SURFACE TREATMENT METHOD AND ELECTROLESS NICKEL PLATING OF MAGNESIUM ALLOY

Method for surface treatment of an object at least in part made of magnesium alloy characterized by comprising the steps of: chemical degreasing of the surface, pickling of the surface, neutralization of the surface, activation of the surface and surface conversion. The aforementioned steps allow to deposit on the treated object a coat of chemical nickel uniform in thickness.
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SURFACE TREATMENT METHOD AND ELECTROLESS NICKEL PLATING OF MAGNESIUM ALLOY

FIELD OF INVENTION

The present invention relates to coatings for metallic material surfaces, in particular galvanic treatments for electroless nickel plating of the surface of a magnesium alloy object.

BACKGROUND ART

Magnesium is an alkaline earth metal and the fourth more widespread element on the planet.

Magnesium is an alkaline metal which offers large advantages to manufacture industry, in particular:

- low density (1.76 g/cm³);
- availability in nature;
- recyclable (up to 99%);
- high stress/weight resistance ratio;
- low melting point;
- good electromagnetic shielding.

Magnesium metal and every magnesium alloy are therefore interesting for the manufacture industry.

Magnesium alloys are compounds of magnesium with other materials, often aluminum, zinc, manganese, silicon, copper, rare metals and zirconium. Magnesium alloys have an extreme low density and higher stress/weight resistance ratio than other structural materials like steel or aluminum.

Thanks to the excellent mechanical properties, magnesium alloys are molded and frequently used in various industrial applications, in particular in the automotive industry where components must be light and at the same time mechanical stress proof.
Nevertheless, magnesium alloys are corrosion sensitive, in particular in moist and salted environments.

Further, magnesium alloys are very reactive to the air and to the water.

To overcome these drawbacks, coatings on magnesium alloy molded objects are carried out through conventional methods, for isolating the surface from the corrosive environment. In particular, for protecting magnesium alloys, metallic and non-metallic coatings are used.

Coating methods of a metallic (or plastic) material with a second coating metallic or organic material having different properties from the first are known from the state of the art. Generally, a base material, as carbon steel, cast iron, aluminum, brass, copper, ABS, polyamide and polycarbonate, may be metallized through methods known from the state of art, for example through electroless nickel plating, chromium plating, zinc plating, copper plating, silvering, palladium plating.

To carry out the metallization, the base material needs a specific preliminary treatment for each kind of material.

In particular, a common problem of metallization processes is the cleaning of the surface of the base material to allow the coating material to best adhere to the base material. Coating layers may also be manifold to sum effects and advantages of each layer.

For example, in the automotive sector, ABS and/or aluminum are coated with copper, nickel and chrome. This specific sequence of copper and nickel allows the chrome to adhere, giving a better aesthetic finishing.

Differently from the cited metals, magnesium alloys are not easily metallizable, there specific surface treatments are conceived.

Some processes known from the state of the art provide a first preliminary superficial treatment followed by further steps of superficial treatment.
A first known process from the state of the art is the passivation/oxidation followed by varnishing. Magnesium alloy, like the aluminum, has an high surface tension and thus a poor wettability. To allow the varnish to fix to the surface of the magnesium object, a passivation or oxidation of the surface is carried out, for giving to the material a spongy layer allowing permeation and thus adhesion of the varnish.

Alternatively, magnesium alloys may be coated with a film of epoxy or acrylic varnish, or varnished through cataphoresis, like occurs in automotive industry. A superficial coating applied with this methodology, does not allow a long average life of the object, the barrier effect is limited to the lifespan of the varnish film.

A second process of superficial treatment known from the state of art is the hard anodizing process. As the previous process, for the surface to coat a passivation is carried out, but with a higher current and for more time, to uniformly compact the coating.

The oxidation, that thus is heavier, may give thicknesses from 2 microns till 20-30 microns. This process is mainly used for applications where aesthetic finishing are not required, to improve functional aspects, namely where a good resistance to the corrosive agents and/or a good superficial hardness to withstand wear.

The main limit of this process, as for all other surfaces electroless nickel plating, is the electrical current distribution. When objects geometries are complex, the risk to expose the manufacture to burnt patches and/or regions not coated increases, compromising the effectiveness of the process or, as an extreme consequence, making the object unusable.

A third treatment process known from the state of art is the plasma ceramisation, also known as keronite®. The keronite® is
a process of superficial conversion of light alloys as aluminum, titanium and magnesium alloys. The functioning principle is similar to the passivation previously described and provides the growth of the natural oxide of the base material, through a source of high energy within a gas (plasma), creating a structure very compact and dense, similar to ceramic carryovers. This compact structure makes the material very wear proof and gives a good corrosion protection degree, significantly lengthening the time span.

For this energy consumption, used gases, appliance dimensions and high cost, keronite® is not a solution easily applicable to all products.

Furthermore, the high current density may bring defects in the objects with complex geometries and in particular in the undercuts and in some critical points where the deposit cannot arrive. Consequently, keronite® brings the risk that some portions of surface be uncovered, with consequences for the manufacture during usage.

A further method known from the state of the art is the one described in the patent application CN102808168.

This process provides, as the keronite®, a process of ceramisation. This ceramisation is followed by a neutralization and a reactivation and after by a nickel plating at environment temperature.

This process joins two known methodologies to sum the effects, but has an high cost because tension used are very high (300-470 volt) and are used for long times.

The solutions known from the state of the art do not solve in economic and effective way the problem to provide a preliminary superficial treatment of a magnesium alloy for subsequent metallization.

In particular, the techniques known from the state of the art do not provide a method avoiding the use of carcinogen
products, as chromic acid and/or its hexavalent salts, often used in metallization processes. A further problem of the prior art is connected to the corrosive phenomenon that often occurs during nickel plating. During this process may happen that the magnesium "sacrifice" corroding itself to "protect" nickel deposit instead of remaining intact.

SUMMARY OF THE INVENTION

The present invention has the aim to overcome drawbacks mentioned, and an object of the present invention is to provide a method for the surface treatment of an object at least in part made of magnesium comprising the steps of: chemical degreasing of the surface; pickling of the surface; neutralization of the surface; activation of the surface; surface conversion. Preferably, the degreasing of the magnesium alloy object occurs in a solution comprising caustic soda (NaOH), sodium carbonate (Na₂CO₃) and surfactant substances. This step allows an intense cleaning of the material and the removal of oily and fatty molecules on the surface. The step of pickling is carried out in a solution comprising formic acid (HCOOH), sodium molybdate (Na₂MoO₄) to delete surface layers of the material through acid solutions. The step of neutralization is carried out in a solution comprising tetra sodium pyrophosphate (Na₄P₂O₇) and sodium nitrate (NaNO₃). To regulate reaction pH between two steps having different pH is possible provide a neutralization step. The activation step of the surface, wherein the molecules are brought in an active (or activated) state and put in condition to react, is preferably performed in a solution comprising ammonium fluoride (NH₄F) and phosphoric acid (H₃PO₄).
The step of surface conversion, wherein the material surface is made chemically more inert (metastable) and thus more resistant to chemical-physical attacks, is preferably performed in a solution comprising sodium fluoride (NaF) and tetra sodium pyrophosphate (Na₄P₂O₇).

The object under treatment with the present method is completely immersed in one or more baths containing compounds for the respective steps of the method. Each of these baths is shaken, for example through air insufflation.

Preferably one bath for each step of the method is provided. Alternatively, polyvalent baths may be provided, namely adapted to provide more steps of the method.

More preferably the chemical degreasing of the magnesium alloy surface is performed with 7-15 g/l of caustic soda (NaOH), with 6-13 g/l of sodium carbonate (Na₂CO₃) and surfactants, for example anionics.

The pickling is performed with 15-23 g/l of formic acid (HCOOH), and 0,15-4,5 g/l of sodium molybdate (Na₂MoO₄).

The neutralization is performed with 5-60 g/l of sodium pyrophosphate (Na₄P₂O₇), and 26,5-33,5 g/l of sodium nitrate (NaN₃).

The activation is carried out with 280-345 g/l of ammonium fluoride (NH₄F), and 20-70 g/l of phosphoric acid (H₃PO₄).

The step of surface conversion is carried out with 1-10 g/l sodium fluoride (NaF), with 20-70 g/l of tetra sodium pyrophosphate (Na₄P₂O₇) and 20-70 g/l of sodium nitrate (NaN₃).

The present surface treatment improves the corrosion potential, making the material more protected from aggressive chemical agents attacks.

A second object of the present invention is providing a nickel plating method of the surface of a magnesium alloy object. Said nickel plating comprises the steps of:

carry out a surface treatment of the magnesium alloy object according the first object of the present invention and carry
out a following chemical nickel plating through immersion of the object in a solution comprising nickel phosphate, sodium hypophosphite, carboxylic acids, ammonium fluoride, ammonium sulfate and sodium citrate.

The aforementioned surface treatment creates on the surface of the magnesium alloy object a thin film of oxides mixed with fluorides that works as cathodic micro-areas for the reaction with the solution of chemical nickel plating. The materials accumulated in the micro-areas work as catalysts for the redox reaction between nickel phosphate and sodium hypophosphite with the consequent formation of metal nickel on the surface of the magnesium alloy object.

Preferably the nickel plating is performed in a tub containing a solution in turn comprising 20-50 g/l of nickel sulfate, 12-24 g/l of sodium hypophosphite, 1-2.5 g/l of carboxylic acids, 3.5-13 g/l of ammonium fluoride, 0.5-3 g/l of ammonium sulfate and 9-26 g/l of sodium citrate.

More preferably may be added 2.5-7 g/l of nickel citrate, 3.3-7.2 g/l of citric acid and 0.1-2 g/l of hydrofluoric acid.

The tub for the nickel plating treatment is dimensioned depending on the surface of the object to treat. Since the nickel plating process is relatively slow, about 15 micron of thickness per hour, is preferable using one or more tubs in parallel to nickel plate more objects at the same time.

The nickel plating treatment is preferably performed at a temperature comprised between 75 and 87 °C, with a pH comprised between 5.8 and 6.7.

The surface treatment methods and following nickel plating are methods entirely chemical and do not provide the use of electrical current or tension. For this reason with the term "chemical nickel" a nickel deposited by mean of a chemical process is intended.

The activation of the nickel plating method is performed through a chemical reaction between the film obtained in the
step of surface treatment and metallic elements in the solution, namely nickel and sodium hypophosphite. The present nickel plating step allows to deposit a chemical nickel film low in phosphor (2-4 %) particularly abrasion and corrosive chemical agents resistant. The present nickel plating method also allows covering each point of the magnesium alloy object surface, even when the latter has a very complex shape and deep cavities. Through this method, a uniform coat in quality and thickness is achieved, with a geometrical drift of about 1 or 2 micron maximum. The optimum covering of the magnesium alloy object through the deposit in chemical nickel allows to further coat the nickel surface to obtain further surface finishing. Furthermore, the deposit in chemical nickel makes the object surface electrically conductive for a possible use of the object in applications requiring such feature, for example in the electronic sector.

20 BRIEF DESCRIPTION OF THE DRAWINGS

Further features and advantages of the method for the surface treatment of the magnesium alloy and nickel plating method thereof according to the invention, will be clearer with the following description of an exemplary and not limiting embodiment, with reference to the attached drawing, wherein figure 1 shows a block diagram of the method for the surface treatment of the magnesium alloy and the following nickel plating.

30 DESCRIPTION OF A PREFERRED EMBODIMENT

The following description of some embodiments of the present invention may refer to the block diagram.
The following detailed description is not limiting for the present invention.

Technical specifications, structures or features of the solution disclosed may combined in any matter.

To carry out the chemical metal finishing on the surface of an object in magnesium alloy, for example an alloy AZ91D thixo-molded by injection, the object surface is subject to a preliminary superficial treatment comprising the following steps:

- chemical degreasing performed in a shacked solution containing 10 g/l of caustic soda (NaOH), 10 g/l of sodium carbonate (Na₂CO₃) and surfactant substances;
- pickling of the surface carried out in a shacked solution containing 20 g/l of formic acid (HCOOH), and 1 g/l sodium molybdate (Na₂MoO₄);
- neutralization carried out in a shacked solution comprising 10 g/l of tetra sodium pyrophosphate (Na₄P₂O₇), and 30 g/l of sodium nitrate (NaNO₃);
- activation carried out in a shacked solution comprising 300 g/l of ammonium fluoride (NH₄F), and 30 g/l of phosphoric acid (H₃PO₄);
- surface conversion carried out in a shacked solution comprising 1 g/l of sodium fluoride (NaF) and tetra sodium pyrophosphate (Na₄P₂O₇).

The previous steps are alternated with intermediate steps of rinsing of the object. The rinsing occurs with line water for the degreasing and with demineralized water for the steps of pickling, neutralization, activation and surface conversion.

The degreasing step is generally 10-30 minutes long, preferably 20 minutes and occurs at a temperature comprised between 60 and 80 °C preferably 70 °C, depending on the quality of the alloy to treat. This step may also occur with the use of a chemical product for the aluminum treatment, for
example the product Uniclean 151 of the company Atotech or the product IP Cleaner 301 SE of the company Mac Dermid.

The step of chemical neutralization occurs at ambient temperature and may last few seconds for compact materials and some minutes, preferably 2-3 minutes, for porous materials or with little defects.

The activation step may occur the product Magnify Activator of the company Atotech, at a temperature of 38-45 °C for 1-2 minutes, or the product Metex Etch Salts of the company Mac Dermid, at a temperature of 40-50 °C for 1-2 minutes. For this latter product is advisable the use of ultrasounds.

The surface conversion step is performed at a temperature of 75-85°C for 2-3 minutes.

After the mentioned steps of superficial treatment, the object may be chemically nickel plated in a shacked solution with filter pump containing nickel sulphate, sodium hypophosphite, carboxylic acid as for example malic, lactic and succinic, 10 g/l of ammonium fluoride (NH₄F), 2 mg/l of ammonium sulfate ((NH₄)₂SO₄) and 10 g/l of sodium citrate (Na₃C₆H₅O₇).

The low phosphor nickel, namely with a percent by weight between 1 and 3, is to be preferred if an high hardness of the object is required (780 - 900 vickers), medium phosphor nickel, namely with a percent by weight between 4 and 9 offers a good hardness (650 - 750 vickers) and corrosion resistance, the high phosphor nickel, namely with a percent by weight between 10 and 12, is less hard (< 500 HV) but resists very well to external agents.

Alternatively to the use of compounds aforementioned for nickel plating bath, is possible to use the products Magnify A, B e C of the company Atotech, or the product EnMAG EN-130130 of the company Enthone, or the product NiKlad™ of the company Mac Dermid.

The compound obtained from the nickel plating process has a uniform and tough deposit with thickness depending on the
length of the process itself. Generally, a minimum thickness of 5 micron is preferable, 8-10 micron for objects with superficial defects.

The alloy AZ91D has the following main chemical elements in percent by weight: Al 9,1%; Zn 0,78%; Mn 0,18%; remaining Mg and impurities.

In magnesium alloys molded by pressure harmful porosities for the next step of nickel plating may generate. In this case, to minimize the problems connected to these defects, the neutralization step allows neutralizing the substances within the porosities, while the activation step allows activating the surface of the neutralized porosities.

Following the nickel plating step a step of reactivation for the object may be provided through immersion in a solution with 300 g/l ammonium fluoride (NH₄F).

When the deposit of nickel of the object has an high content of phosphor, in particular between 10 e 12 %pp in alloy, a further superficial reactivation step is provided, through a treatment electro-cathodic at 2 ampere/dm² based on 30 g/l of caustic soda.

This last reactivation step may also be alternative to the first, for example for alloys with low content of phosphor.

For objects realized with different manufacturing techniques than the injection, for example through die casting, is preferable to repeat pickling and activation steps.

The same process of superficial treatment and next nickel plating may be preferably be implemented with a ZK60 alloy obtained by forging and with alloys AM50, MA60 and AZ31, obtaining results the same satisfactory for uniformity and for quality of the coating.

The aforementioned methods of first and/or second superficial reactivation may be repeated several times if more layers of nickel have to be realized.
The reactivated object according to one or both of the previous reactivation steps, may be newly superficially coated through galvanic, chemical-physical or organic deposition techniques.

In particular, through known galvanic methods is possible to: chrome, silver, gild, copper the object chemical nickel plated. For example, a magnesium knob, nickel plated according the method, may be reactivated by immersion in an ammonium fluoride solution and next coated with a deposition of copper electrolytic nickel and finally with a thin deposition of chrome. The knob chromed in this way has a pleasant aesthetic finishing and high resistance to corrosion associated with a particular lightness of the device.

Alternatively, further metallic deposits to the material may be brought through plasma technologies or in vacuum as for example the PVD process (physical vapor deposition). These chemical-physical processes may be used on objects nickel plated according the method, because the coating has a thickness and a uniformity sufficient to conduct a sufficient quantity of electricity to adopt these processes.

In a another embodiment, is possible to bring a further deposit to the object nickel plated using an organic coating. Since the deposit of nickel obtained through the present method has a low surface tension, is easily wettable and thus may be coated with any organic coating as epoxy varnishing, cataphoresis or similar technologies.

The deposition process of an organic coating further improves if preceded from a further reactivation process.

For maximizing the superficial finishing, the first and/or second reactivation with said new superficial coating may be repeated several times, according to the thickness obtainable for new coating and from the phosphor percentage in the nickel coating.
The method according the present invention is versatile and does not imply the use of substance harmful for the environment.

It is further easy to make the present method an industrial process allowing a large scale production of nickel plated components in magnesium alloy.

Object coated with chemical nickel according the present invention have high resistance to environments rich in corrosive agents, passing without alteration 24 hours of test in saline mist.

Advantageously, the present method may be used in a large number of technical sectors, in particular in the automotive sector and generally where the metallic components have a key role: spatial vehicles, airplanes, boats, containers, sport equipment.

The chemical nickel plating obtained through the present method has the particular advantage that does not require electrical current usage, since the magnesium alloy object is completely immersed in the nickel plating solution, with the entire surface in contact with the liquid containing the covering metal.
CLAIMS

1) Method for surface treatment of an object at least in part made of magnesium alloy characterized by comprising the steps of:
- chemical degreasing of the surface;
- pickling of the surface;
- neutralization of the surface;
- activation of the surface;
- surface conversion.

2) Method according to claim 1, wherein the steps of degreasing, pickling, neutralization, activation, surface conversion are in sequence.

3) Method according to claim 1 or 2, wherein the step of chemical degreasing occurs in a solution comprising caustic soda, preferably with a concentration of 7-15 g/1, sodium carbonate, preferably with a concentration of 6-13 g/1, and surfactant substances.

4) Method according to any of the preceding claims, wherein the step of pickling is carried out in a solution comprising formic acid, preferably with a concentration of 15-23 g/1, and sodium molybdate, preferably with a concentration of 0,15-4,5 g/1.

5) Method according to any of the preceding claims, wherein the step of neutralization is carried out in a solution comprising tetra sodium pyrophosphate, preferably with a concentration of 5-60 g/1, and sodium nitrate, preferably with a concentration of 26,5-33,5 g/1.

6) Method according to any of the preceding claims, wherein the step of activation is carried out in a solution comprising ammonium fluoride, preferably with a concentration of 280-345 g/1, and phosphoric, acid preferably with a concentration of 20 - 70 g/1.
7) Method according to any of the preceding claims, wherein the step of surface conversion is carried out in a solution comprising sodium fluoride, preferably with a concentration of 1-10 g/1, and tetra sodium pyrophosphate.

8) Method according to any of the preceding claims, comprising the further step of nickel plating.

9) Method according to claim 8, wherein the nickel plating is carried out in a solution comprising nickel phosphate, sodium hypophosphite, carboxylic acids, preferably malic, lactic and succinic, ammonium fluoride, preferably with a concentration of 3.5-13 g/1, ammonium sulfate, preferably with a concentration of 0.5-3 g/1, and sodium citrate, preferably with a concentration of 9-26 g/1.

10) Method according to any of the preceding claims, comprising the further step of first surface reactivation through immersion of the object in a solution of ammonium fluoride, preferably with a concentration of 300 g/1.

11) Method according to any of the preceding claims, comprising the further step of second surface reactivation through treatment with electrolytic cathodic, preferably carried out at 2 ampere/dm² based on caustic soda, preferably with a concentration of 30 g/1.

12) Method according to any of the preceding claims, comprising the further step of superficial coating through galvanic, chemical-physical or organic process.

13) Method according to claim 12, wherein the steps of first and second reactivation and superficial coating are repeated for improving the coating.

14) Method according to any of the preceding claims, wherein said steps occur by immersion of said object in tubs, preferably shacked.

15) Method according to any of the preceding claims, wherein said steps are alternated with rinsing of the object.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
INV. C23C18/18

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

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 practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Name and mailing address of the ISA:
European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040<br>Fax: (+31-70) 340-3018

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