the method is applied to an end-product made of one or more of the following materials: steel, stainless steel, cast iron, copper, copper alloys, nickel, nickel alloys, magnesium and/or magnesium alloys, aluminum and/or aluminum alloys, cobalt, cobalt alloys, zinc, zinc alloys, composite materials with a metallic matrix, polymers and composite materials with a polymeric matrix, glass, ceramic, wood, leather, cellulose yarns, fabrics and materials.

With particular reference to figure 1, the method according to the invention can, in the case of the production of end-products with particular demands for resistance to corrosion, wear or the like, envisage a phase for the coating with a transparent protective layer RIV of said thin coloured layer COL following the formation of the outer surface protective oxide.

The surface of the material of which the end-product B is made, is pretreated to allow a better reception of the metallic coating.

The pretreatment can consist of various phases, depending on the type of material used as substrate.

The structure of the coating which is formed is in the most general case of the type shown in figure 2.

Starting from the surface of the end-product B, this structure has a barrier layer SB overlaid by the deposition layer DEP which is subdivided into a metallization layer ME and a coloured oxide layer COL on the surface of the former.

In the case of specific resistance demands there is also a final protection layer RIV.

The deposition DEP or metallization is effected under vacuum with the PVD, physical vapour deposition, technique. The colouring of the metallic layer ME deposited with the PVD technique is effected by oxidation in atmospheres containing oxygen (for example by heating in air) or by the direction deposition of titanium oxide (reactive PVD), or, electrolytically (anodic oxidation) to obtain the oxidized layer COL.

The vacuum metallization phase is preceded by a preparation phase of the surface of the end-product B or deposition substrate. The preparation of the surface B of the deposition substrate can comprise, in relation to the material to be treated, a chemical cleaning phase (with an organic or aqueous solvent) and/or mechanical phase (sandblasting, grinding) and a cleaning and activation phase under vacuum by bombarding the surface with ions of inert gas or with oxygen plasma.

The deposition of a basic organic film SB (which is advantageously applied typically in the metallization of plastics) can also be conveniently applied in the case of other materials, for example metals. In this case, the organic layer SB offers further protection against corrosion to the metallic substrate of the end-product B during the electrochemical colouring phase of the metallization layer deposited with the PVD technique (titanium and the like) and during the life of the end-product.

As far as the transparent protective layer RIV is concerned, it should be noted that, every possible outer protection layer, deposited on the titanium oxide or the like, should be effected so that it is transparent - so as not to hide the colouring - and this can be achieved by the application of a filmogenic organic material or a layer of quartz (SiOx) deposited by means of PECVD (Plasma Enhanced Chemical Vapour Deposition).

With particular reference to figures 3a, 3b, 4 and 5, in the particular case of magnesium, aluminum and/or magnesium or aluminum alloys, the method for the protection/selective colouring of light alloys (magnesium and aluminum), comprising the following phases: preparing an end-product made of a light alloy; pretreating said end-product to prepare its surface for a coating treatment; coating said end-product with one or more protective layers; colouring the most external layer of said coating by the formation of an outer surface protective oxide.

The method is based on the use of light alloy coating technologies (magnesium or aluminum) based on the physical vapour deposition of titanium and the like (Ti, Ta, Nb, Zr, Hf, W, V, Mo) and the subsequent colouring of the metal (Ti, Ta, Nb, Zr, Hf, W, V, Mo) by electrochemical oxidation.

A variation of the technique consists in the physical vapour deposition of a layer of titanium or the like (Ti, Ta, Nb, Zr, Hf, W, V, Mo) and the subsequent reactive physical deposition of a layer of TiO_2 (or similar oxide for the metals Ta, Nb, Zr, Hf, W, V, Mo).

The most commonly used magnesium alloys are listed in Table A below, together with the nominal composition.

Table A. Nominal composition (wt %) of magnesium alloys

Alloy	Al	Mn	Zn	Rare earth	Zr	Y
AM60	6	0.15				
AZ 31	3	0.2	1			
AZ 61	6.5	0.15	1			
AZ 91	9	0.13	0.68			
WE 54				3.5	0.5	5.25
ZE 63			5.8	2.6	0.7	
ZK 21			6		0.8	
ZM 21		1.2	2.2			

The series of the aluminum alloys most commonly used is listed in Table B.

Table B. Commonly used aluminum alloys.

Series	Main alloy element. Notes
1000	These alloys have an aluminum percentage of at least 99.0% The other elements present as impurities, are iron, silicon and copper. They are used for the production of sheets, kitchenware and food containers.
2000	The main alloy element of this group is copper, but magnesium is also added to most of them. They have excellent mechanical properties and offer good creep resistance. They are used for aeronautical structural applications.
3000	Manganese is the main alloy element: this increases resistance to Al through the hardening mechanism by alligation.
4000	The main alloy element of these alloys is silicon.
5000	The main alloy element of these alloys is magnesium, added to obtain hardening by a solid solution. They are used for producing sheets (for buses and lorries), for marine applications (parts of ships), thanks to their excellent resistance to corrosion and for oil and aqueduct pipelines.
6000	The main alloy elements of this group are magnesium and silicon which are combined to form an intermetallic compound, Mg_2Si, which gives good mechanical properties, for structural uses. These alloys also have a good weldability and good resistance to oxidation.
7000	The main alloy element of this group is zinc, to which magnesium and copper are very often added. Zinc and magnesium are combined to form the intermetallic compound $MgZn_2$, which, together with other precipitates formed due to the relatively high solubility of Zn and Mg in Al, give these alloys resistance values which are among the highest. Thanks to these properties and to the easy weldability, they are used for structural purposes.
8000	This group does not have a main alloy element but comprises various types of alloys: Al-Li, Al-Ni-Fe, Al-Sn alloys, etc.
9000	Particular alloys

In order to be coated by a thin layer R (in the order of micrometers) of titanium or the like (Ti, Ta, Nb, Zr, Hf, W, V, Mo), the surface of the base metal indicated with *LL* in figures 3a, 3b, 4, (light magnesium or aluminum alloy) must be adequately prepared.

The pretreatment *PR* of the surface does in fact play an important part for allowing the development of a protective coating *R* on magnesium and its alloys, or on aluminum and alloys.

The most common pretreatment operations *PR* are mechanical finishing, chemical cleaning and the deposition of a galvanic coating (typically zinc, copper and nickel). The mechanical finishing and chemical cleaning are indispensable for bringing the surface of the product to the optimal degree of roughness and decontamination, allowing it to receive a coating without problems of adhesion between the end-product, the substrate *LL*, and coating *R* (figure 3a). Furthermore, the use of an intermediate coating *SB* of a galvanic nature, which forms a barrier layer, (figure 3b), can be recommended for having a greater guarantee of protection of the substrate made of light alloy.

If, for example, the end-product made of a magnesium alloy were not sufficiently protected from the titanium film, during the subsequent electrochemical colouring operation *COL* in an aqueous environment, there would be the dissolution of the magnesium rather than the titanium colouring.

This marks a great difference with respect to the case of massive titanium colouring (tantalum, niobium, and the like), for which there are no problems of this type.

It could therefore be necessary to insert further intermediate protective layers between the film of titanium or similar products (Ti, Ta, Nb, Zr, Hf, W, V, Mo) and the magnesium or aluminum alloy. The pretreatment phases of the surface of the end-product made of light alloy, before the deposition of thin layers of metallic titanium and other products (Ti, Ta, Nb, Zr, Hf, W, V, Mo) and their colouring, are therefore extremely important.

Magnesium or aluminum alloys are metals which are difficult to cover with humid methods. The layer of oxide which covers them must be removed before the deposition.

In all cases, the coatings must have a very low porosity and the deposition solutions must not react violently with the light alloy forming the substrate. The quality of the coating depends on the quality of the preparation of the end-product made of magnesium or aluminum alloy; pretreatment methods suitable for the type of base alloy are therefore necessary.

Figure 4 represents the sequence of operations starting from the end-product made of light alloy *LL*; the pretreatment *PR*; the coating *R* by the physical vapour deposition of a metal selected from titanium, tantalum, niobium, zirconium, vanadium, hafnium, molybdenum, rhenium, tungsten; and the colouring *COL* by oxidation according to the invention.

Table C below summarizes the function of the pretreatment operations which precede the galvanic deposition whereas, with reference to figure 5, two pretreatment procedures of light magnesium or aluminum alloys are illustrated.

Table C. Pretreatment operations of the surface of the end-product made of a light alloy (Mg or Al)

Type of treatment	Observations
Surface cleaning	Removal of dirt, oil, grease
Alkaline cleaning	Mg is passive in alkaline environments. It removes dirt, grease, etc.
Acid pickling	This removes flakes and oxides, forming a higher-quality oxide to be subsequently removed. Cavities are formed on the surface which act as mechanical gripping sites for the coatings.
Acid activation	This removes residual oxides, minimum attack, it makes the surface uniform.
Zinc by immersion in an alkaline solution	This forms a layer of zinc on the end-product
Thin copper layer	Zinc is a very reactive metal: not all metals can be deposited on Zn. The copper acts as a base for a subsequent plating from an aqueous solution.
Activation with fluorides	This removes oxides and, in the case of magnesium, it forms a thin layer of MgF_2. Treatment with fluorides seems to control the deposition rate of zinc or nickel and produces more adherent deposits.
Chemical nickel (electroless)	A nickel alloy is deposited on the surface. It acts as a base for a subsequent deposition.

In the scheme of figure 5, it can be seen how the pretreatment *PR* is effected according to two plating procedures with zinc *Zn* or with chemical nickel *NiA*.

After a cleaning *PR* and pickling *DEC* common to the two methods in the case of the zincate process, the activation *ZnA* is effected followed by zincing in an alkaline solution of zinc *Zn* and the deposition of a copper *Cu* layer and a subsequent further coating *R′* is effected, if necessary.

In direct plating, on the contrary, the activation *NiA* is effected by means of fluorides followed by plating *PL* with chemical nickel (electroless) and a further coating R′, if necessary.

In the case of a generic end-product made of the mentioned materials, with reference to figures 6a and 6b, the metallization and colouring process can also be applied with a method of the "web coating" type. A suitably pre-treated material (for example: yarns, plastic films for packaging, galvanized sheet iron for cars, etc..) can be coated in continuous: the tape 2 (or thread) is unwound from the spool 1 following the direction of the arrow F, coated with a metal layer of titanium, in a reactor PVD, by means of the ionic beam assisted deposition technique, and rewound on the reel as a bobbin 3. The tape 6 coated with a titanium film is subsequently passed to the colouring step, for example electro-chemically. Also in this case, the technique can be adopted for unwinding the bobbin 3 of metallized tape, sending it into the colouring tank 4 equipped with a cathode 5, making it to act as anode, and then rewinding it on a reel 7. Finally the metallized and coloured tape (or yarn) is possibly protected by a transparent protective layer.

The metallization can be effected by means of air-air systems, in which the tape enters the metallization reactor through low-medium-high vacuum zones, is metallized, and then exits passing through high-medium and low vacuum zones, until it returns into the atmosphere.

As an alternative, the operation can be effected by implementing the whole unwinding-winding system in the metallization reactor.

The electro-chemical colouring can be effected by means of brush methods. A brush soaked with an electrolytic solution is put in contact with the surface to be electrochemically oxidized. A metal push-rod is present on the brush, which is connected to the negative pole (cathode) of a generator, the metal film is put in contact with the positive pole (anode). In this way, the anodic oxidation region can be localized and the colouring is subsequently effected by anodic oxidation in the areas in which the brush is in contact with the metallized surface.

It is extremely important for the deposited layer to be sufficiently thick and adherent to the substrate, in order to electrochemically oxidize the surface of the metal deposited with the PVD technique.

Furthermore, the thickness of the film deposited plays an important role in the current distribution in the film during the anodic oxidation operation.

It is extremely important for the current to suitably reach all the surface points in order to electrochemically oxidize the metal surface with the PVD technique.

Appropriate contact systems must therefore be prepared for the objects to be coloured, or with a high number of electric current points in contact with the metal film.

Colouring can be also effected directly in the metallization reactor, for example by introducing in the magnetron sputtering reactor, at the end of the deposition of the metal layer, an oxygen/argon mixture so that oxygen reacts with the metal (titanium and similar) forming a layer of coloured oxide.

The deposition of titanium (Ti, Ta, Nb, Zr, Hf, W, V, Mo and alloys thereof) in the form of a thin layer can be effected using several techniques.

The deposition technique and the operative parameters greatly influence the structure of the metallic films produced (dimensions, form and crystallographic orientation of the grains, defects, porosity, residual stress in the coating, and similar). The film structure, in turn, influences the chemical and physical properties of the film itself.

The PVD deposition is the preferred technique for depositing metals such as titanium and similar (Ti, Ta, Nb, Zr, Hf, W, V, Mo and alloys thereof).

The main physical vapour phase deposition techniques are listed hereunder:

- vacuum evaporation, wherein the material emitted from a thermal vaporization source, reaches the substrate without collisions with the gas molecules in the area between the source and the substrate;
- sputtering (cathodic ablation) in which the source of the vaporized material is the surface of one or more targets (cathode), which are subjected to physical ablation (sputtering).
- arc deposition, wherein a high current and low voltage electric arc is shot in a low pressure gas, to erode the solid cathode or to melt and evaporate the anode;
- ionic deposition which uses the bombardment of the

developing film on the part of atomic particles having sufficient energy, to modify and control the composition and property of the film.

These processes normally operate at pressures lower than (or close to) 1 mTorr or, according to the I.S. lower or close to 7.5 pascal (Pa) as 1 Pa corresponds to about 7.5 mTorr.

These pressures can be reached by means of a pumping system equipped with a diffusion or turbo-molecular pump and a preliminary pump.

The conceptual scheme of a physical vapour deposition process (PVD) is shown in figure 7. The atoms of the metal to be deposited are emitted EV from a liquid or solid source (target) T to form the gas G1 (due to the heating, as a result of collision with ions of inert gas, and similar) and with a transport mechanism TR, mediated by the gas G2 which is present at low pressure in the deposition reactor, CND are deposited on the substrate under the form of a film F.

In general it can be said that the structure of the deposited layer is determined by the competition between the atomic mobility (which depends on the substrate temperature) and the arrival rate of the particles on the surface.

The ratio between the substrate temperature and the melting temperature of the metal deposited, Ts/Tf, is an extremely important parameter.

Another very important parameter is the gas pressure in the reactor.

The problem of the porosity of the titanium (tantalum, niobium, etc..) metal coating is represented by the high melting point of the metal deposited. In a PVD process the metal is vaporized and re-condensed on the substrate. If the conditions are not suitable, the film structure formed is porous.

A densification effect is observed in deposition processes wherein a beam of energy particles (ionic bombardment) hits the developing metal.

The deposition temperatures must be lower than the stability temperatures of the substrate B or the barrier layer SB, if present.

Good adhesion, uniformity and low porosity of the titanium coating or similar (Ti, Ta, Nb, Zr, Hf, W, V, Mo and alloys thereof), must be obtained. In PVD processes, the high substrate temperature favours the formation of coatings having a compact structure. High temperatures of the substrate however are not practicable in the case of low-melting substrates.

It has been observed that other technical expedients can be used in order to reduce the temperature of the substrate without lowering the quality of the deposit: for example, by electrically polarizing the substrate.

Physical vapour deposition assisted by ionic bombardment (IBAD : ion beam assisted deposition), allows good quality films to be obtained.

During the deposition phase, the film is struck, continuously or periodically, by highly energetic atoms of inert gas and by reactive particles which modify the development and properties of the film.

The technique allows the film adhesion and the covering of the film on the substrate, to be improved; moreover, by controlling the ionic bombardment, it is possible to operate on the film properties (density, morphology and residual stress).

With reference to figure 8, the light interference is due to the optical path difference between the luminous rays reflected on the oxide surface A and those reflected by the surface of the metal B. This phenomenon gives rise to interference colouring. The colour depends on the thickness of the oxide film.

Metals such as titanium, niobium, tantalum and similar, oxidize in the air at room temperature, but the oxide film which is formed is too thin to provide interference colours. The simplest thickening method of the oxide film consists of heating the metal in air.

The colouring of the metal layer, vapour deposited, can be effected by means of thermal or galvanic oxidation.

The colouring can also be obtained by reactive physical vapour deposition of the metal oxide. In this case, argon/oxygen mixtures are used in the deposition reactor.

By controlling the emission rate of the metal, the ionization degree of the gas and the ratio of the partial oxygen and argon pressures, an oxide layer is obtained which creates interference colours.

The colours which are formed by heating the metal in air, depend on the time and temperature of the treatment. Table 1 of figure 9 indicates a chromatic scale example obtained by thermal oxidation of titanium in air.

The electrochemical colouring of titanium is a technique which is effected at room temperature by dipping the piece to be oxidized in an electrolytic solution and connecting it to the positive pole of a current generator.

A metal is connected to the negative pole, which acts as cathode (titanium, stainless steel and similar).

The electric scheme is shown in figure 10 (anode: manufactured product coated with Ti and similar; cathode: titanium, stainless steel and similar).

The electrolytic solution can contain sulphuric acid (5%) or phosphoric acid (15%) or ammonium sulphate (10%). Other solutions are possible. There are numerous colouring techniques: by immersing the piece in an electrolytic cell, or by brush anodization. The oxidation active area can be delimited by shields, lacquers and the like so as to localize the formation of the coloured oxide.

The different colours are formed by varying the cell voltage. This method is extremely accurate as the electric parameters, voltage and current, are easily controlled. In this way wide colour ranges can be obtained as shown as an example in table 2 of figure 11.

The electrochemical oxidation is generally effected by anodic polarization of the end-product covered by a cell voltage ranging from 5 to 300 volt, according to the desired colour.

The surface pre-treatment of massive titanium end-products plays an important role in the electrochemical development of the coloured titanium oxide.

Before the electrochemical oxidation, the surface of the metal (Ti, Ta, Nb, Zr, Hf, W, V, Mo and alloys thereof) must be suitably prepared.

The preparation cycles of the metals which can be coloured by electrochemical oxidation are based on mechanical finishing, cleaning and surface activation steps.

For example, the acidic activation of titanium can be effected by immersion in 10% by weight solutions of nitric acid and 2.5% hydrofluoric acid, for various tens of seconds. Tantalum can be attached by very aggressive acidic solutions: for example concentrated acids at boiling point. Niobium can be attached in solutions of sulphuric acid (20%) and hydrofluoric acid (10%) at a warm temperature. Other solutions can be used.

In the case of thin films produced by vapour deposition, the preparation can be extremely simplified. The deposition of thin films is in fact effected under conditions of low oxygen concentration and if the target is extremely pure, the surface of the metal film which is deposited is also extremely pure. This makes the removal of the surface oxides before the electrochemical colouring less complex.

The deposition phase comprises the deposition of a layer of metal selected from titanium, tantalum, niobium, zirconium, vanadium, hafnium, molybdenum, rhenium, tungsten and their alloys in thicknesses preferably ranging from 1 to 20 micrometers.

A very important problem which makes the electrochemical oxidation of titanium (or similar) films with respect to massive titanium lies in the fact that in the anodic oxidation of titanium films, a correct current distribution must be obtained on the whole surface of the film. This aspect is linked to problems of electric conductivity through a metallic film which can also have the thickness dl of a micrometer or even less.

The difficulty can be overcome by using massive conductor substrates on which the film is deposited, or by using barrier layers which contain metallic films deposited with the PVD or also galvanic technique, capable of sustaining the current in the anodization phase. The metallic film, for example copper, beneath the titanium (or similar) film will act, together with the titanium film itself, as a conductor in the oxidation operation.

When the substrate or base B is of the *metallic* type, a good adhesion of the metallic film to the metallic substrate is typically obtained using surface preparation techniques (with wet or vacuum methods) capable of removing the surface contamination and any possible layer which negatively influences the adhesion, and subsequently depositing a material which easily binds with the base material. High surface temperatures stimulate the diffusive phenomena and often allow a better adhesion. Metal-metal pairs non-mutually soluble should be avoided, a good adhesion however can be obtained with non-mutually soluble metallic systems if the nucleation density during the PVD development is high.

In order to obtain a good adhesion of the film deposited with the PVD technique on metallic substrates, use is made of the continuous variation in the properties of the interfacial region, by controlling the PVD deposition parameters. The barrier layer must also act as an adhesion promoter, in the sense of attenuating all states of interfacial stress between the substrate and the film deposited. These states of interfacial stress can cause delamination and are due, for example, to different dilation coefficients of the materials or to differences in the crystalline or morphological structure. For this reason, nickel is often a good material as it binds with many metals and is ductile.

In many cases, the metal oxide is removed during the outer cleaning process and the small quantities reformed after the cleaning are removed by activation *in situ* in the deposition reactor. If the natural oxides on the surface are not removed, then the metal deposited should have a high affinity for oxygen.

With respect to the application field relating to the metallic materials of the present application, distinction should be made between ferrous and non-ferrous metallic materials.

Ferrous metallic materials for the application of the present invention are: steels, cast irons, inox steels.

Non-ferrous metallic materials for the application of the present invention are: copper and copper alloys, nickel and nickel alloys, cobalt and cobalt alloys, zinc and zinc alloys.

The surface of the metallic materials used as substrate must be pretreated before the application of the barrier layer and metallization layer or the direct application of the metallization layer. The pretreatment operations depend on the type of metallic material used.

It can generally be said that the pretreatment operations can be of the mechanical type or chemical or electrochemical type.

Among important operations of the mechanical type, sandblasting and mass finishing can be mentioned in particular.

Among important operations of the chemical or electrochemical type, cleaning with organic or aqueous solvents, acid or alkaline surface activation, the chemical deposition of metallic layers (copper and nickel), the galvanic deposition of metallic layers or electrofinishing, can be mentioned.

Polymeric materials offer numerous possibilities from a metallization and colouring point of view.

The chemical properties of a polymeric surface depend on the functional groups present on the surface.

The mechanical properties of the surface region depend on the quantity and type of bonds which are formed there and are generally different from those of the material body.

In order to obtain a good adhesion, the surface of the polymer must be free of contaminants.

The adhesion of a metallic film to a polymeric surface can be obtained using metals which form organometallic bonds with the substrate. Among the main metals, Al, Cr, Ti (Ta, Nb, etc) can be mentioned. The surface of the polymer can be pretreated in plasma to make the surfaces more reactive with an increase in the nucleation density and of the bonds.

Oxygen or nitrogen plasmas are generally used to activate the surfaces.

Also in this operation, care should be taken not to overexpose the surfaces to the plasmas, with the consequent formation of weakened interfacial regions and therefore with a reduced adhesion.

Improved adhesion can be obtained by roughening the surface and having a mechanical hooking between the film deposited and the surface.

Plastic materials which are industrially subjected to vacuum metallization are: acrylics, acrylonitrile-butadiene-styrene (ABS), polyamide (PA), polybutyleneterephthalate (PBT), polycarbonate (PC), polyester, polyethersulfone (PES), polyethylene (PE), polyethyleneterephthalate (PET), polyphenyleneoxide (PPO), polypropylene (PP), polysulfone, polyvinylchloride (PVC).

Plastic materials require an adequate pretreatment before metallization. The primary purpose is to remove the contaminants which can cause poor adhesion, a low-quality finishing, etc.

The cleaning is effected by means of organic or water-based solvents.

An example of a metallization process with titanium or the like, of plastic materials consists in the application of three layers:

- A base layer, this is an organic coating, also called base-coat, whose main function is to produce a smooth surface so that the metal deposited is shiny; it is also used for improving adhesion between the metallic coating and the substrate. The base layer also acts as a seal of the substrate surface for the gases which are released from the plastic material during the vacuum set-up of the deposition reactor. Many plastic materials can be metallized directly but the results are generally unsatisfactory, except for acrylic materials and polycarbonates. In the case of thin films, all surface edges and faults are faithfully reproduced. For this reason, the surfaces are generally prepared by the application of an organic base layer (SB). This layers allows a satisfactory adhesion, it fills small defects or holes in the surface of the substrate and provides a smooth surface for the metallization.

- A metallization layer deposited with vacuum techniques (PVD). This is the titanium layer (or similar and their alloys).
- A coating layer applied on the metallic oxide which produces interference colours; this layers is also called top-coat and its main function is to protect the metal and metal oxide. In some cases, the top-coat is not applied. The top-coat can be deposited directly in the reactor (quartz layer deposited with the PECVD technique). The top-coat can be an organic material which hardens due to UV or thermal action.

One of the main factors which cause the durability of a coating is adhesion to the substrate. Metals which form strong stable chemical bonds with the substrate firmly adhere, whereas metals which only form physical bonds can become more easily detached from the substrate.

The maximum thermal treatment temperatures of the organic layers, used as barrier layer (SB) and protective layer (RIV) of the metallization, should be selected in relation to the type of plastic material. As an indicative example: polystyrene 60-65°C; acrylic 65-80°C; ABS 80-90°C; phenol and urea 110-150°C; polycarbonate, polypropylene and polysulfone 130-150°C.

The type of plastic material to be metallized is the determinant factor in selecting the composition of the organic layers. There are numerous specific commercial organic formulations for the various types of plastics and for the protection of the metallization layer. Examples of formulations for organic layers can be the following:

a) base layer:

1) nitrocellulose resin modified in a solvent (system of ketones, alcohols, glycol ether and aromatic hydrocarbons) which easily evaporate in air;

2) alkyd resin amino-modified in solvents based on aromatic hydrocarbons, alcohols and esters;

3) alkyd resins modified in aromatic and aliphatic hydrocarbons, or glycol ether;

4) epoxy-acrylate resins, unsaturated acrylate, acrylate esters in a solvent based on methylisobutylketone and isopropyl alcohol, with photo-setting agents which, when exposed to UV radiation, begin the setting process;

b) protective layer:

Epoxy modified acrylic resin in n-butanol and xylol, sometimes with the addition of 2-ethoxyethanol.

The formulations for the base layer can have a non-volatile content ranging from 30% to 50% by weight, whereas the formulations for the protective layer can have a non-volatile content ranging from 20% to 30% by weight.

The application of the organic layers can be effected automatically or manually by: a) immersion; b) flow or shower; c) spraying.

The setting of the organic layers is extremely important, it must in fact be complete, especially in the case of the base layer.

In the contrary case, there is the release of gases during the vacuum deposition. The volatile substances entrapped in the organic product can migrate during evaporation allowing penetration of the metal and creating iridescence phenomena.

The production of plastic components requires a good surface preparation.

It is preferable to clean the plastic surfaces upstream of the coating treatment with organic film, using, for example, water-based or organic-based solvents. If the organic solvent can have a good capacity of eliminating the organic contaminants, it can, on the other hand, damage the plastic material on which the metallic layer is to be deposited. Environmental problems relating to the release of solvents into the atmosphere should also be taken into consideration.

The cleaning can be effected in solvent vapours, by immersion in liquid phase - or a combination of both. The stirring of the plastic components in ultrasounds can help to remove the contamination from recesses, blind holes, etc.

When the plastic components are not coated by an organic layer, the cleaning can be effected in the vacuum deposition chamber, by adding a plasma assisted activation station and subsequently eliminating the cleaning as a separate process step. In this way, excellent adhesion of the metallic film to the plastic can be obtained.

The vacuum metallization of plastic materials offers many openings for engineering and design, as it can be used for the substitution of components previously made with other materials. The plastics to be metallized must have a uniform composition and should not release volatile substances under vacuum. As plastic materials are good insulators, they have the disadvantage of becoming electrostatically charged, attracting dust. This necessitates cleaning and preparation treatment.

Non-removed volatile substances can contaminate the metallization system and ruin the work. Furthermore, plastics (unlike glass and metals) desorb gases with vapours extremely slowly. In many cases the metallization plants are generously equipped with adequately powerful vacuum systems.

Examples of pretreatment of plastic materials before metallization are based on chemical activation in tetrachloromethylene, or in concentrated sulphuric acid and subsequent washing in water.

A further example is represented by activation with oxygen or ionic bombardment treatment.

One of the most common types of pretreatment consist in surface roughening by means of sandblasting. The micropores act as nucleation and anchoring sites of the metallic film.

These types of pretreatment are important in the case of multiphase polymers in which one of the phases is preferably attacked. By attacking ABS, styrene-butadiene polymer, for example, the butadiene component is preferably attacked and solubilized. Problems can arise in attacking materials reinforced with fibres as they require long activation times of the fibre with the risk of degrading the matrix of the material.

One of the problems of chemical pretreatment is that the use of additives, which increase the thermal and mechanical resistance of the polymer, requires more aggressive chemical agents, and this can be a limitation.

Other techniques frequently used for improving adhesion are treatment with flames (flaming), crown discharge, activation in oxygen plasma. For these types of pretreatment, the surface modification mechanism is the formation of a wide range of functional groups containing oxygen. These modifications, however, change the surface of the polymer. The plastic material ABS, for example, is treated with an oxygen plasma before the metallization application.

The surfaces can be treated in the plasma of inert gases. The activation in this case is probably due to the UV radiation from the plasma.

The treatment of polymers in plasma can cause textures and improves the adhesion strength with a mechanical interlocking mechanism. The texture can be accompanied by a variation in the chemistry of the surface due to the variation in the terminal species.

For depositing an aluminum film on Kapton, for example, an optimum surface treatment for Kapton has proved to be a detergent washing followed by caustic attack to roughen the surface and subsequently UV treatment under partial oxygen pressure which oxidizes the surface.

The activation of the polymeric surfaces can be effected by the deposition of an additional polymer layer which is more subject to the formation of bonds.

Mechanical brushing of the surface is a technique which destroys the oxide and exposes the metal producing an improved adhesion of the coatings deposited under vacuum on a steel tape.

The sensitisation consists in the addition of small particles of material on the surface which act as nucleation sites.

Ionic implanting can also be used for introducing foreign elements into the material and improving adhesion.

The pre- and post-metallization varnishes can be of the traditional type: with solvent, water, hardenable with UV rays.

The premetallization varnishes can be applied for example to polymeric materials (PP, Nylon, ABS, etc.), metals, glass, etc.

Mixed water and solvent treatment cycles can be used.

The UV hardening varnishes require short hardening times.

Wood, leather and natural fibres of an animal or vegetable origin and cellulose materials can be protected and decorated with the application by means of PVD techniques of one or more metallic layers and an oxide layer which creates interference colours.

Among the most common types of wood, the following can be cited: soft wood (fir, pinewood, sequoia, etc.), hard wood (birch, cherry, beech, nut, oak, etc.) and exotic hard wood (ebony, mahogany, teak, etc.).

The metallization of these materials should take into account the fact that they degas under vacuum. The metallization can be preceded by the application of a base layer, for example of a photo-polymerizable filmogenic material with UV radiation, suitable for sealing the material to prevent the release of gas and to promote the uniformity and adhesion of the metallic coating.

The sealing phase of the pores with a base layer which can consist, for example but not exclusively, of a thermosetting polymeric material, UV setting, or metallic material (for example nickel deposited with a wet autocatalytic method), is extremely important.

A layer of titanium is then deposited with PVD processes on the metallized wood material.

The metallization treatment and colouring can be applied to *glass and ceramic*.

On the basis of their composition and utilization, the following types of glass can be distinguished: silica glass, 96% silica (Vycor^{TM}), sodium-calcium glass, lead silicate, high lead silicate, borosilicate, aluminum-boro-silicate, aluminumsilicate.

Upon heating some types of glass in air, the mobile species (sodium) segregate on the surface and form nodules which, if not removed in the pretreatment phase, cause dotting in the metallization film.

"Float" glass is the type which is most commonly metallized with the PVD technique. The side of the glass which has been in contact with the molten tin can be contaminated by a tin oxide. In the pretreatment phase, the tin oxide can be removed with a light attack with a solution of ammonium bifluoride.

A further cause of the surface contamination of glass is represented by the packaging and storage phases.

In some cases, the adhesion of the metallic film to the surface of glass increases with time after the deposition, as reactions in the solid state take place at the interface, which can proceed very slowly after deposition. This can be due to the diffusion of reactive species such as oxygen at the interface or by the release of the film stress with time. The cleaning with plasma of a glass surface before deposition of the metallic film has proved, for example, to improve the adhesion of the film with time.

Metals having a strong affinity for oxygen generally form well-adhering coatings on glass. It is known that in the first moments after the deposition of titanium on pyrex glass, a layer of TiO is formed, which facilitates adhesion.

Adhesion to the surface of glass is generally obtained by preparing a decontaminated surface and using a material having a high affinity for oxygen, such as for example, Ti and similar products. Furthermore, in order to reduce internal stress of the film, the thickness of the titanium film should be limited and the desired properties generated using a multilayer structure.

If the first atomic interfacial layers do not have an affinity for oxygen, a surface chemistry or conductive deposition can be used which forms a high density of nuclei. In some cases, the nucleation density can be increased by initiating the deposition with oxygen, residual in the environment or adsorbed on the surface of the substrate, which has a strong affinity with the film of material which is deposited.

In some cases, a high initial deposition rate increases the nucleation density on the surface. The surface chemistry of the oxides can be altered with selective treatment which modifies the composition and nucleation of the ad-atoms on the surface.

In the deposition of a film of compounds on oxides, good adhesion can be obtained by generating an interface with a composition gradient and being certain that a minimum residual stress is exerted.

Ceramic materials can also be subjected to metallization and colouring. Traditional ceramic materials are classified as follows: traditional ceramics, brickwork, tiles, sanitary products, technical porcelains, refractory materials.

Ceramics for traditional use can be subdivided according to their structure into porous or greified, depending on the surface state into glazed or unglazed, and in relation to the colour into white or coloured.

In the colouring of massive metals by oxidation, thermal or galvanic, the thin layer of oxide is produced by the reaction of the metal with oxygen, according to the reactions:

$Ti + O_2(g) = TiO_2$ thermal

$Ti + 2H_2O = TiO_2 + 4H^+ + 4e^-$ electrochemical

In the case of titanium, for example, with an increase in the time and treatment temperature of the oxide, there is a colour variation along chromatic scales.

End-products made of magnesium or aluminum alloys do not tolerate high temperatures and consequently the thermal oxidation of the titanium (or similar) film which covers the light alloy end-product must be carried out at sufficiently low temperatures for longer times, depending on the type of light alloy used.

Vice versa, the electrochemical colouring of titanium is a technique which is effected at room temperature by immersing the piece to be oxidized into an electrolytic solution and connecting it to the positive pole of a current generator.

A metal which acts as cathode (titanium, stainless steel, etc.) is connected to the negative pole.

The electric scheme is shown in figure 7 (anode: light alloy coated with Ti and similar products; cathode: titanium, stainless steel, and the like).

The electrolytic solution can contain sulphuric acid (5%) or phosphoric acid (15%) or also ammonium sulfate (10%). Other solutions are possible. There are a numerous colouring techniques: by immersion of the piece in an electrolytic cell, or by brush anodization. The active oxidation area can be delimited by shields, lacquers, and the like so as to localize the formation of coloured oxide.

The various colours are formed by varying the cell voltage. This method is extremely accurate as the electric parameters, voltage and current can be easily controlled. In this way wide colour ranges can be obtained.

Electrochemical oxidation is generally effected by anodically polarizing the coated end-product at a cell voltage ranging from 5 to 300 volts, in relation to the desired colour.

The preparation of the titanium surface plays an important role. The mechanical resistance of anodic films made of titanium and similar metals (Ti, Ta, Nb, Zr, Hf, W, V, Mo) is greatly conditioned by the state of the surface downstream of the physical vapour deposition.

Before the electrochemical oxidation, the surface of the metal (Ti, Ta, Nb, Zr, Hf, W, V, Mo) must be suitably prepared.

The preparation cycles of metals which can be coloured by means of electrochemical oxidation are based on mechanical finishing, cleaning and acid activation stages. The acid activation of titanium, for example, can be effected by immersion in solutions of nitric acid 10% by weight and hydrofluoric acid 2.5%, for tens of seconds. Tantalum can be attacked with very aggressive acid solutions: for example, acids concentrated at boiling point. Niobium can be attacked in solutions of sulphuric acid (20%) and hydrofluoric acid (10%) at a warm temperature. Other solutions can be used.

In the case of thin films produced by vapour phase deposition, the preparation can be extremely simplified. The deposition of thin films, in fact, takes place under conditions of low oxygen concentration, and if the target is very pure, the surface of the metal film which is deposited is just as pure. This makes the removal of the surface oxides before the electrochemical colouring less complex.

The deposition phase comprises the deposition of a metal layer selected from titanium, tantalum, niobium, zirconium, vanadium, hafnium, molybdenum, rhenium, tungsten in thicknesses preferably ranging from 0.5 to 50 micrometers, and even more preferably ranging from 1 micrometer to 10 micrometers.

Deposition and colouring tests

The experimental tests were carried out using samples made of magnesium alloy AM60B. Metal plates (10 cm x 10 cm x 0.5 cm), were cut from ingots of magnesium alloy AM60B, using a belt saw. The surface finishing was improved, by smoothing the surface of the samples with sandpaper (up to 1200 grits). The samples were washed in acetone, abundantly rinsed with distilled water, pickled in diluted nitric acid, rinsed again in distilled water. At this point, the samples were subjected to coating treatment with titanium by means of the physical vapour deposition technique.

The deposition reactor is of the *sputtering magnetron* type and is equipped with an ionic source. The ionic source was used to clean and activate the surface of the sample before deposition, effected with the sputtering magnetron technique. Both the activation and cleaning phase with the ionic source and the sputtering magnetron deposition phase were carried out in an argon atmosphere at a low pressure (in the order of mTorr).

The electrochemical colouring was effected by anodizing the titanium film having a thickness of a few micrometers and deposited on magnesium alloy. An electrolyte based on sulphuric acid (at 5%) was used, exerting cell voltages in the order of tens of volts.

Test 1 (Mg)

Ionic source

Parameter	Value
Argon pressure	2 mTorr
Voltage	1.48 kV
Current	0.28 A
Time	10 minutes

Magnetron sputtering

Parameter	Value
Argon pressure	2 mTorr
Current	6.8 A
Target-substrate distance	8 cm
Time	60

The magnesium alloy substrate was uniformly coated on the whole surface.

The thickness of the coating is a few microns.

There are no signs of delamination of the coating.

The porosity is extremely low: upon placing a drop of acid on the titanium surface, no hydrogen development due to the attack of the magnesium, was observed, even after prolonged exposure.

If the titanium film were porous, a strong hydrogen development due to the dissolution reaction of the underlying magnesium, would in fact be observed.

The colouring of the titanium film on magnesium alloy was effected electrochemically.

The sample of magnesium alloy AM60B coating with titanium (5-10 micrometers) was anodically polarized in sulphuric acid at 5% against a massive titanium electrode, at a cell voltage of a few tens of volts.

After a few seconds, the titanium was coated with a bluish-purple-coloured oxide.

Test 2 (Mg)

Ionic source

Parameter	Value
Argon pressure	2 mTorr
Voltage	1.4 kV
Current	0.28 A
Time	10 minutes

Magnetron sputtering

Parameter	Value
Argon pressure	2 mTorr
Current	6.3 A
Target-substrate distance	8 cm
Time	60

The coating is compact and uniform. It does not delaminate from the substrate and with the drop of sulphuric acid test, it proves to be non-porous.

Under slightly different voltage conditions with respect to Test 1, the colouring obtained is a uniform blue colour on the surface.

Test 3 (Al)

A coating and colouring test of a sample made of aluminum alloy 6060 was effected. The aluminum sample (10 cm x 5 cm x 0.2 cm) was smoothed with paper (up to 1200 grits), was washed in acetone and subsequently with deionized water. This pretreatment phase was followed by the ionic cleaning phase in the deposition reactor. A titanium layer was then deposited.

Ionic source

Parameter	Value
Argon pressure	2 mTorr
Voltage	1.2 kV
Current	0.32 A
Time	10 minutes

Magnetron sputtering

Parameter	Value
Argon pressure	2 mTorr
Current	6.5 A
Target-substrate distance	8 cm
Time	40 minutes

The coating is compact and uniform. A tear test was effected with adhesive tape. There were no delaminations of the titanium film from the substrate.

The aluminum alloy sample coated with titanium was electrochemically coloured with a light blue colour, under identical voltage conditions to those of test 2.

Some examples of the colouring of end-products are provided below.

Example 1

A flat UNS 316 stainless steel sample was subjected to titanium coating followed by electrochemical colouring. The surface of the sample was degreased with isopropylic alcohol. The deposition cycle of the titanium layer envisaged an initial activation phase with the use of an ionic source: the activation treatment lasted 5 minutes at 1.9 mTorr of argon pressure at a voltage of 1.4 kV. This was followed by a coating phase using the physical deposition technique of the magnetron sputtering type: the coating treatment lasted 20 minutes at 1.9 mTorr of argon pressure; the sputtering current was 6.6 A. The result was a deposit in the order of a micrometer with a dark grey shiny appearance. There was an extremely good adhesion of the titanium to the stainless steel. The titanium layer was coloured by anodic oxidation in a solution of phosphoric acid, at a voltage of 20 V, obtaining a violet-blue-coloured layer of titanium oxide. This was followed by the varnishing phase with a layer of transparent varnish with protective water for metals.

Example 2

A flat CZ 121 M brass sample was subjected to coating with a barrier layer of the metallic type followed by titanium coating and finally electrochemical colouring. The surface of the brass sample was degreased with acetone and deoxidized by immersion for 5 minutes in a sulphuric acid solution (20% by weight) at room temperature. The brass substrate was activated with a commercial solution of Sn/Pd by immersion at room temperature for 2 minutes. This was followed by metallization by the autocatalytic deposition of Ni-P alloy in a bath having the following composition and characteristics: nickel acetate 0.12 M, sodium hypophosphite 0.32 M, lactic acid 0.5 M, pH 4.7, operating temperature 85°C. The deposition of nickel-phosphorous was carried out for 30 minutes producing a deposit having a thickness of 10 µm. The deposition cycle of the titanium layer was based on an initial activation phase with the use of an ionic source: the activation treatment lasted 5 minutes at 1.9 mTorr of argon pressure at a voltage of 1.4 kV. This was followed by the coating phase by means of the magnetron sputtering technique: the coating treatment lasted 20 minutes at 1.9 mTorr of argon pressure; the sputtering current was 6.6 A. A deposit was formed in the order of a micrometer with a dark grey shiny appearance. There was an extremely good adhesion of the titanium to the stainless steel. The titanium layer was coloured by anodic oxidation in a solution of phosphoric acid, at a voltage of 20 V, obtaining a violet-blue-coloured layer of titanium oxide.

Example 3

A sample made of copper-tin alloy (white bronze) was coated with a layer of tantalum by means of the magnetron sputtering technique. The layer was deposited after cleaning the surface of the sample with acetone and activation in sulfamic acid. The tantalum deposition was effected for a period of 10 minutes at an argon pressure of 1.9 mTorr and a sputtering current of 6.4 A. The deposit was electrochemically coloured in a solution of sulfuric acid.

Example 4

A product made of ABS plastic material was subjected to coating with zirconium and subsequently electrochemical colouring. The metallization was effected with the magnetron sputtering technique: 15 minutes at 1.9 mTorr of argon pressure, a sputtering current of 6.6 A. A thin deposit was formed which was subjected to electrochemical colouring by means of anodic oxidation in a solution of phosphoric acid. The result was an object made of ABS plastic coated with a coloured layer of zirconium oxide.

Example 5

A product made of ABS plastic material premetallized with a copper layer, was subjected to coating with titanium and subsequently electrochemical colouring. The titanium deposition was effected with the magnetron sputtering technique: 15 minutes at 1.9 mTorr of argon pressure, a sputtering current of 6.6 A. A thin deposit was formed (less than a micrometer) which was subjected to electrochemical colouring by means of anodic oxidation in a solution of phosphoric acid. The result was an object made of ABS plastic coated with a coloured layer of titanium oxide. The metallic copper barrier layer acted as an adhesion layer for the titanium and also as a current-carrier in the electrochemical colouring phase.

Example 6

A product made of ABS plastic material was subjected to coating with titanium with the magnetron sputtering technique and then colouring with the reactive magnetron sputtering technique. The surface of the ABS plastic object was subjected first to the deposition cycle, with activation in oxygen plasma (2.20 mTorr) for 5 minutes.

The metallization was effected with the magnetron sputtering deposition technique: 2 minutes at 1.6 mTorr of argon pressure. At 6.6-6.7 A of sputtering current.

The colouring of the ABS plastic object was effected with the reactive magnetron sputtering technique: the deposition was effected for 3 minutes and 30 seconds at 6.6-6.9 A of sputtering current using an argon-oxygen mixture whose total pressure was 2.5-2.7 mTorr.

The result was an ABS plastic object coated with a yellow-coloured layer of titanium oxide.

Example 7

Several sheets of boron silicate glass (4 cm x 5 cm x 0.5 cm) were subjected to metallization by coating with titanium and subsequent electrochemical colouring.

The titanium deposition was effected using a reactor of the magnetron sputtering type.

The glass sheets were degreased in acetone. The deposition cycle envisaged an initial activation phase using an ionic source: the activation treatment lasted a few minutes at 2.0 mTorr (argon) at a voltage of 1.3 kV. A coating phase followed, by means of magnetron sputtering: the coating treatment lasted 20 minutes at 1.9 mTorr (argon); the sputtering current was 6.6 A. The result was a deposit in the order of a micrometer with a dark grey shine appearance. The glass sheets coated with the titanium layer were coloured by anodic oxidation in a solution of phosphoric acid. Glass sheets were produced with varying colours depending on the cell voltage applied.

Example 8

A quartz glass ball was metallized and coloured with the technique described above. The metallization was carried out with the magnetron sputtering technique preceded by ionic activation with argon. The colouring was effected electrochemically in a solution of sulfuric acid. A bulb was produced with a blue-coloured outer layer.

Example 9

A ceramic tile (glazed stoneware), having dimensions of 10 cm x 10 cm x 1 cm, was subjected to a coating cycle with titanium and subsequent electrochemical colouring.

The titanium deposition was effected using a reactor of the magnetron sputtering type.

The surface of the tile was degreased with acetone. The deposition cycle envisaged an initial activation phase using an ionic source: the activation treatment lasted 5 minutes at 1.9 mTorr of argon pressure at a voltage of 1.4 kV. A coating phase followed, by means of magnetron sputtering: the coating treatment lasted 20 minutes at 1.9 mTorr of argon pressure; the sputtering current was 6.6 A. The result was a deposit in the order of a few micrometers with a dark grey shine appearance. The titanium adhesion was extremely good. The ceramic tile coated with the thin layer of titanium was subjected to an electrochemical colouring test, by means of anodic oxidation in a solution of phosphoric acid. The result was a ceramic tile metallized with a blue-coloured layer of titanium oxide.

Example 10

A ceramic tile (glazed stoneware), having dimensions of 10 cm x 10 cm x 1 cm, was subjected to a coating cycle with titanium with the evaporation technique and subsequent electrochemical colouring.

The evaporation was carried out under a vacuum of 0.1-10 mPa. A titanium layer of about 1.5 micrometers was deposited.

The titanium layer was electrochemically coloured, with a similar technique to that described in the previous examples.

Example 11

A ceramic tile (glazed stoneware), having dimensions of 10 cm x 10 cm x 1 cm, was subjected to a coating cycle with titanium with the cathodic arc technique and subsequent electrochemical colouring.

The evaporation was carried out under a vacuum of 0.001-0.1 Pa. A titanium layer of about 2 micrometers was deposited, which was well adhered to the substrate.

The titanium layer was electrochemically coloured, with a similar technique to that described in the previous examples.

Example 12

A ceramic tile (glazed stoneware), having dimensions of 10 cm x 10 cm x 1 cm, was subjected to a coating cycle with titanium with the magnetron sputtering technique and subsequent electrochemical colouring.

The surface of the tile was degreased with acetone. The deposition cycle envisaged an initial activation phase using an ionic source: the activation treatment lasted 5 minutes at 1.9 mTorr of argon pressure at a voltage of 1.4 kV. A coating phase followed, by means of magnetron sputtering: the coating treatment lasted 20 minutes at 1.9 mTorr of argon pressure; the sputtering current was 6.6 A. The result was a deposit in the order of a few micrometers with a dark grey shine appearance. The adhesion of the titanium to the tile was extremely good. The ceramic tile coated with the thin layer of titanium was subjected to an electrochemical colouring test, by means of anodic oxidation in a solution of phosphoric acid. It was possible to obtain a multicoloured surface by acting on the cell voltage during the anodic oxidation.

Example 13

A ceramic tile (glazed stoneware), having dimensions of 10 cm x 10 cm x 1 cm, was subjected to a coating cycle with titanium with the magnetron sputtering technique and subsequent electrochemical colouring.

The surface of the tile was degreased with acetone. The deposition cycle envisaged an initial activation phase using an ionic source: the activation treatment lasted 5 minutes at 1.9 mTorr of argon pressure at a voltage of 1.4 kV. A coating phase followed, by means of magnetron sputtering: the coating treatment lasted 1 minute at 1.7 mTorr of argon pressure; the sputtering current was 6.6 A. At the end of the deposition, the deposition of titanium oxide was effected with the reactive magnetron sputtering technique by introducing an argon-oxygen mixture (total pressure of 2.6 mTorr) for a time of 3 minutes at 6.7-6.8 A. At the end of the test a coloured surface of titanium oxide was produced.

Example 14

A sample of beech-wood was sealed with a thermosetting organic layer. It was then metallized by thermal evaporation. A metallic titanium layer was formed, having a thickness of 1 micrometer. The titanium layer was electrochemically coloured.

Example 15

A 5 cm x 5 cm sample of cotton fabric was subjected to titanium deposition by means of vacuum evaporation. The thermal evaporation was effected in a reactor at a pressure of 0.1-10 mPa for a few minutes. The titanate fabric was subjected to electrochemical colouring.

Example 16

A 20 cm x 20 cm sample of cotton fabric was subjected to the deposition of titanium by means of magnetron sputtering and titanium oxide by means of reactive magnetron sputtering. The titanium deposition was effected in an argon atmosphere (1.7 mTorr) for 30 seconds. At the end of the titanium deposition, an argon/oxygen mixture was introduced into the reactor, regulating the total pressure at a value of 2.13 to 2.7 mTorr for a period of 4 minutes. A sample of cotton fabric was produced, coloured (purple-brown) on the side exposed to the target.

Example 17

A polyethylene sheet was subjected to metallization with titanium using the thermal evaporation technique. The thermal evaporation was effected in a reactor at a pressure of 0.1-10 mPa for a few minutes. The titanate fabric was subjected to electrochemical colouring.

Example 18

The metallization and colouring of various glass containers (perfume bottles). The glass bottles were cleaned in acetone and in isopropylic alcohol. They were placed inside the deposition reactor under vacuum. The magnetron sputtering deposition was preceded by an activation phase with argon plasma (1.85 mTorr at 1.6 kV and 0.3 A) which lasted 5 minutes.

The titanium deposition via magnetron sputtering lasted 20 minutes at 1.70-1.80 mTorr of argon pressure, at a sputtering current of 6.6-6.9 A and a voltage of 365÷385 V. At the end of the deposition the bottles were uniformly coated by a titanium layer. The titanium layer is compact, shiny and adherent. There are no signs of detachment.

The bottles coated with a titanium film were subjected to electrochemical colouring in a solution of phosphoric acid. Bottles were obtained, having a uniform blue colour and a uniform blue-cobalt colour.

Example 19

A pyramid-shaped glass bottle (used for food) was metallized adopting the deposition parameters of the previous test. The metallization with titanium was effected via magnetron sputtering with a correct result. The titanium layer is uniform and adherent on the whole layer. The electrochemical colouring was effected in a solution of phosphoric acid at room temperature and produced a uniform dark-yellow-coloured titanium oxide.

Example 20

A glass container (such as a sugar bowl) was subjected to metallization with titanium by means of the magnetron sputtering technique and colouring by the deposition of titanium oxide using the reactive magnetron sputtering technique. The basic vacuum in the deposition reactor was 3 x 10^{-3} Pa. The titanium deposition was preceded by an ionic activation phase (Kauffman-type source) in argon plasma at 1.80 mTorr of pressure for 5 minutes at 1.4 kV and 0.22 A.

The titanium deposition via magnetron sputtering lasted 4 minutes, at 6.7-6.8 A, with pressure values of 1.69-1.93 mTorr of argon. At the end of the deposition, the deposition of titanium oxide was effected with the reactive magnetron sputtering technique introducing an argon-oxygen mixture (total pressure of 2.50-2,80 mTorr) for a time of 4 minutes at 6.7-6.9 A. At the end of the test, a glass container was produced, uniformly coated by a layer of titanium and coloured titanium oxide with typical interference colours.

Example 21

A C70 carbon steel sheet with a thin perlite structure was metallized and coloured using the parameters of the previous test. The dimension of the sheet was 15 cm x 20 cm with a thickness of 0.5 mm.

The titanium deposition was effected in a magnetron sputtering reactor, starting from a basic pressure of $2.5\text{-}10^{-3}$ Pa. The sample was subjected to ionic activation in argon at 1.76 mTorr, 16 kV and 0.26 A for a period of 5 minutes.

The steel sheet was then coated with a layer of titanium by means of the magnetron sputtering technique, at an argon pressure of 1.5-1.7 mTorr and a sputtering current of 6.8 A and a voltage of 375 V.

The sheet coated with titanium was then coated with titanium oxide by means of the reactive magnetron sputtering technique, using an argon-oxygen mixture at a pressure of 2.2-2.5 mTorr, for 4 minutes at 6.5-6.8 A.

A steel sheet was produced coated by a layer of titanium and a layer of titanium oxide with the typical colours of light interference phenomena.

A transparent organic layer was applied to the coloured sheet. The organic layer was applied with a brush. A drying phase followed for a few minutes at room temperature.

Example 22

A glass bottle (of the type used for food) was subjected to metallization with titanium (magnetron sputtering) and colouring with titanium oxide (reactive magnetron sputtering).

The bottle was cleaned in acetone and isopropylic alcohol. The bottle was then placed in the deposition and ionic activation reactor.

The ionic activation (Kauffman source) took place with an argon pressure of 1.84 mTorr and a voltage of 1.4 kV and 0.22 A.

The titanium deposition (magnetron sputtering DC) was effected for 3 minutes at 1.7-1.8 mTorr of argon pressure at 6.8 A of sputtering current.

The deposition of titanium oxide (reactive magnetron sputtering DC) was effected for 6 minutes in an argon-oxygen mixture at a total pressure of 2.4-2.6 mTorr and 6.8 of sputtering current.

The result was a bottle coloured with light interference colours.

Example 23

A cardboard sheet (of the type used for food) was subjected to metallization with titanium (magnetron sputtering) and colouring with titanium oxide (reactive magnetron sputtering).

The titanium deposition (magnetron sputtering DC) was effected for 1 minute at 1.6 mTorr of argon pressure at 6.7 A of sputtering current.

The deposition of titanium oxide (reactive magnetron sputtering DC) was effected for 3 minutes in an argon-oxygen mixture at a total pressure of 2.6-2.7 mTorr.

The result was a cardboard sheet coloured with light interference colours.

Example 24

A flat carbon steel sample whose surface was degreased in acetone and activated in sulfamic acid, was pretreated with a cataphoretic organic layer. A layer of zirconium was deposited on this layer with the magnetron sputtering technique. The zirconium film having a thickness of a few micrometers was electrochemically coloured.

Example 25

A glazed stoneware tile was coated with a layer of titanium by means of the cathodic arc deposition technique. The coated tile was treated in an air oven for colouring by thermal oxidation. After about ten minutes at 370°C, a yellow-coloured layered was obtained.

Example 26

A hollow ball, having a diameter of 12 cm, consisting of a mixture of polyester resin and alabaster powder was coated with a layer of titanium by means of the magnetron sputtering technique. The deposition lasted 1 minute at 1.72 mTorr of argon pressure. At the end of the titanium deposition a layer of titanium oxide was deposited with the reactive magnetron sputtering technique, using an argon/oxygen mixture at 2.5-2.7 mTorr of total pressure. The deposition lasted 3 minutes: the result was a surface coated with titanium oxide and characterized by typical interference colours.

Example 27

A flat chromium-plated sample (10 cm x 10 cm x 0.5 cm) was degreased with acetone and activated in diluted sulfuric acid at 3% for a few minutes at room temperature. The surface was coated with an organic layer hardened with UV rays. A metallic nickel layer was deposited on this organic layer using the procedure of Example 1. A titanium layer was deposited on the composite barrier layer (organic + nickel) with the magnetron sputtering technique. Titanium oxide was deposited on this layer by reactive sputtering. A sample with a coloured surface was produced.

Example 28

A sample of polyacrylonitrile organic fibre was subjected to coating with a barrier layer of the metallic type, followed by coating with titanium and finally electrochemical colouring. The surface of the fibre was activated with a commercial solution of Sn/Pd by immersion at room temperature for 2 minutes. Metallization was then effected by the autocatalytic deposition of copper in a bath based on formaldehyde at room temperature for 10 minutes. The deposition cycle of the titanium layer on the copper-coated fibre was based on an initial activation phase with the use of an ionic source: the activation treatment lasted 5 minutes at 1.9 mTorr of argon pressure at a voltage of 1.4 kV. This was followed by the coating phase by means of the magnetron sputtering technique: the coating treatment lasted 20 minutes at an argon pressure of 1.9 mTorr; the sputtering current was 6.6 A. The result was a deposit in the order of a micrometer with a dark grey shiny appearance. The titanium layer was coloured by means of anodic oxidation in a solution of phosphoric acid.

Example 29

A sample of polyacrylonitrile organic fibre was subjected to coating with a barrier layer of the metallic type, followed by coating with titanium and finally electrochemical colouring. The surface of the fibre was activated by immersion at room temperature for 2 minutes in a commercial solution of Sn/Pd. Metallization was then effected by the autocatalytic deposition of copper in a bath based on formaldehyde at room temperature for 10 minutes. A second activation of the copper base was subsequently effected with a commercial solution of Sn/Pd by immersion at room temperature for 2 minutes. Metallization was then effected by the autocatalytic deposition of an Ni-P alloy in the composition bath with the following characteristics: nickel acetate 0.12 M, sodium hypophosphite 0.32 M, lactic acid 0.5 M, pH 4.7, operating temperature 85°C. The nickel-phosphorous deposition was carried out for 30 minutes, producing a deposit having a thickness of 10 micrometers. The deposition cycle of the titanium layer was based on an initial activation phase with the use of an ionic source: the activation treatment lasted 5 minutes at 1.9 mTorr of argon pressure, at a voltage of 1.4 kV. This was followed by the coating phase by means of the magnetron sputtering technique: the coating treatment lasted 20 minutes at an argon pressure of 1.9 mTorr; the sputtering current was 6.6 A. The result was a deposit in the order of a micrometer with a dark grey shiny appearance. The titanium layer was coloured by means of anodic oxidation in a solution of phosphoric acid, at a voltage of 20 V, obtaining a violet/blue-coloured layer of titanium oxide.

CLAIMS

1) A method for the protection/selective colouring of an end-product, comprising the following phases:

- preparing an end-product (B, LL);
- pretreating (PRE, PR) said end-product (B, LL) to prepare its surface for a coating treatment;
- coating said end-product by the deposition of thin layers (DEP, R);
- colouring the most external layer of the coating by the formation of an outer surface protective oxide (COL).

2) The method for the protection/selective colouring of an end-product according to claim 1, wherein said end-product (B, LL) is made of one or more of the following materials: steel, stainless steel, cast iron, copper, copper alloys, nickel, nickel alloys, magnesium and/or magnesium alloys, aluminum and/or aluminum alloys, cobalt, cobalt alloys, zinc, zinc alloys, composite materials with a metallic matrix, polymers and composite materials with a polymeric matrix, glass, ceramics, wood, leather, cellulose yarns, fabrics and materials.

3) The method for the protection/selective colouring of an end-product according to claim 1 or 2, wherein a coating phase is envisaged, with a transparent protective layer (RIV), of said thin layer subsequently coloured by the formation of the outer surface protective oxide

(COL).

4) The method for the protection/selective colouring of an end-product according to claim 1, wherein a coating phase of said end-product (B, LL) with a protective layer (PRE, PR) is also envisaged before the deposition phase (DEP, R).

5) The method for the protection/selective colouring of an end-product according to claim 1, wherein an application phase on said end-product (B, LL) is also envisaged, of a barrier layer (SB) which also acts as an adhesion layer for the metallic layer.

6) The method for the protection/selective colouring of an end-product according to claim 1, wherein the deposition of thin layers (DEP, R) is effected by means of the physical vapour deposition process (PVD) such as, for example, vacuum evaporation, sputtering, arc deposition, ionic deposition.

7) The method for the protection/selective colouring of an end-product according to claim 6, wherein said coating phase of said end-product by the deposition of thin layers (DEP, R) of metals is of the ionic beam assisted type (IBAD - ion beam assisted deposition).

8) The method for the protection/selective colouring of an end-product according to claim 6, wherein said deposition phase of thin layers (DEP, R) of metals is effected

by means of a deposition reactor of the magnetron sputtering type with an unbalanced field.

9) The method for the protection/selective colouring of an end-product according to claim 1, wherein said deposition phase of thin layers (DEP, R) comprises the deposition of a metal layer selected from titanium, tantalum, niobium, zirconium, vanadium, hafnium, molybdenum, rhenium, tungsten and their alloys in thicknesses ranging from 0.5 to 50 micrometers, and more preferably from 1 to 20 micrometers and even more preferably from 1 to 10 micrometers.

10) The method for the protection/selective colouring of an end-product according to claim 1, wherein said selective colouring phase is effected by electrochemical oxidation by anodically polarizing the coated end-product at a cell voltage ranging from 5 to 300 volts, in relation to the desired colour.

11) The method for the protection/selective colouring of an end-product according to claim 1, wherein said selective colouring phase is effected by means of reactive physical deposition.

12) The method for the protection/selective colouring of an end-product according to claim 1, wherein said selective colouring phase is effected by means of thermal oxidation.

13) The method for the protection/selective colouring of an end-product according to claim 1, wherein said end-product is made of magnesium or of an alloy having a composition according to Table A.

14) The method for the protection/selective colouring of an end-product according to claim 1, wherein said end-product is made of Aluminum or an alloy having a composition according to Table B.

15) The method for the protection/selective colouring of an end-product according to claim 1, wherein said pre-treating phase of the end-product comprises mechanical finishing and chemical cleaning.

16) The method for the protection/selective colouring of an end-product according to claim 1, wherein said pre-treating phase of the end-product comprises cleaning, chemical pretreatment, degreasing, alkaline immersion, acid pickling and a galvanized process comprising acid activation, immersion in a Zinc alkaline solution, the deposition of a copper layer and, if necessary, the deposition of a further coating.

17) The method for the protection/selective colouring of an end-product according to claim 1, wherein said pre-treating phase of the end-product comprises the cleaning, chemical pretreatment, degreasing, alkaline immersion, acid pickling and an activation by means of fluorides,

plating with chemical nickel in deposition from a bath of fluorides, and, if necessary, the deposition of a further coating.

Fig. 1

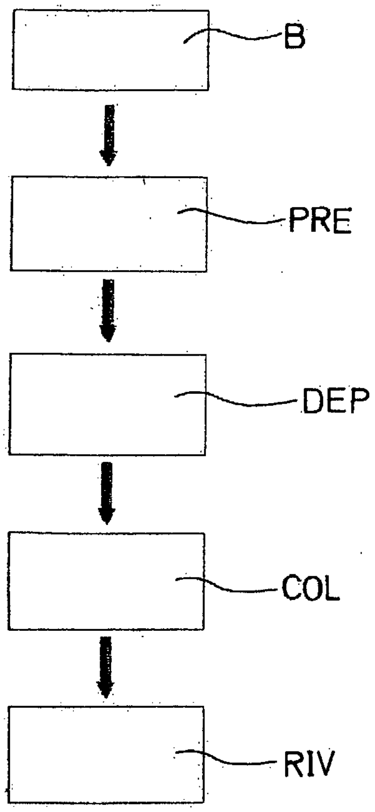
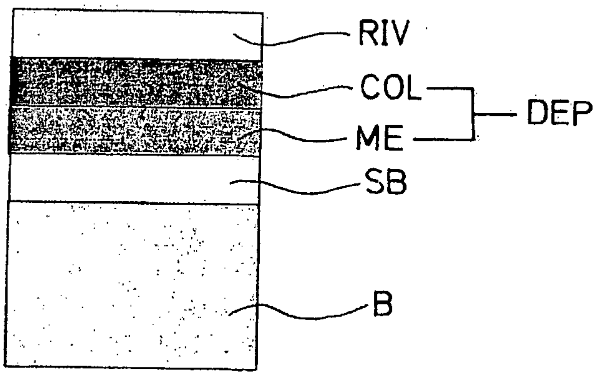


Fig. 2



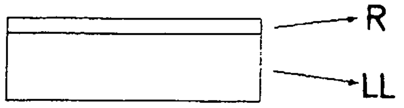


Fig. 3a

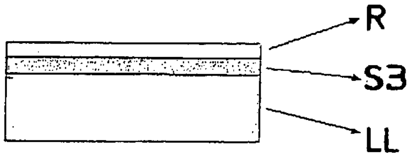


Fig. 3b

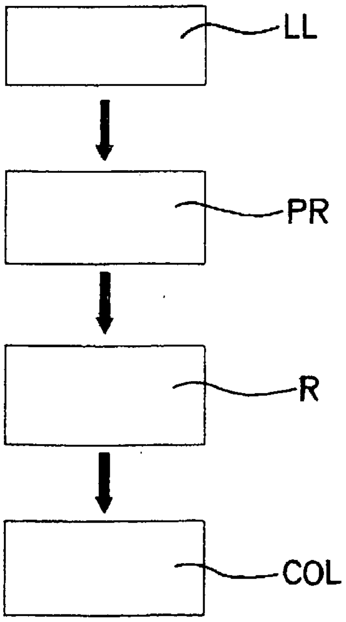


Fig. 4

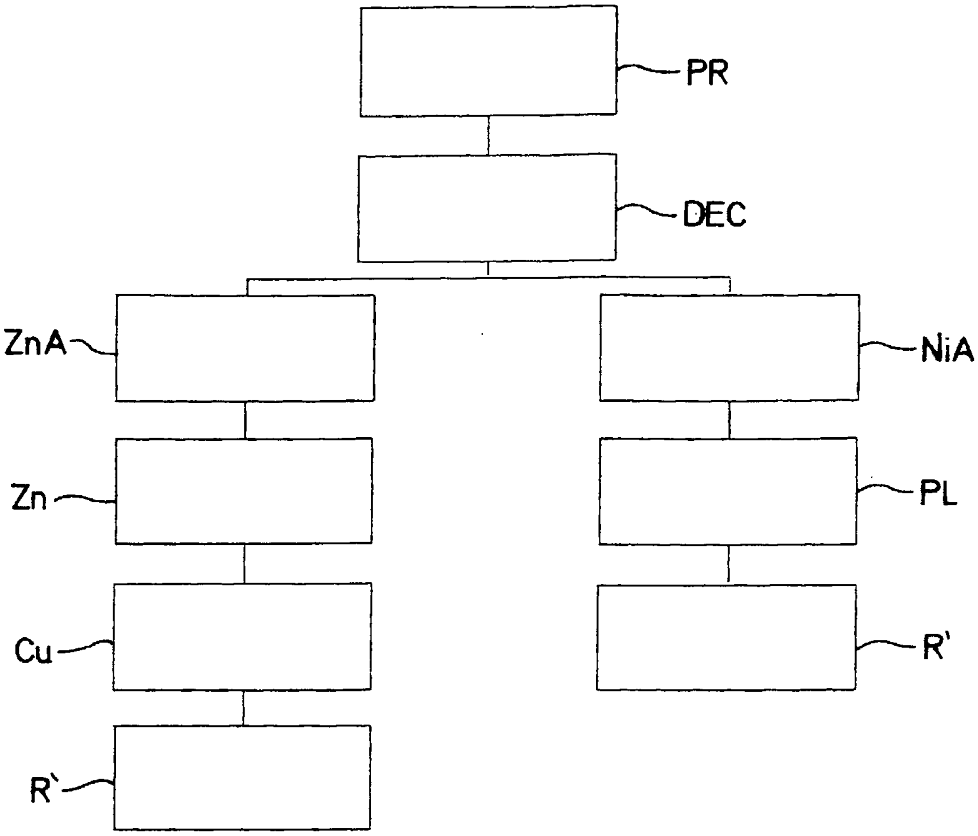


Fig. 5

Fig. 6a

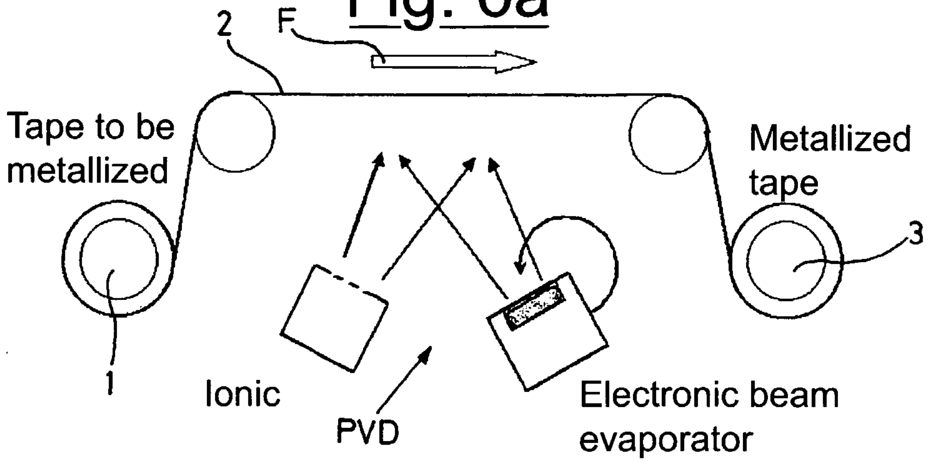


Fig. 6b

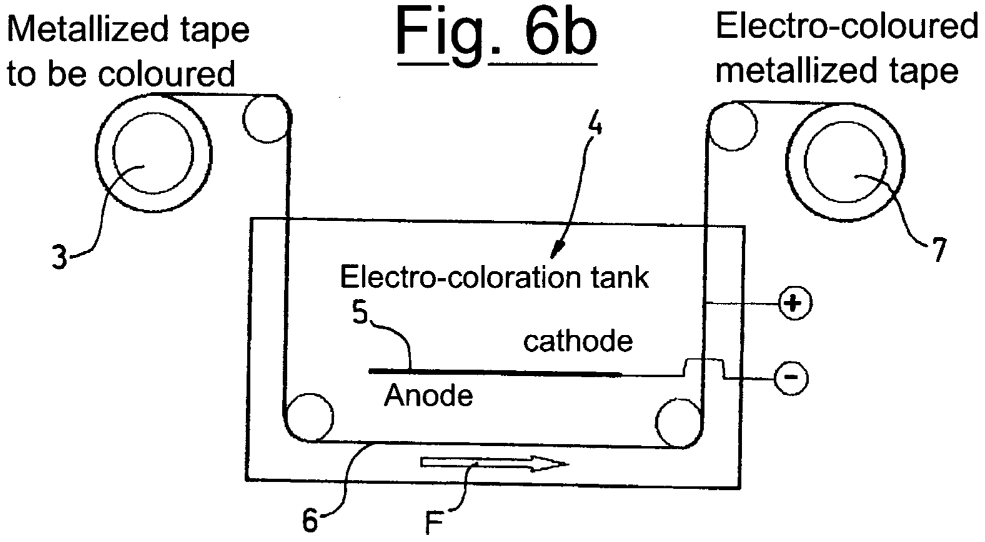


Fig. 7

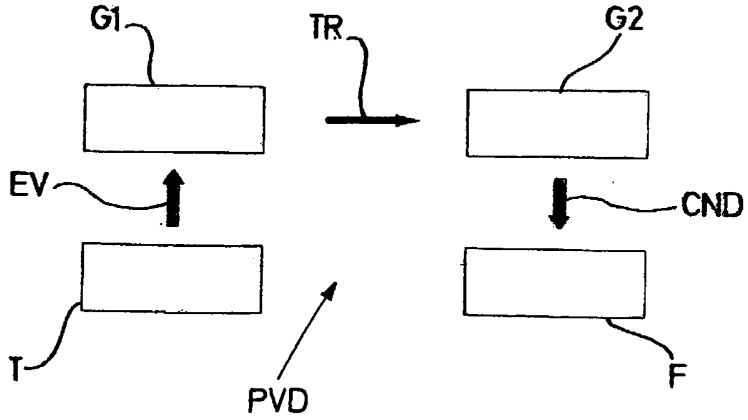


Fig. 8

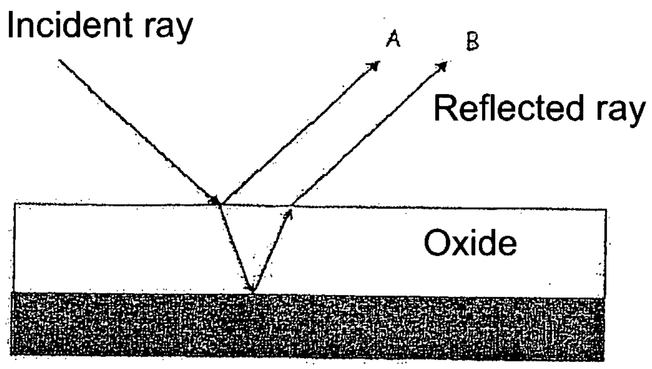


Fig. 9

Table 1

Colour	Temp. (°C)	Thick. (nm)	Colour	Temp. (°C)	Thick. (nm)
Yellow	371	30	Light green	510	95
Brass	385	35	Purple	523	110
Purple	398	40	Green	537	120
Violet blue	412	46	Pink gold	551	130
Purple blue	426	53	Purple red	565	140
Light blue	440	60	Bronze	579	150
Grey blue	454	63	Purple gold	593	160
Light sky blue	468	66	Pink	607	170
Green blue	482	70	Dark green	621	180
Light bronze	496	80	Grey	635	190

Fig. 10

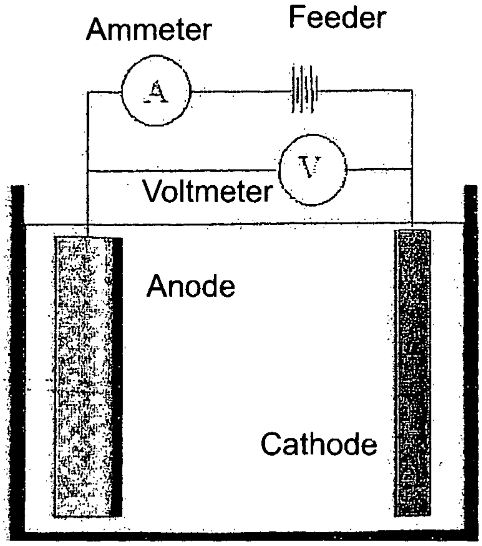


Fig. 11

Table 2

Cell voltage (V)	Titanium	Niobium	Tantalum
5	Yellow	Yellow	- - -
10	Brass	Brass	- - -
15	Purple	Plum	Brass
20	Violet Blue	Violet blue	Yellow
25	Purple blue	Sky blue	Purple
30	Light blue	Bluish grey	Violet blue
35	Grey blue	Light grey blue	Silver blue
40	Light sky-blue	Green gold	Sky blue
45	Green blue	Orange gold	Blue silver
50	Light bronze	Pink	Silver
55	Light green	Purple blue	Silver
60	Purple	Green blue	Silver
65	Green	See green	Light yellow
70	Pink gold	Gold green	Yellow
75	Purple red	Green brass	Gold
80	Bronze	Opaque gold	Copper
85	Purple gold	Green	Light orange
90	Pink	Plum pink	Gold orange
95	Dark green	Magenta	Purple Pink
100	Grey	Blue magenta	Purple

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2005/008750

A. CLASSIFICATION OF SUBJECT MATTER
C23C14/58 C23C28/00 C25D11/26 C23C4/08 C23C4/18
C04B41/52 C03C17/36 B05D5/06 D06M11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C23C C25D C04B C03C B05D D06M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; LEE, JI HWAN ET AL: "Method for coloring non-ferrous metal using titanium deposition" XP002352777 retrieved from STN Database accession no. 2002:64121 abstract & KR 2000 008 860 A (NEWMAT CO., LTD., S. KOREA) 15 February 2000 (2000-02-15) -----	1-10, 13-17

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search 7 November 2005	Date of mailing of the international search report 28/11/2005
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Mauger, J

INTERNATIONAL SEARCH REPORT

Inte[illegible]ional Application No
PCT/EP2005/008750

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	DE 101 18 763 A1 (FRIEDRICH-SCHILLER-UNIVERSITAET JENA) 17 October 2002 (2002-10-17) paragraph ‘0009! - paragraph ‘0016!; claims; examples -----	1-10, 13-17
X	DATABASE WPI Section Ch, Week 197847 Derwent Publications Ltd., London, GB; Class M11, AN 1978-84786A XP002352823 -& JP 53 119734 A (MITSUBISHI METAL CORP) 19 October 1978 (1978-10-19) abstract -----	1-10, 13-17
X	DE 198 09 932 C1 (AESCULAP AG & CO. KG) 28 October 1999 (1999-10-28) claims -----	1-10, 13-17
X	PATENT ABSTRACTS OF JAPAN vol. 012, no. 373 (C-534), 6 October 1988 (1988-10-06) -& JP 63 125660 A (SEIKO EPSON CORP), 28 May 1988 (1988-05-28) abstract -----	1-9,11, 13-17
X	PATENT ABSTRACTS OF JAPAN vol. 015, no. 112 (C-0815), 18 March 1991 (1991-03-18) & JP 03 002385 A (MITSUBISHI HEAVY IND LTD), 8 January 1991 (1991-01-08) abstract -----	1-9, 12-17

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[illegible]ormation on patent family members

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