METHOD FOR PLATING METALLIC WIRE OR TAPE AND PRODUCT OBTAINED WITH SAID METHOD

The present invention refers to a method for plating a metallic product (10) having a prevailing dimension, like wire or tape, comprising a cycle of treatments of electrolytic type in continuous cycle so as to progressively obtain a metallic product (30) with multilayer plating with low release of nickel; the method comprising the following phases:
- Preparatory phase (A, B, C, D);
- Phase of electrolytic nickel-plating (E);
- Phase of chromium electroplating (G) following the electrolytic nickel-plating phase (E). The metallic product (10) goes through all the phases in a continuous manner and at a substantially constant speed.

The invention also refers to a metallic product obtained through said plating method.
Description

TECHNICAL FIELD OF INVENTION

[0001] The present invention refers to a method for obtaining a laminated and/or drawn metallic product of wire or tape type, in coils or reels, which is plated by electroplating with layers of nickel and chromium. The product obtained through the method hereof is, moreover, characterized by a low release of nickel.

[0002] With particular reference to the paper-transformation industry, the invention finds its application in the industrial production of objects having a high aesthetic quality, obtained from the processing of wire or metallic tape.

STATE OF THE ART

[0003] The main industrial processes used to plate metallic materials, so as to provide specific characteristics of hardness, resistance to wear and/or to corrosion, are known as processes of galvanic type.

[0004] These processes rely on electrochemical principles to obtain an electroplating that can vary according to the material to deposit and the type of object to be plated. The most widely used galvanic processes are nickel-plating, zinc-coating and chromium-plating.

[0005] In particular, the nickel-plating process is used both as coating and as primer base for subsequent treatments, as it is enduring, ductile, fast clinging and also of attractive appearance, a characteristic that makes nickel-plating preferable over zinc-coating, being the latter less appealing in appearance.

[0006] The chromium-plating process makes it possible to obtain an especially hard surface layer of bright glossy white color, which is thus greatly appreciated in products or accessories requiring such characteristics of aesthetic finish.

[0007] The prior art chromium-plating process is however at the same time more complex and costly compared to nickel coating.

[0008] The prior art galvanic treatments require the use of a tank, usually containing an aqueous solution of the metal salt to be deposited, in which are immersed two electrodes, a cathode and an anode respectively, both connected to an electrical circuit.

[0009] The cathode consists of the object to be plated, while the anode can consist of the metal that must be deposited, or it can be another inert metal or graphite.

[0010] If a difference of potential is applied to the two electrodes, by means of the electrical circuit to which they are connected, the cations of the metal to be deposited move toward the negatively charged cathode, while the anions move toward the positively charged anode.

[0011] The known treatments differ principally on the basis of the type and form of the pieces being processed, as they can be pieces that can be processed entirely in a bath in which they remain for a certain time or pieces that are processed only partially or at different times.

[0012] The conventional treatments, for pieces that are processed entire and simultaneously, include processing the whole piece through a static permanence of the same pieces in the different stations or tanks of the production process. In other words, there is a subdivision of the process and of its progressive phases in different stations, in which the product is held while it is being plated, until the desired result is obtained.

[0013] The phases that follow the cleaning and preparation of the piece and that make it possible to achieve the plating consist, therefore, of immersing the piece in the respective bath, so that an electric current can be applied that is functional to the type of plating metal, which progressively builds up on the piece being plated.

[0014] An example of such galvanic processes is disclosed in the US patent application US2010/0167085 (BYD Co. Ltd.), which suggests a method of plating articles made of aluminum alloy with a multilayer, being free of nickel and with the last layer, in contact with the skin, being a chromium layer.

[0015] In the scope of methods carried out in the continuous mode, to obtain a galvanic plating of wires or tapes with nickel, processes are known that employ a plurality of tanks or passage stations and act on the portion of wire or tape that is dipped or submerged in each of them.

[0016] The galvanic treatment of wires or tapes in the continuous cycle presents specific problematic and critical aspects unlike those found in treatments involving single pieces.

[0017] The single pieces, such as for example car or motorcycle items, in fact remain substantially motionless inside the same tank until the completion of the galvanic process, while in the case of wires or tapes the treatment is applied in a continuous mode, depending on the tanks being crossed and on the time during which each portion remains immersed in the respective tank while moving through it.

[0018] An example of a known method to obtain the continuous-cycle nickel-plating of a wire or bar is disclosed in GB 938192 (Manson and others), in which is described a galvanic multilayer plating for metallic wire, bars or tape, achieved in continuous cycle, in which the product being processed is given a helical shape and placed in rotation, so that it can pass through a bath of a first plating metal, and subsequently undergoes cold processing and is finally subjected to a further bath, in a second plating metal, to obtain a desired thickness.

[0019] According to said document, an improved surface that is resistant and free of pores or flaws is achieved, in which the metals used in the two plating cycles can be the same or different, for example nickel, tin, copper, aluminum, steel or alloys.

[0020] In the paper-transformation field and in related fields, such processes can be used to obtain steel wires or strips, to which is applied a nickel-plating treatment to improve the aesthetic quality.
The nickel-plating treatment itself has recently received particular attention from doctors, manufacturers and lawmakers, due to the proven high allergenic and irritating properties of nickel, which is thus classified as a harmful, polluting and also carcinogenic substance.

In particular, it is well known that the absorption of nickel in allergy sufferers, even through the skin, generates a pathological condition called "allergic contact dermatitis".

Companies operating in the galvanic field, particularly companies manufacturing metallic objects intended for continuous contact with the skin, like costume jewelry, or even for occasional contact, such as for example in the paper transformation field, have been engaged in finding innovative solutions and safer galvanic coatings with low or no nickel release, while trying to maintain the know characteristics of resistance and aesthetic appeal.

European Directive 94/27/CE has also introduced the ban on the sale of products designed to come in direct and prolonged contact with the skin of the wearer if they release a quantity of nickel (Ni) higher than a minimum established value, measured according to a specific measuring protocol.

This characteristic is conventionally referred to as "nickel-free", even though it does not necessarily imply the total absence of nickel in the component but only in the external coating, as is specifically the case foreseen in the present invention. Alternatively, it is possible to define such products as being "low nickel release products".

The metallic articles used in the paper-transformation field, even if their contact with the skin is brief and not continuing, may be prudently likened to the products of the related field of costume jewelry, for the purposes of verifying the release of nickel according to norms.

A possible improvement may essentially result, at the technological level, from two solutions: the elimination and the substitution of the nickel or, alternatively, from a further protective coating applied on the nickel.

The first solution, that is, the elimination and replacement of the nickel with other processes, used in the clothing field, for example in belt buckles, or also in costume jewelry, involves resorting to treatments that deposit substitute materials having an overall higher cost or being more intricate to make, which prevents their use in the paper-transformation field, where moderate costs and high volumes of production are required.

Therefore, if a further protective coating is to be implemented in the production of wires or tapes in the paper-transformation field, the process of research and development that led up to the present invention considered the application of a layer of chromium plating on top of the one or more nickel-plating layers, and at the same time many problems were observed, as exemplified below.

In the first place, chromium plating is a more complex galvanic process to manage compared to nickel-plating, due to the process parameters and conditions required to achieve a satisfactory result, which makes it very problematic in the case of continuous processing of wires or tapes, so that it is not yet applied in known methods. In fact, methods are known in which, after having performed nickel-plating in a continuous process and at a substantially constant speed, chromium plating is performed in a so-called "batch" or discontinuous process.

A problem found at the experimental level and not solved in the prior art is due to the quality of the surface finish, which proved to be strongly influenced by the vibrations, although very slight, suffered by one or more wires inside the relative electrolytic chromium-plating tank, tested with a bath of hexavalent chromium.

In other words, the portion of wire or tape that is temporarily immersed in the electrolytic chromium-plating tank, with a bath of hexavalent chromium, if subjected to vibrations or false contacts, incurs process complications that lead to undesirable surface defects, called "scorchings", as they appear more opaque than the typical finish of the chromium-plating operation.

The main objective of the present invention is to overcome the shortcomings of the prior art by providing a method for metallic wire or tape that makes it possible to obtain in a continuous cycle a product coated with a nickel-plating layer and with a chromium-plating layer, with a finish that at least minimizes the so-called "scorchings".

In the scope of the above objective, one purpose of the present invention is to devise a method of galvanic treatment that is suitable for plating wires or metallic tapes in a continuous mode while avoiding finishing flaws.

A further objective of the present invention consists of providing a method of galvanic treatment, used in a continuous mode at a constant speed, that makes it possible to obtain a wire or a tape coated with nickel and chromium, by treating in a continuous mode a whole wire or tape wound in coils or reels.

A not secondary purpose is to realize a product for the paper transformation field that makes it possible to obtain a wire or tape coated with nickel and chromium and having a low nickel release.

The above objective and purposes, and others that will become more evident in the ensuing description, are achieved by a method as defined in claim 1 or with a product as defined in claim 9.

Further characteristics and the advantages of the present invention will become more evident from the following description of a particular, but not exclusive, embodiment illustrated purely by way of a non-limiting
example with reference to the enclosed drawings, where:
- Figure 1 is a schematic view of a processing cycle according to the present invention;
- Figure 2 is a graph showing the trend in the voltage applied to the wire or tape being processed in relation to the length of the chromium-plating tank, according to a first configuration;
- Figure 3 is a graph showing the trend in the voltage applied to the wire or tape being processed in relation to the length of the chromium-plating tank, according to a second configuration;
- Figure 4 is a schematic view of an element realized according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0039] With reference to figure 1, hereunder is described a process according to a first experimental configuration of the present invention. A decoiler 20 holds a coil 12, from which is unwound a wire 10 that, in a continuous treatment line, runs through the following stations at a substantially constant speed and in series:

A) Electrolytic degreasing, at a temperature between 30 and 80°C and a permanence time of 1 to 60 seconds;
B) Washing, preferably in countercurrent;
C) Electrolytic pickling, at a temperature between 20 and 60°C and a permanence time of 1 to 60 seconds;
D) Washing, preferably in countercurrent;
E) Electrolytic nickel-plating, at a temperature between 30 and 70°C and a permanence time between 10 and 500 seconds, so as to achieve a continuous deposition of nickel (Ni) with a thickness between 1 and 5 micron;
F) Washing, preferably in countercurrent;
G) Chromium electroplating, with a permanence time of between 1 and 30 seconds, so as to achieve a continuous deposition of chromium (Cr) of a thickness of 0.01 to 1 micron;
H) Washing, preferably in countercurrent;
I) Neutralization;
J) Drying, at a temperature between 60 and 90°C and a permanence time of 3 to 30 seconds.

[0040] The wire 10, after having undergone the above treatments, is a treated wire 30 that is wound in a second coil 32 housed in a coiler 40 that also turns at a substantially constant speed.

[0041] The set of phases preceding the electrolytic nickel-plating E is referred to as the preparation phase, for example comprising phases A, B, C and D.

[0042] The intervals relating to the permanence times are, as described, obtained by adjusting the substantially constant wire feeding speed comprised between 10 and 100 meters a minute.

[0043] Naturally, if a tape is being processed, the tape is unwound from a reel housed in a relative decoiler, in order to be treated and turned into a treated tape that is rewound in a second reel housed in a relative rewinder, in a continuous-cycle mode and at a substantially constant speed.

[0044] The treated wire 30 or the treated tape is thus obtained from a drawn and/or rolled metallic product in reels and coils, obtained from a base material of ferrous type, that is nickel-plated and also coated in a continuous cycle, at a substantially constant speed, with a superficial metallic layer without nickel so as to substantially limit the release of nickel from the substrate.

[0045] In particular, according to such first configuration, the portion of wire or tape that is temporarily immersed in the electrolytic plating tank, if subjected to vibration or false contacts, as previously described, incurs process shortcomings that lead to undesirable surface flaws, called "scorchings", as they appear more opaque than the typical finish of the chromium-plating operation.

[0046] Subsequent to painstaking and costly experimental tests, the inventors were able to understand the problems at the basis of the formation of "scorchings", identified, as shown in figure 2, in the trend of the voltage, indicated with V, applied to the wire or tape being processed in relation to the length of the chromium-plating tank. Within the station G, the chromium-plating tank is schematically illustrated in figure 2, with a length included between a first length L1 and a second length L2.

[0047] The voltage was in fact seen as being substantially decreasing, starting from an optimal value V1, representative of the difference of potential between the wire or tape to be treated and the anode, at the entrance of the chromium-plating tank, decreasing to a low value V2, representative of the difference of potential at the exit from the same chromium-plating tank according to the first configuration.

[0048] The voltage difference given by the passage from the optimal value V1 to the low value V2 proved to be excessive and harmful, so as to determine, in case of even slight vibrations or false contacts, the undesirable "scorchings".

[0049] Advantageously, through a second preferable configuration of the invention shown schematically in figure 3, a trend of the difference of potential that remains around the optimal value V1 is maintained, therefore without descending to the low value V2.

[0050] Thus were determined some points of actuation within the chromium-plating tank, respectively at a third length L3 and at a fourth length L4 within the chromium-plating station G, in which to operate with stabilizing means or restoring elements that are capable of restoring, or at least approximate, the difference of potential at the optimal value V1, to the length of the portion of the immersed wire that is close to reaching a voltage threshold value V3.

[0051] Preferably, such restoring elements are placed in contact with the wire or tape in motion, when the latter
is outside the chromium-plating bath, thus avoiding deposing chromium on the same restoring element.

[0052] Advantageously, two or more chromium-plating tanks are used, so that the total sum of the lengths of the two or more chromium-plating tanks is equal to the length of one chromium-plating tank according to the first configuration.

[0053] As can be seen in figure 3, according to the invention the schematic length from the first length L1 to the second length L2 of the chromium-plating station G is preferably subdivided into three operating lengths: of a first tank G1, a second tank G2 and a third tank G3, respectively.

[0054] According to a manner of embodiment of the invention, visible in figure 4, at each point of actuation singled out, for example at the third length L3 and at the fourth length L4, is placed, in contact with one portion of processed product 110 on which to operate, a sliding contact 120, to which is applied a predetermined voltage, so as to restore the difference of potential toward the value V1.

[0055] The sliding contact 120, according to one embodiment of the same, includes a sliding element 122 that comes into direct contact with a portion of the processed product 110. The sliding element 122 is coupled to the free end of a boom 124 that is connected, at the opposite end, to an arm 126, itself connected to the frame of the machine or to another suitable support.

[0056] Advantageously, the chromium-plating bath is provided with trivalent chromium, which experimentally has made it possible to obtain better and less polluting results compared to a bath of hexavalent chromium.

[0057] Preferably, the trivalent chromium bath is based on chlorides or sulfates.

[0058] Thanks to the presence of actuation points to restore the difference of potential between the wire or tape being processed and the anode in the chromium-plating bath, it is possible to limit, and even to eliminate, the results of undesirable "scorchings".

[0059] This innovative application has demonstrated experimentally the possibility of performing a chromium-plating treatment in a continuous mode with wires or tapes, that can be carried out at a substantially constant speed, avoiding undesirable effects that were previously unresolved in the field of galvanic treatments for the production of metallic elements, for example for applications in the paper-transformation field.

[0060] The valuable and innovative result achieved thanks to the present invention has therefore allowed the mass-produced nickel-plating and chromium-plating treatment of wires or tapes, in a continuous cycle and at a substantially constant speed. It is thus possible to achieve the continuous processing, without interruptions, of a whole coil 12 of wire 10 or respective reel of tape, guaranteeing an optimal surface finish and avoiding "scorchings".

[0061] This solution is applicable, in particular, to the metallic wire or tapes that are subsequently processed by plastic deformation in order to obtain the finished product such as finds application, by way of example but without limits, in the paper-transformation field for the ring and lever mechanisms used in loose-leaf binders.

[0062] In general, the prior-art continuous-cycle industrial processes of galvanic type to obtain superficially plated metallic wires and tapes are conventional and known for some time, being diversified on the basis of the specific industrial field, with different materials and thicknesses; the paper-transformation industry, in particular, generally uses conventional nickel-plated wires and tapes.

[0063] The invention therefore provides an innovative multilayer plating that consists of a first coating of nickel-plating type, as a substrate, to which is added an extremely thin second surface coating of the chromium-plating type; said surface coating has both protective purposes, being in contact with the skin of the final user, and aesthetic purposes, being superficial and visible. In particular, the proposed innovative treatment is one with a low release of nickel responding to European Directive 94/27/CE and can be implemented at the industrial level starting from a conventional continuous-treatment line of the mono-wire or mono-tape type, or also of the multiwire or multi-tape type; the invention also makes it possible to subsequently implement, without detectiveness, the ensuing processes that are typical of the conventional articles found in the paper-transformation field, and still more.

[0064] Generally, in metallic articles designed for industry, the coatings are considered to be of technical and functional type when the thickness exceeds an average value of about 6 or 8 micron, as for example in conventional nickel-platings and in chrome platings intended to increase the hardness and resistance to wear, while they are considered as being of decorative type when the thickness is smaller than this value.

[0065] In the specific case considered in the invention, the limitation in the release of nickel and the other purposes are achieved with a layer of nickel of 1 to 5 micron in thickness, additionally coated with an extremely thin layer of chromium, with a thickness of 0.01 to 1 micron.

[0066] This productive approach makes it possible to meet the requirements of technical, functional and aesthetic quality expected, for example, in the industrial paper-transformation field.

[0067] In fact, a proper ductility of the nickel-plating is maintained, allowing the conventional folding and bending achieved afterward in the cold processing step on automatic machines, thus avoiding surface defects.

[0068] The chromium layer, although it is extremely thin, achieves the purpose of substantially limiting the transfer of nickel, increasing at the same time the resistance to corrosion of the processed wire or tape.

[0069] Naturally, the present invention is amenable to many applications, modifications or variants without thereby departing from the scope of patent protection as defined by the independent claims 1 or 9.

[0070] Furthermore, the materials and equipment used
to implement the present invention, as well as the shapes and dimensions of the individual components, may be the most suitable in accordance with the specific requirements.

Claims

1. Method for plating a metallic product (10) with a prevailing dimension, the type wire or tape, comprising a treatment cycle of the electrolytic type in continuous cycle so as to progressively obtain a metallic product (30) with a multilayer plating with low release of nickel, said method comprising the following phases:

- Preparatory phase (A, B, C, D);
- Phase of electrolytic nickel-plating (E);

characterized in that it also comprises a stage of electrolytic chromium plating (G) that follows the phase of electrolytic nickel-plating (E), and in that the metallic product (10) passes through all the stages in a continuous manner and at substantially constant speed.

2. Method for plating in accordance with claim 1, wherein the crossing speed of the phases is between 10 and 100 meters per minute.

3. Method for plating in accordance with one of the preceding claims, wherein the step of electrolytic chromium plating (G) comprises passing the metallic product through at least one bath of trivalent chromium.

4. Method for plating in accordance with claim 3, wherein said at least one bath of trivalent chromium is based on chlorides or sulfates, or both.

5. Method for plating in accordance with one of the preceding claims, wherein the step of electrolytic chromium plating (G) comprises at least two galvanic baths (G1, G2, G3) which allow to separate the passage of the metallic product for a total length (L1, L2, L3, L4) that is equal to a length (L1, L2) which allows the permanence of each portion of metallic product (10) for a time comprised between 1 and 30 seconds or which allows to obtain a chromium plating having a thickness comprised between 0.01 and 1 microns.

6. Method for plating in accordance with claim 5, in which is included an anode and wherein the step of electrolytic chromium plating (G) comprises stabilizing means (120, 122, 124, 126) interposed between the at least two galvanic baths (G1, G2, G3), said stabilizing means (120) being adapted to maintain the electric potential difference between the metallic product and the anode between an optimum value (V1) and a threshold value (V3) in the stage of electrolytic chromium plating (G).

7. Method for plating in accordance with claim 6, wherein the stabilizing means (120) comprise a sliding element (122) adapted to go into direct contact with the metallic product being processed.

8. Method for plating in accordance with one of the preceding claims, comprises the following steps:

A) Electrolytic degreasing, with temperature between 30 and 80 °C and a permanence time of between 1 and 60 seconds;
B) Countercurrent washing;
C) Electrolytic pickling, with temperatures between 20 and 60 °C and a permanence time of between 1 and 60 seconds;
D) Countercurrent washing;
E) Electrolytic nickel-plating, with temperature between 30 and 70 °C and a permanence time of between 10 and 500 seconds, so as to provide a continuous deposit of nickel (Ni) with a thickness between 1 and 5 microns;
F) Countercurrent washing;
G) Chromium electroplating, with a permanence time of between 1 and 30 seconds, so as to provide a continuous deposit of chromium (Cr) of a thickness comprised between 0.01 and 1 micron;
H) Countercurrent washing;
I) Neutralization;
J) Drying, at a temperature between 60 and 90 °C and a permanence time of between 3 and 30 seconds.

9. Metallic product (30) with a prevailing dimension, the type wire or tape, obtained starting from a metallic product (10) by a method for plating according to one of the preceding claims.

10. Metallic product (30) with a prevailing dimension, the type wire or tape for use in the paper industry, obtained starting from a metallic product (10) by a method for plating according to one of the claims from 1 to 8.
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ANNEX TO THE EUROPEAN SEARCH REPORT
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