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(54) Multivalent electrolytic process for the surface treatment of non ferrous metallic material

(57) A process for the electrolytic treatment of non-ferrous metal materials, such as for example magnesium, aluminium, titanium, vanadium and alloys thereof, particularly a process for the production of a surface coating which has both an aesthetic and a protective function.

Said process comprises at least one main treatment stage or anodic stage carried out in a tank or cell, using an alkaline solution which allows the simultaneous treatment of metal materials, even different metals, and/or materials made from alloys and/or combinations and/or other kind of various metals coupled together.

An object of the present invention is also products made from non-ferrous metal materials, provided with surface coatings obtained according to the above process.

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Description

OBJECT OF THE INVENTION

[0001] The object of the present invention is a process for the electrolytic treatment of non-ferrous metal materials, such as for example magnesium, aluminium, titanium, vanadium and alloys thereof, particularly a process for the production of a surface coating which has both an aesthetic and a protective function. Another object of the present invention is products made from non-ferrous metal materials, provided with surface coatings obtained according to said process.

BACKGROUND OF THE ART

[0002] In recent years, there has been significant development in the use of metals such as magnesium, titanium, and alloys thereof, while the use of aluminium and alloys thereof, for example high silicon content alloys, has remained constant and even increased. The increasing demand for the use of such materials has not been matched by the reciprocal development of surface treatment technologies, essential for the subsequent metal processing and for the uses to which they are intended.

[0003] Currently, there is an increasing interest in the possibility of manufacturing products from several different metals, for example, in order to be able to combine and exploit the light weight of magnesium with the rigidity or mechanical characteristics of titanium. For example, among the above-mentioned metals, aluminium, magnesium and titanium have always been treated separately and, frequently in relation to the latter two, in a manner that is unsuited to the technical requirements of the market.

[0004] In its extrusion and lamination alloys, aluminium is subjected to well-defined treatments, such as for example, anodic oxidation treatment or anodisation and painting.

[0005] With reference to the anodic oxidation treatment, this is carried out conventionally, in sulphuric acid solutions (160 - 220 g/l). The anodic layer thus formed may be further treated, for example it can be stained either by absorption, i.e. by immersing the aluminium pieces in solutions of organic or inorganic dyes, or electrolytically by treating the pieces with currents in suitable tin or nickel salt-based solutions. After treatment to close the pores of the oxide which has formed during the anodisation step and which is conventionally known as "fixing", the aluminium pieces thus produced show excellent corrosion resistance and, if dyed, the dyes have suitable light solidity.

[0006] Similarly to other metals, aluminium can also be painted. In this case, it is necessary to include a preliminary stage, providing a "chemical conversion" treatment, upon completion of which, it is possible to apply a paint which may be of the "powder" or "liquid" type. Once painted, the pieces must be subjected to a "curing" treatment, which generally consists of heat curing of the paint. The material thus obtained shows good light solidity and good corrosion resistance.

[0007] Finishings for aluminium have been known for some years, but, among others, the problem of how to treat high-silicon content alloys, such as for example, certain pressure casting alloys, is still unresolved. When the percentage of silicon in the aluminium alloy exceeds 5%, both the anodic oxidation process and painting become difficult, and frequently the quality of the product obtained is poor. Indeed, due to the silicon content, the usual chemical conversion treatments prior to painting do not ensure adequate paint adhesion during the subsequent painting stage. Likewise, during the anodisation stage, the anodic oxide forms badly and, frequently, appears greyish and soft, providing the product with poor corrosion resistance.

[0008] On the other hand, with regard to magnesium, it is essential to consider that up to ten years or so ago, it was considered to be a metal for special applications, where it was desired to better exploit its mechanical characteristics and light weight. However, more recently, due to the large price reduction as a result of the increased market availability, its use has become more widespread and competitive, with respect to aluminium for example, also due to its lightness and malleability. In practice, a magnesium alloy weighs 35% less than an analogous aluminium alloy with similar mechanical characteristics, and furthermore, can be "cast" much thinner without forming "bubbles". Furthermore, magnesium is frequently used in place of plastic for delicate applications such as for example laptop computer, camera and CD player casings, and is beginning to be used in place of aluminium in mechanical pressure casting applications.

[0009] The corrosion resistance of magnesium, and the alloys thereof, is very poor and, in the absence of surface treatments, is unsuitable for the majority of applications. Up to a few years ago, all magnesium materials were destined for painting after chemical conversion treatment. The most commonly used chemical conversion treatments are based on chromic acid, chromates or dichromates (known by the trade names Dow 1, Dow 9, etc.. because they were introduced by Dow Chemicals at the end of the 1940s) and are considered suitable for indoor use, and for products subjected to mild wear. Recently, chromium-free conversion treatments have been introduced which, even though they should be preferred due to their reduced toxicity, from the quality viewpoint, the results are similar to those obtained using traditional treatments.

[0010] In any case, even in relation to magnesium, the best treatments, both as such and even those prior to treatment, involve anodisation.

[0011] The anodisation processes mostly used in the past (which can be traced to US patent US 2901409 and known commercially as Dow 17 and Dow HAE) are still valid today as a pre-treatment to painting, in as much as in any case they give good adhesion and satisfactory corrosion resistance, even in comparison to the above mentioned conversion processes.

[0012] With passing time, the operational complexity, the toxicity of the processes mentioned and/or the less than perfect resistance to corrosion and abrasion of the materials thus treated, have led to the formulation of new technologies.

[0013] A typical outline for anodisation treatment, common to all routinely used treatments, is as follows:

a) Alkaline degreasing
b) Washing in running water
c) Acid pickling (activation)
d) Washing in running water
e) DC or AC anodisation
f) Washing in running water
g) Washing in deionised water
h) Washing in hot deionised water
i) Fixing (chemical or resin).

[0014] Generally, it can be said that the more recently developed treatments, which are chromium-free and have lower toxicity, have the following characteristics:

1. they produce colourless coatings,
2. they use medium or high alkalinity treatment solutions,
3. they ensure a substrate with optimal paint adhesion properties,
4. they ensure a substrate with medium to high corrosion resistance (depending on the type of treatment),
5. they ensure a substrate with medium to high abrasion resistance (depending on the type of treatment),
6. they allow the use of AC or DC current, characterized by high voltage (150 - 600 V) and in some cases, even high current density (3 - 30 A/dm^2).

[0015] It should be considered that, in certain processes, there is an intense "luminosity" surrounding the piece undergoing treatment, due to a dense series of discharges reaching it and which contribute towards the formation of the protective layer.

[0016] With reference to titanium, it is only recently that there have been developments making it essential to study specific surface treatments for this metal. Again, in this case, the most commonly used treatment is anodic oxidation, achieved in a similar manner to that for aluminium, in either acid or alkaline environments. Anodising in an acid environment (regardless of whether produced by sulphuric or phosphoric acid) produces coloured coatings (due to the interference effect), the tone of which depends on the voltage applied (15-100 Volt) and the purity of the alloys. The oxide layer thus formed contributes to the aesthetic appearance of the pieces, and can be particularly applied to dentistry and prosthetics in general, because the colour imparted is used to characterize the mechanical characteristics of the piece itself. However, when particular mechanical or structural pieces must be treated, anodising must always be alkaline as prescribed, for example in US standard AMS 2488D currently in force for the use of titanium in the aerospace sector.

[0017] There are no processes described for the treatment of pieces formed by coupling pieces of various different metals, selected from aluminium, magnesium, titanium or the alloys thereof.

[0018] According to the prior art, the solutions used for anodising treatments may contain anions such as fluorides, borates, silicates and phosphates, which are all capable of forming complex salts with the metals undergoing treatment, for example, with magnesium.

[0019] For adjusting the alkalinity, alkaline metals (Li, Na, K) or ammonia or amines may be used as cations. The metal immersed in the solution necessary for the anodising treatment, is normally connected to one pole of a current supply, with a second piece of metal connected to the other pole (if conventional AC will be used) or an inert cathode (for example stainless steel) in the case where DC must be used. With passing the electrical current, a salt compound, containing those anion(s) present in the solution will form on the surface of the metal piece, with the cations(s) being, other than the metal, one of more of the cations used to adjust the pH of the solution. This is anodisation of the metal and not anodic "oxidation" of the metal, since the quantity of oxide produced is noticeably less than that of the complex salts mentioned above.

[0020] Preferably, the formation of the layer occurs when the piece acts as an anode in the electrical cell, also when alternating current or complex waveforms with one negative part are used, whereby the term "anodisation", for the most part, remains correct.

[0021] If operating at constant current density, since the layer is highly insulating during formation, the voltage applied will increase rapidly with the increasing thickness of the oxide layer being formed.

[0022] Beyond certain values (for example, 200- 300 V, depending on the type of alloy treated and the composition of the solution) a visible formation of electrical discharges between the cathode and anode are observed (giving rise to the definition of "micro arc" (MAO) or plasma anodisation). In some processes, the voltage can reach 700 V with a ΔV of even 1000 V if a negative part is inserted.

[0023] The oxide layer formed by discharge (for example both in the case of magnesium and aluminium materials) is mainly made of two components: one more compact with a thickness of 10-20 microns, depending on the duration of the process, and another rougher with a thickness of 2-3 microns. This occurs because the discharges which reach the surface of the metal compress the underlying layers, thus increasing the compactness and hardness thereof and, obviously, the outermost parts are made rough by the discharges themselves. Standard industrial practice is to eliminate the first 2-3 microns of the product layer in order to be able to completely exploit the hardness properties of the remaining part of the layer. With this system, it is possible to obtain, for example on aluminium, up to 2000 HV of hardness (and 400-600 HV on magnesium).

[0024] As the thickness of the layer produced is solely a function of the intensity of current passed (i.e. the Ampere hours - Ah), it is understood that the cost of the process is highly associated with the voltage required for maintaining the current used for the production of the desired layer. This voltage depends on the composition and temperature of the solution, as well as the resistivity of the layer.

[0025] In brief, the processes according to the prior art have the following drawbacks.

- ➢ All processes involving the discharge effect (micro-arc or plasma) are very expensive.
- ➢ Anodising bath solutions containing silicates and/or aluminium are not very stable and tend to form precipitates which must be eliminated for the solution itself to operate optimally. It is also difficult to constantly monitor the composition of the solution.
- ➢ Compositions containing fluorine, boron and amines are toxic, and difficult to handle and store.
- ➢ Frequently the compositions contain mixtures of anions and/or cations, the monitoring and balancing of which, while managing an industrial anodizing treatment bath, can be difficult.
- ➢ All the processes according to the prior art (independently of the metal in question), provide one or more preliminary cleaning, pickling and/or activation stages of the surface to be treated. The degreasing products which must be used frequently contain borates, while the "activation" products contain mostly fluorinated compounds in an acid environment (hydrofluoric acid, and the compounds or derivatives thereof).
- ➢ None of the claimed processes provides being able to treat coupled or mixed materials, or materials made by the association of various metals in alloys or the like.
- ➢ Furthermore, anodising baths, according to the prior art, do not allow the simultaneous treatment of several different metals, but require a different bath for each type of metal to be subjected to the anodising process, and hence additional costs for the replacement of the bath, each time a different metal has to be treated.

OBJECTS OF THE INVENTION

[0026] The object of the present invention is that of providing a process for the surface treatment of non-ferrous metal materials, which is both economical and does not involve the use of toxic or potentially hazardous substances.

[0027] Another object of the present invention is that of providing a process for the surface treatment of non-ferrous metal materials providing the use of stable solutions, with constant composition, and which do not require frequent replacement of the solutions used.

[0028] Another object of the present finding is that of providing a process for the surface treatment of non-ferrous metal materials, which does not provide separate preliminary stages of cleaning, and/or degreasing and/or activation of the metallic surfaces which must be subjected to treatment, and which thus allows performing the surface treatment of the metal material in a single main stage.

[0029] An additional object of the present invention is that of providing a process for the surface treatment of non-ferrous metal materials, which allows the simultaneous treatment of different metals and/or products manufactured in different parts using different metals and/or in non-ferrous metal alloys, inside the same bath.

[0030] Another object of the finding is that of providing a process for the surface treatment of non-ferrous metal materials which allows the simultaneous surface treatment of coupled or mixed materials, or materials made by combining various metals in alloys or the like, with consequent advantages, even from the economic viewpoint.

[0031] A further object of the present invention is that of providing non-ferrous metals, materials and products made using said metals and/or alloys thereof, provided with a surface coating obtained by means of the process being the object of the present invention.

DESCRIPTION

[0032] These and further objects and the advantages thereof which will be better appreciated from the description below, are achieved by means of an electrolytic process for the treatment of non-ferrous metal materials which comprises at least one main treatment stage or anodic stage, carried out in a bath or cell, said stage being carried out using an alkaline solution allowing the simultaneous treatment of metal materials even different from each other, and/or alloys and/or combinations and/or any other kind of association of various metals.

[0033] Particularly, said alkaline solution consists of phosphoric acid, ammonia and/or alkaline hydroxides and/or phosphates, and has a pH value comprised of between 7 and 10. Particularly, said alkaline hydroxides are selected from lithium hydroxide, sodium hydroxide, potassium hydroxide and said phosphoric acid is present in concentrations comprised of between 1 and 50 g/l, preferably at a concentration comprised of between 15 and 20 g/l, while said ammonia and/or said alkaline hydroxides are present at a concentration comprised of between 3 and 150 g/l, preferably at a concentration comprised of between 45 and 60 g/l. Said non-ferrous metals are advantageously selected from aluminium, titanium, magnesium and vanadium.

[0034] The process according to the present finding offers numerous advantages, and particularly allows eliminating the pre-treatment stages, normally provided in the processs according to the prior art. In practice, with the process being the object of the invention, the separate preliminary stages of cleaning, and/or degreasing and/or activation of the metal surfaces to be treated, for example in order to carry out surface anodising, are completely eliminated, and it is possible to use a single tank or bath for the main treatment stage, without requiring a succession of different baths, containing different solutions, in order for example to carry out the cleaning stage, then the degreasing, and finally the activation of the surface of the material to be treated. Thereby, it is possible to perform the main anodising treatment as a single stage, and it is thus possible to create a system avoiding a series of successive tanks, but a single main tank, with consequent significant advantages, both in relation to the size of the system, in addition to economic advantages.

[0035] Again, with the process being the object of the invention, it is possible to perform the main anodising treatment simultaneously on non-ferrous metal materials even different from each other, or even on products made of different non-ferrous metals in combination with one another inside the same material or on materials made, at least partially, from non-ferrous metal alloys. All the above is a significant technical advance with respect to the anodising processs according to the prior art, where tanks required to be always provided, which were separate and distinct from the main tank, in order to perform the aforementioned pre-treatments (cleaning, and/or degreasing and/or activation). Indeed, the pre-treatments according to the prior art are carried out using several solutions, at different concentrations and, in some cases, even just using water. For this reason, it is essential to perform each individual step in a different tank or bath, in order to be able to use the solution most suited to the type of treatment to be carried out in view of the main anodizing treatment. Furthermore, according to the present invention, the use of a basic solution as described above, allows simultaneous treatment, in the same anodising tank or bath, of non-ferrous metals even different from each other, or even products made from different metals coupled or fused together or even products made from non-ferrous metal alloys. On the other hand, with the processes of the prior art, it was necessary to perform a specific anodising treatment for each type of metal, and it was not possible to treat different metals at the same time, and in the same bath.

[0036] Therefore, one of the main objects of the present invention is that of simplifying the existing technology by reducing the operational complexity and costs thereof and allowing materials such as magnesium, aluminium and titanium (and alloys thereof), or pieces coupled together in any way, to be treated in the same solution, and even simultaneously.

[0037] For example, in the case of magnesium, for many years it has found specific and highly appreciated use in advanced mechanics above for military or aerospace use, where even the very high finishing costs were easily absorbed by the high added value of the finished product. However, since the cost of magnesium metal became comparable, even if not lower than that of aluminium, its use has expanded enormously to consumer products, with the consequence that the cost of the finishing must be proportional to the actual value of the item manufactured.

[0038] In order to contain costs and to make the product competitive, even with respect to consumer materials, it is therefore essential to simplify both the chemical and electric parts (power consumed) of the anodising process. The process according to the invention allows the achievement of the objectives set out above, while boasting the characteristics described below.

[0039] With the process being the object of the invention, it is possible to provide the elimination of all preliminary cleaning, degreasing, and above all activation treatments. Such treatments, which are absolutely essential if the anodising process is conducted according to the prior art, provide treating the metal materials with solutions based on, for example fluorinated acids or fluoride salts, which constitute both significant operational complexity and an environmental and health problem for the workers involved in the process.

[0040] The process being the object of the present invention is further a significant simplification in relation to the solution used for the main treatment, the composition of which is not binding, but can be selected on the basis of low cost and operational practicability. The solution must be suitable for the treatment of magnesium, vanadium, aluminium and titanium, even simultaneously. For example, a small amount of phosphoric acid or alkaline phosphate (for example

15 g/l) is essential, along with a varying amount of ammonia or alkaline hydroxides (lithium, sodium or potassium) in amounts sufficient to adjust the pH of the solution to values of between pH 7 and 10. Higher pH are only essential if systematically producing high thickness layers (in excess of 20 microns). The preferred temperature is comprised of between 20-25 °C, without the need for any specific accurate temperature control. This solution is easily managed, as a filter pump can keep it scrupulously clear by eliminating any traces of contamination and precipitates.

[0041] The electrolytic treatment of the anodising stage is preferably carried out using a known power supply, such as described in EP 0619643. Said power supply is well suited to the purposes indicated, in that it has an automatic supply current parameter adjustment system. An electrolyte of the type described above is introduced into the electrolytic cell, i.e. into the treatment tank, and two plates, preferably made of stainless steel, which will essentially act as the cathode, are positioned along the long walls of the tank itself, while arranged in parallel to these, in the middle section of the cell or tank, will be immersed one or more pieces to be subjected to the treatment.

[0042] The following tables report some treatment examples, and some examples (on magnesium) of how the process according to the invention allows the attainment of different thicknesses of surface oxide layer which is formed on the metal, depending on the treatment time and not the intensity of the current, which is the case in the process according to the prior art.

Table 1 - Example treatment program

	Stage			
Description	**Wait time**	**Cleaning/activation**	**Wait time**	**Anodising**
	No current	Negative current (cathodic stage)	No current	Positive current (anodic stage)
	Duration 30 s	Ramp 30 seconds Current 2.0 A/dm^2 Duration 2 minutes	Duration 5 s	Ramp 1-5 minutes Current 2.0 A/dm^2 Duration 1-20 minutes
Function	Allows the pieces to be suitably bathed in the solution	Eliminates dirt and grease from the surface, activating it and making it reactive to the subsequent anodisation	Allows depolarization of the pieces and the elimination of the gasses produced.	Forms the layer, the thickness of which will be a function of the treatment time.

Table 2 - Product thickness (indicative) as a function of treatment time in the anodisation stage and maximum voltage (indicative) reached (with reference to magnesium alloys)

Thickness (μm)	**Program**	**Maximum voltage (V)**	**Application**
< 5	Ramp 5 minutes Current 2.0 A/dm^2 Duration 1 minute	180	Pre-treatment to painting.
Approx. 10	Ramp 5 minutes Current 2.0 A/dm^2 Duration 5 minutes	225	Pre-treatment to painting.
15-20	Ramp 5 minutes Current 2.0 A/dm^2 Duration 10 minutes	275	Unpainted layers, With aesthetic properties
20-25	Ramp 5 minutes Current 2.0 A/dm^2 Duration 15 minutes	315	Unpainted layers, with aesthetic properties

(continued)

Thickness (μm)	Program	Maximum voltage (V)	Application
Approx. 30	Ramp 5 minutes Current 2.0 A/dm^2 Duration 20 minutes	350	Special applications
Notes about the table.			

[0043] It should be considered that in any case it is difficult to accurately measure the thickness of the layer obtained, using the induced current process (the same used for anodized aluminium in an acid environment), since on certain alloys the finished surface is rough. It should be furthermore considered that there are many factors which affect the maximum voltage reached at the end of the process, for example, the kind of alloy, the temperature of the solution used and the type of material used for holding the material to be subjected to treatment.

[0044] Again, according to the invention, it is possible to perform treatments subsequent to the main anodisation described above. These subsequent treatments, also known as post-treatments, must be commensurate with the final application, whereby we will now outline various options.

[0045] For example, again considering magnesium as the selected material, following thorough washing in water, the magnesium material is either sent for drying, if intended for painting, or if it is desired to keep the satin white appearance obtained by the anodic oxidation process, the material is sent for a fixing treatment. Three types of "post treatments" are provided, depending on the type of quality it is desired to achieve. If we use corrosion resistance in a neutral saline cloud, according to ASTM B 117 as a parameter, then the following treatment *1.a)* ensures corrosion resistance of about 100 hours (even though for many applications 8-24 hours are required), the subsequent treatment *1.b)* may exceed 200 hours, while option *1.c),* besides increasing corrosion resistance significantly beyond 200 hours, it confers a surface "lubricity" (slipperiness) frequently required for mechanical pieces.

> *1.a) Fixing with surfactants.* A solution is prepared containing an anionic surfactant (for example an alkyldiphenyloxide sulphate disodium salt - CAS No. 11935-04-9, sold as Dowfax 2A1 by "Dow Chemical Company) at a concentration of 10 g/l. The process operates at a temperature of at least 80 °C for an immersion time of at least 5 minutes. The subsequent wash step is optional. Preferably the pieces are then dried using conventional systems.
>
> *1.b) Fixing with silicates and surfactants.* The anodized pieces are first treated in a solution of sodium silicate (soluble glass) at an indicative concentration of 10 g/l, at a temperature of at least 50 °C for a time of at least 5 minutes. After washing in running water, the treatment continues as in point *1.a.* The pieces are then dried in a kiln at a temperature of at least 80 °C.
>
> *1.c) Fixing with PTFE (Teflon or the like).* The anodized and subsequently washed pieces are immersed in a solution containing a transparent or black coloured PTFE polymer, depending on the final application (or the aesthetic requirements of the piece) scrupulously adhering to the manufacturers instructions. After treatment, the piece is dried appropriately in order to aid polymerization of the impregnated or surface layer.

[0046] Always according to the invention, the materials anodized by the main treatment as described above can be subjected to special treatments. For example, in the case of magnesium materials, there are two possible absorption colouring systems, using azoic dyes.

> *2.a) Two stage colouring.* The layer produced by means of the process being the object of the invention, may be coloured by immersing the material, following anodising and subsequent washing, into the colouring solution prepared at the concentrations and following the conditions of use provided by the manufacturer. In practice, all the dyes used for colouring anodized aluminium can also be used to colour the layer produced on magnesium, preferably selecting those which operate in alkaline or only weakly acid environments, so as to avoid slight chemical etching on the composite layer formed previously on the magnesium. It is preferable to "fix" the coloured layer thus obtained using the process described in part *1a)* or apply a transparent varnish to protect both the anodic layer and the colour imparted from any alterations due to corrosion or exposure to light.
>
> *2.b) Single step colouring.* Almost all the dyes indicated for the above described process dissolve and are also stable in the solution used for anodising according to the present invention, and their chemical structure is not altered by passing the current necessary for the process in question. Under such conditions, by adding a suitable quantity of dye (for example between 1 and 50 g/l depending on the type of dye and the manufacturers instructions) to the solution used for anodising, the layer formed during the electrolytic or anodising process, will incorporate particles of dye, taking on the same basic colour. After thorough washing, it is preferable to "fix" the coloured layer thus obtained using the process described in part *1a)* or it is preferable apply a transparent varnish to protect both the

anodic layer and the colour imparted from any alterations due to corrosion or exposure to light. For example, said process becomes advantageous when it is desired to repeatedly produce large quantities of materials of the same colour.

[0047] The electrolytic solution used for the main anodising treatment forming the subject of the process according to the invention, has shown itself to be polyvalent (or multi-use), since it can be advantageously used for both metals such as magnesium, and for titanium or aluminium, even when in alloys with one another, when coupled together or when held in the same piece holder for treatment.

[0048] The object of the present invention is, accordingly, an electrolytic process for producing a coating that is both aesthetic and protective, on non-ferrous materials such as magnesium, titanium, vanadium and aluminium (and alloys thereof), even when such metals are coupled together in various ways to form a single product. The process is carried out by providing the pieces to be treated, duly immersed in an electrolyte solution contained in a cell with adequate characteristics and fitted with "counter-electrodes", with a preferably DC current, but with particular characteristics.

[0049] The electrolyte solution is alkaline in nature and has been specially formulated to be free of toxic ions such as chromium, both hexavalent and trivalent, fluorides, borates or amine derivatives in any form.

[0050] Said process is characterized by not providing any preliminary degreasing or activating treatments, whereby the treatment is carried out in an individual tank or cell, allowing considerable simplification of the system, besides significant financial savings.

[0051] Suitable use of current, preferably supplied by a special power supply, allows producing a coating of the thickness desired, just by essentially varying the treatment time.

[0052] The treatment thus described improves both the corrosion resistance properties and the aesthetic properties of the starting material, which can be further increased according to particular needs, by means of a further specific post-treatment.

[0053] The process being the object of the invention allows treating said metals even when they are in special alloys (for example aluminium casts containing up to 10% silicon) or when coupled together in various ways to form a single piece or product.

[0054] The process, as stated above, further allows resolving the problem of using the same system to treat for example magnesium, aluminium, especially if in high silicon alloys, titanium and the like, and of treating mixed pieces (with parts for example made of aluminium and magnesium coupled together).

[0055] The above will now be better exemplified through the series of 5 examples reported below, given by way of non-limiting indication of the present invention.

Applicative examples

Preliminary notes

[0056] 1) All samples have been produced under the same operational conditions, in order to highlight the simplicity and flexibility of the process proposed.

2) The electrolytic cell (treatment bath) was made of Moplen and sized 700 x 300 x 700 mm. 316L stainless steel sheets were positioned along the long walls of the tank and connected to a ring- closed aluminium crossing and connected to the negative pole (cathode) of the current power supply. A piece holding bar was positioned longitudinally at the centre of the tank and connected to the positive pole (anode). Holders can be strips of titanium 99.5 or small pieces of extruded aluminium alloy 6060, regardless of the type of material to be treated. The use of aluminium holders slightly increased the voltage used. Individual pieces were fixed to holders using standard plastic clips used in the traditional anodic oxidation of aluminium.

3) The treatment tank was fitted with a heat exchanger connected to a refrigerator.

4) The treatment tank was fitted with compressed air by means of agitation.

5) The solution was held filtered by means of a filter pump with paper disks with a porosity of 5 microns.

6) The current supply, of the type indicated above, delivered a maximum power output of 450V x 50 Ampere.

7) For each individual treatment or test, one or more pieces (indifferently), up to a maximum immersed surface area of 20 dm^2 were used.

8) After each treatment, the holders were suitably pickled in order to remove the layer previously produced.

9) The solution used for anodising was the following:

Phosphoric acid	15 g/l
Ammonia (25%)	50 g/l
Temperature	20 - 25 °C

(continued)

Current density	2 A/dm^2

and the programs indicated in tables 1 and 2 are used. In practice, the duration of the anodic stage is varied, as required, leaving all the other parameters unchanged.
The individual alloys treated are indicated in the separate examples.
10) Post-treatments optionally applied to the layer produced.
a) Painting using epoxide powder (e.g. RAL 7001 - DuPont code No. 9003461)
b) Fixing with surfactant

Dowfax 2A1	10 g/l
Temperature	80 °C
Immersion time	20 minutes

c) Fixing with silicate

Sodium silicate (soluble glass)	10 g/l
Temperature	70 °C
Immersion time	20 minutes

d) Fixing with PTFE, according to the suppliers data sheet.
[0057] For descriptive simplicity, the tables report the most significant applicative examples

Table 3 - Applicative examples on magnesium alloys.

Example	**1**	**2**	**3**	**4**
Alloy	AZ91	AZ 91	ZK60	AZ31

Type of piece	Small pressure cast tool sheath	Pressure cast motorcycle wheel block	Forged motorcycle wheel block	Thixo glued cell phone casing
Layer thickness (microns)	20	20	20	10
Post treatment	Varnishing	Varnishing	Varnishing	Fixing with surfactants
Quality control Result	Adhes. ISO2409	Adhes. ISO2409	Adhes. ISO2409	ASTM B117
	OK	OK	OK	
	Machu test	Machu test	Machu test	
	OK	OK	OK	
	Pressure cooker	Pressure cooker	Pressure cooker	Corrosion sets in after 70 hours
	OK	OK	OK	
	ASTM B117	ASTM B117	ASTM B117	
	OK after 1000	OK after 500	OK after 500	
Notes	1	2	2	3

Notes:

1) The conventional dichromate system on the same piece does not exceed 200 hours.

2) Test stopped since for this application, the minimum limit is 384 hours.

3) For this application, only 24 hours are required.

Table 3 (cont.).

Example	**5**	**6**	**7**	**8**
Alloy	AZ31	AZ 91	AZ91	AZ91
Type of piece	Thixo glued cell phone casing	Pressure cast car wheel block	Pressure cast car wheel block	Piece of photographic

Layer thickness (microns)	20	20	20	20
Post treatment	Surfactant + silicate fixing	Colouring + surfactant fixing	Colouring + surfactant fixing	Colouring + surfactant fixing
Quality control	ASTM B117	ASTM B117	Not done	Not done
Result	Corrosion sets in after 250 hours	Corrosion sets in after 50 hours		
Notes	4	5-6	7	8

***Notes** (cont.)*

4) Value required for this 200 hour application.

5) Colouring has been carried out in a solution of

MLW black (Clariant)	20 g/l
Temperature	50 °C
Immersion time	20 minutes

6) Reference value: 24 hours

7) Colouring has been carried out by adding 20g/l of MLW black Clariant directly to the anodising solution.

8) The resulting coloration is uniform. Colouring has been carried in a solution of

RI Orange (Clariant)	20 g/l
Temperature	50 °C
Immersion time	20 minutes.

Colouring was correct

Table 4 - Applicative examples on aluminium alloys

Example	**1**	**2**	**3**	**4**
Alloy	6082	5754	6063	2024
Type of piece	Flat sheet	Flat sheet	Extruded	Mechanical detail
Layer thickness (microns)	< 10	< 10	< 10	----
Colour	Porcelainised white	Porcelainised greyish white	Straw white	Porcelainised white
Post treatment	Surfactant fixing	Surfactant fixing	Surfactant fixing	Colouring + surfactant fixing
Quality control	ASTM B117	ASTM B117	Not done	Not done
Result	No corrosion after 2000 hours	No corrosion after 2000 hours		
Notes	1			2

Notes.

1) The material has a covering, porcelainised white colour.
2) This is a high copper content alloy.

Table 4 (cont.)

Example	**5**	**6**	**7**	**8**
Alloy	GAISi9	GAISi8	GAISi12	GAISi18
Type of piece	Pressure cast mechanical piece	Lorry piston	Motorcycle piston	Car piston
Layer thickness (microns)	approx. 15	approx. 15	approx. 15	approx. 15
Colour	Porcelainised grey	Porcelainised grey	Porcelainised grey	Porcelainised white
Post treatment	Surfactant fixing	Surfactant fixing	Surfactant fixing	Surfactant fixing
Notes	3	3	3	3

***Notes* (cont.)**

3) The material has a smooth porcelainised grey appearance.

Table 5 -Applicative examples on titanium alloys

Example	1	2	3	
Alloy	99.5	99.5	Ti6Al4V	
Type of piece	Flat sheet	Flat sheet	Flat sheet	
Layer thickness (μm)	> 20	> 20	> 20	
Colour	Porcelainised white	Porcelainised white	Yellowish	
Post treatment	Surfactant fixing	Varnishing	Surfactant fixing	
Quality control	Not done	Adherence ISO2409	Not done	
Result		OK		
Notes	1		2	
Notes 1) Titanium is easily anodized at voltages slightly lower than those for magnesium. Alkaline anodising of this type can fall within US MIL specifications, and the materials thus produced are suitable for the aeronautics industry. 2) The colour depends on the composition of the alloy. Even vanadium can be anodized in an alkaline environment, analogously to magnesium, aluminium, titanium and zinc.				

Table 6 -Applicative examples of mixed pieces

Example	1	2	3	4
Alloys	Titanium 99.5 Magnesium AZ31	Aluminium ASTM6060 Magnesium AZ91	Titanium 99.5 Aluminium ASTM 5005	Magnesium ZK60 Aluminium 6060 Titanium Ti6Al4V
Type of piece	Flat sheet	Aluminium extrudate Pressure moulded magnesium	Flat sheet	Motorcycle wheel hub Hub (MG)-Flange (Al) - Flange fixing screws (Ti)
Layer thickness (μm)	> 20 on both metals	> 20 on Magnesium < 10 on aluminium	> 20 on titanium < 10 on aluminium	>20 on magnesium and titanium < 10 on aluminium
Post treatment	Surfactant fixing	Surfactant fixing	Surfactant fixing	Surfactant fixing

Claims

1. An electrolytic process for the treatment of non-ferrous metal materials comprising at least one main treatment stage or anodic stage carried out in a tank or cell, said stage being carried out simultaneously even on different metallic materials, and/or materials made by association in alloys and/or coupling and/or other types of association of different metallic materials, using an alkaline solution.

2. The process according to claim 1, **characterized in that** said alkaline solution comprises phosphoric acid and/or phosphates and/or ammonia and/or alkaline hydroxides, and has a pH value comprised of between 7 and 10.

3. The process according to claim 2, **characterized in that** said alkaline hydroxides are selected from lithium hydroxide, sodium hydroxide, potassium hydroxide.

4. The process according to claim 2, **characterized in that** said ammonia and/or said alkaline hydroxides are present at a concentration comprised of between 3 and 150 g/l, preferably at a concentration comprised of between 45 and

60 g/l.

5. The process according to claim 2, **characterized in that** said phosphoric acid is present at a concentration comprised of between 1 and 50 g/l, preferably at a concentration comprised of between 15 and 20 g/l.

6. The process according to claim 1, **characterized in that** said non-ferrous metal materials are selected from aluminium, titanium, magnesium, vanadium.

7. The process according to claim 1, **characterized in that** it is carried out in an individual tank or cell, by immersion of said non-ferrous metal materials in said alkaline solution.

8. The process according to claim 1, **characterized in that** it further comprises a stage in which said metal material is degreased and/or activated by means of a step without current lasting between 5 and 300 seconds, preferably 30-60 seconds.

9. The process according to claim 8, **characterized in that** said stage, in which said metal material is degreased and/or activated, is followed by a cathodic stage with an overall duration of 10 to 600 seconds at a current density comprised of between 1 and 10 A/dmq, preferably 2 A/dmq, reached by a ramp up with an overall duration of 5 to 60 seconds, preferably 30 seconds.

10. The process according to claim 9, **characterized in that** following said cathodic stage, there is a pause without current lasting 1 to 100 seconds, preferably 5-10 seconds, followed by said anodic stage.

11. The process according to claim 1, **characterized in that** said anodic stage has a duration of 10 seconds to 60 minutes, at a current density comprised of between 1 and 10 A/dmq, preferably 2 A/dmq, with a ramp up with an overall duration of 10 to 600 seconds, preferably 60 to 300 seconds.

12. The process according to claim 1, **characterized in that** said anodic stage is followed by a colouring treatment by the immersion of said metal materials in solutions of organic dyes, preferably at a concentration of 20 g/l, a temperature of 50°C for a duration of 20 minutes.

13. The process according to claim 1, **characterized in that** said metal material is subjected to colouring during said anodic stage by the addition of organic dyes to said alkaline solution, preferably at a concentration of 20 g/l.

14. The process according to claim 1, **characterised in that** said anodic stage is followed by a fixing treatment in an aqueous solution comprising at least one anionic surfactant at a concentration comprised of between 1 and 100 g/l, preferably 10 g/l, at a temperature in excess of 80 °C and for an immersion time in excess of 5 minutes.

15. The process according to claim 1, **characterised in that** said anodic stage is followed by a fixing treatment in an aqueous solution comprising at least one silicate and at least one surfactant, preferably sodium silicate at a concentration of between 1 and 30 g/L, preferably 10 g/l , and at a temperature in excess of 50 °C for a period of time in excess of 5 minutes, followed by an optional additional fixing in accordance with claim 13.

16. The process according to claims 14 and 15, **characterised in that** said fixing treatment is followed by a treatment with demineralised water followed by drying at a temperature of at least 120°C.

17. Use of the process of the preceding claims, for the preparation of non-ferrous metal products.

18. Non-ferrous metal products made by means of the process being the object of the preceding claims.

19. Products according to claim 18, made from magnesium, aluminium, titanium and vanadium, and/or alloys thereof, and/or combinations thereof and/or other kind of association thereof.

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- US 2901409 A **[0011]**
- EP 0619643 A **[0041]**