METHOD FOR TREATING IN CONTINUOUS THE SURFACE OF A LAMINATE MADE OF STAINLESS STEEL IN A SOLUTION BASED ON SULFURIC ACID

Fig. 1

The present invention refers to a method for treating in continuous the surface of a laminate made of stainless steel that comprises at least the steps of: (a) making said laminate (11) pass in continuous in a tank (12) containing an aqueous electrolytic solution (SE) of sulfuric acid; said laminate (11) passing between at least two electrodes (150, 170) immersed in said electrolytic solution (SE) and arranged in a direction substantially parallel to the movement direction of the laminate (11) and having a length L_x measured along said direction, said electrodes (150, 170) facing the opposite faces of said laminate (11) and being arranged in a position facing each other, (b) subjecting said laminate (11) to an electrolytic pickling treatment by applying an alternating current having a frequency f comprised between 5 Hz and 150 Hz, said frequency f being correlated to said forward velocity v of the laminate (11) and to said length L_x of said electrodes (150, 170) by the relation $F \geq (A^* \pi / L_x)$, where $A^*$ is a rational number greater than 1, preferably greater than 2; (c) subjecting said electrolytically pickled laminate (11) to a surface finishing and a surface passivation treatment.
METHOD FOR TREATING IN CONTINUOUS THE SURFACE OF A LAMINATE MADE OF STAINLESS STEEL IN A SOLUTION BASED ON SULFURIC ACID

The present invention concerns a method for treating in continuous the surface of a laminate made of stainless steel in a solution based on sulfuric acid.

The method of the present invention is particularly suitable for treating a laminate made of stainless steel in order to remove the surface oxide layer (so-called "scale") which inevitably forms during the various heat treatments to which the laminate is subjected, including the hot lamination process itself.

As known, the removal of scale from a laminate made of stainless steel is necessary to restore to the surface thereof the base chemical composition of the steel, so as to give the laminate the well-known properties of resistance to corrosion.

The process for removing scale, known as "pickling", aims to remove both the outermost surface layer of metal oxide (richer in chrome with respect to the basic composition of steel) and the layer of alloy beneath it that, on the other hand, has a lower chrome content with respect to the base chemical composition of steel (dechromatized layer).

The pickling processes of the prior art generally provide three distinct steps. In the first step (descaling) a chemical-physical modification of the scale is induced in order to promote detachment from the laminate. This step is carried out, for example, by immersing the manufactured product in baths of molten...
oxidizing salts, such as Kolene baths (mixtures of NaOH, NaN0₃ and NaCl) at temperatures around 500 °C (thermochemical descaling), or electrolytically (electrolytic descaling) in neutral or acidic aqueous solutions (for example, aqueous solutions of sodium sulfate or sulfuric acid). As a function of the type of steel and the composition of the scale, the descaling step can also be preceded by mechanical scale-removal treatments (so-called "scale-breaking" treatments), like sand-blasting, shotblasting and abrasive brushing.

In the second step (the actual pickling), the residual scale is removed from the surface of the laminate together with the dechromatized layer beneath. This step is generally carried out by immersing the laminates in acid baths with high oxidizing capability, such as the baths of mixtures of mineral acids (e.g. mixtures of HNO₃ and HF, mixtures of H₂SO₄, HCl and H₃PO₄, etc.) in the presence of oxidizing compounds, like for example permanganates, persulfates or hydrogen peroxide.

In the third step (finishing and passivation), the protective layer of chromium oxide forms on the surface of the laminate. This step is generally carried out immersing the manufactured product in baths containing nitric acid or mixtures of mineral acids (generally at lower concentrations with respect to the pickling step and with a lower content of the metal ions making up the steel). In certain cases, in the pickling step, in addition to the removal of the scale and of the dechromatized layer, there is also surface oxidation of the laminate that thus makes the finishing/passivation step superfluous.
The pickling processes of the prior art have various drawbacks concerning their potential environmental impact, safety of the work spaces, operative control of the process as well as the equipment costs and the consumption of raw materials.

The use of pickling baths of nitric acid and hydrofluoric acid, for example, leads to the formation of large quantities of nitrogen oxides (NOx) and waste water contaminated by nitrates and fluorinated compounds, which make it necessary to adopt specific measures to keep down gaseous emissions and to purify the waste water. The quantity of contaminating compounds to be treated or disposed of depends on the quantity of material removed from the laminate in the baths containing nitric acid and hydrofluoric acid, a quantity that in turn depends - all other conditions being the same - on the duration of the treatment in these baths.

The efficiency of pickling processes of the prior art is also such that an adequate removal of the scaling can be obtained only with prolonged contact of the laminate with the pickling baths. This means that the processes are rather slow and necessarily carried out in large sized plants.

In the field of pickling of stainless steel, the use of pickling baths based on nitric and hydrofluoric acid is currently considered unavoidable for obtaining high quality products. In general, in modern plants for annealing and pickling in continuous, the quantities of material that are removed using these baths are comprised between 60% and 80% of the material removal overall in the pickling process. Consequently, in
industrial plants, the lines for the surface treatment of laminates of stainless steel are of dimensions such as to carry out, at the maximum process speed, the pickling and passivation finishing steps with a minimum duration of no less than 60 s for hot rolled laminates and not less than 30 s for cold rolled laminates. Such durations are typically added to with the time necessary to carry out the chemical descaling in acid solution for the hot rolled strips (30-40 s) and that necessary for the electrolytic descaling in neutral or acid solution for cold annealed laminates (35-45 s). Clearly, strips of greater thickness with respect to those of the laminates able to be processed at the maximum speed, being heat treated in the annealing oven for longer times, involve proportionally longer descaling and pickling steps.

Processes for pickling laminates made of stainless steel having improved efficiency and less environmental impact are described, for example, in WO 02/12596 A2 and WO 00/15880 A1.

The process described in WO 02/12596 comprises an electrolytic pickling step in alternating current carried out in an aqueous solution of sulfuric acid in the presence of Fe$^{3+}$ ions or in the presence of at least one second acid selected from hydrofluoric acid and phosphoric acid.

The process described in WO 00/15880 comprises an electrolytic pickling step in continuous current carried out in an aqueous solution of sulfuric acid in the presence of ions Fe$^{3+}$ ions. The process can also comprise steps of descaling (in baths of molten salts), chemical pickling (in solutions of H$_2$SO$_4$ and HF in the
presence of Fe\(^{2+}\) and Fe\(^{3+}\) ions) and/or final passivation (in H\(_2\)SO\(_4\) and H\(_2\)O\(_2\)).

EP 2102376 A1 and JP 5222449 describe processes in which the annealing treatment that precedes the pickling is carried out in temperature and oxygen concentration conditions such as to reduce the amount of oxide that forms overall on the laminates.

WO 03/052165 describes an electrolytic descaling process (in continuous current) of the laminates made of stainless steel carried out in a bath of sulfuric acid containing ferric ions, ferrous ions and hydrofluoric acid, followed by a chemical pickling treatment in aqueous solutions of sulfuric acid. The duration of the anode treatment in the electrolytic descaling process is correlated to the current density applied and to two parameters that are experimental in nature.

EP 1307609 A1 describes an electrolytic pickling process of laminates made of stainless steel carried out in a bath of sulfuric acid with an alternating current of frequency comprised between 40 and 70 Hz and with current density comprised between 10 and 250 A/dm\(^2\) for a duration comprised between 3 s and 60 s.

Document WO 02086199 A2 describes an electrolytic descaling process of laminates made of stainless steel carried out with a continuous or alternating current inside an aqueous electrolytic solution of a strong acid (for example hydrochloric acid, sulfuric acid, hydrofluoric acid, etc.), the duration of which is correlated to the current density applied and to two parameters that are experimental in nature.

The main purpose of the present invention is to
avoid the drawbacks of the pickling processes of laminates made of stainless steel of the prior art.

In such a general purpose, a purpose of the present invention is to provide a method for pickling a laminate made of stainless steel that makes it possible to obtain a high-quality treated product, but with low environmental impact and lower consumption of raw materials, such as mineral acids and additives.

Another purpose of the present invention is to provide a method for pickling a laminate made of stainless steel with improved efficacy, so as to reduce the duration of the pickling treatments and the bulk of the plants necessary to carry it out.

The Applicant has found that these and other purposes are accomplished by the method for treating in continuous the surface of a laminate made of stainless steel comprising at least the following steps:

(a) making said laminate pass in continuous in a tank containing an aqueous electrolytic solution of sulfuric acid, said laminate passing between at least two electrodes immersed in said electrolytic solution and arranged in a direction substantially parallel to the movement direction of the laminate and having a length $L_e$ measured along said direction, said electrodes facing the opposite faces of said laminate and being arranged in a position facing each other;

(b) subjecting said laminate to an electrolytic pickling treatment by applying an alternating current having a frequency $f$ comprised between 5 Hz and 150 Hz, said frequency $f$ being correlated to the forward velocity $v$ of the laminate and to said length $L_e$ of said electrodes by the relation $f \geq (A - v) / L_e$, where $A$ is a
rational number greater than 1;
(c) subjecting said electrolytically pickled laminate to a surface finishing and surface passivation treatment.

For the purposes of the present invention, by laminate made of stainless steel (hereafter also "laminate") it is meant a semi-worked product made of stainless steel of the type like a plate, a strip, (a wire, a rod iron, a wire rod, a section bar or similar), of indefinite length. These semi-worked products are generally obtained through lamination processes, either hot or cold, possibly accompanied by annealing heat treatments.

In the description of the present invention the electrolytic solutions, the pickling solutions and the descaling solutions are also indicated, without distinction, as "pickling baths".

The method according to the present invention can be applied to effectively remove the layer of metal oxide (scale) from the surface of the laminate and the dechromatized layer beneath, forming a layer of chrome oxide in its place that protects the laminate from corrosion.

Advantageously, the method according to the invention can be used to pickle various types of steel, in particular austenite, martensitic and ferritic steels, whether they are obtained through hot and cold lamination processes (hereafter respectively indicated as "hot rolled laminates" and "cold rolled laminates").

The method according to the invention comprises at least one electrolytic pickling step of the laminate carried out in alternating current (AC) in an aqueous
electrolytic solution comprising at least sulfuric acid.

The electrolytic pickling in AC is carried out by suitably selecting the frequency of the alternating current applied as a function of the position of the electrodes with respect to the laminate subjected to treatment, as will be illustrated in detail later on.

The Applicant has, indeed, found that the efficacy of the electrolytic pickling is greater if, during the crossing path of the electrolytic bath, a given surface portion of the laminate is prevented from being exposed substantially to the same polarization at the pairs of electrodes through which the laminate is made to pass. In this case, indeed, there would be regions of the laminate treated unevenly.

The concentration of sulfuric acid in the electrolytic solution is selected in the range 30 g/l - 300 g/l according to the type of steel and the type of treatments to which the laminate has been exposed. For example, in the case of hot rolled laminates, the concentration of sulfuric acid is more preferably comprised in the ranged 70-300 g/l. In the case of cold rolled austenite steels, the concentration of sulfuric acid is more preferably comprised in the range 40-200 g/l. In the case of cold rolled ferritic steels (stabilised and not), the concentration of sulfuric acid is more preferably comprised in the range 30-100 g/l.

In the present description, the concentration values of sulfuric acid should be taken as in reference to the concentration of the free acid in the aqueous solution, as measurable, for example, through an acid-
base titration or conductometric analysis.

The electrolytic solution can also comprise variable concentrations of metal ions in solution deriving from the dissolution of steel, such as Fe, Cr, Ni, Mn, Mo, etc.

The total content of metals in solution (dissolved metals) is typically comprised in the range 0 g/1 - 120 g/1.

The concentration of dissolved metals depends on the type of steel and on the type of treatments to which the laminate has been subjected. In the case of cold rolled steels, for example, the concentration of dissolved metals is preferably comprised in the range 20-50 g/1. In the case of cold rolled ferritic steels (stabilized and not), the concentration of the dissolved metals is more preferably comprised in the range 30-100 g/1.

As the electrolytic treatment proceeds, through the effect of the dissolution reactions of the scale, of the dechromatized layer and of the steel as well as of the reactions between species in solution, the concentration of the free acid in the solutions progressively decreases, whereas that of the metal ions, in particular that of the ferrous Fe\(^{2+}\) ions, increases. In order to have an effective pickling action it is thus preferable to replenish the sulfuric acid consumed and keep the concentration of dissolved metals within the ranges indicated above. The concentration of sulfuric acid can be kept to desired levels through periodic addition of fresh acid or by recycling the aqueous solutions of the acid used in other steps of the method, provided that they have
greater concentrations than that desired.

The electrolytic pickling is carried out keeping the electrolytic solution at a temperature comprised in the range 30-100°C. In the case of hot rolled laminates, the temperature is more preferably comprised in the range 40-95°C, whereas for cold rolled, the temperature is more preferably comprised in the range 30-95°C. In particular, for cold rolled steels, the temperature is preferably comprised in the range 40-70°C for steels of the austenitic type, in the range 30-50°C for stabilized ferritic steels and in the range 30-45°C for unstabilized ferritic steels.

The alternating current (AC) used in the electrolytic pickling has a density (referring to the unit surface of the laminate) comprised in the range 5-60 A/dm².

For hot rolled laminates, the current density is preferably comprised in the range 15-60 A/dm², even more preferably in the range 20-50 A/dm².

For cold rolled laminates, the current density can preferably be selected as a function of the type of steels, for example, as follows:

- austenite steels 10-40 A/dm²;
- ferritic steels 5-30 A/dm².

The frequency of the AC current is comprised in the range 5-150 Hz. Typically, the frequency is kept at a constant value during the treatment. However, it can also be varied as a function of the process requirements, for example to increase the quality of the treatment or to control the pickling speed as a function of the feeding speed of the laminate to the
pickling plant.

Typically, the electrolytic pickling has a duration comprised between 3 and 40 seconds, both for hot rolled laminates and for cold rolled laminates.

For hot rolled laminates, the duration of the electrolytic pickling is preferably comprised in the range 8-60 seconds, even more preferably in the range 10-50 seconds; in the case of hot rolled austenite steels, the duration is preferably comprised in the range 10-20 seconds.

For cold rolled laminates, the duration of the electrolytic pickling in AC current can preferably be selected as a function of the type of steels, for example, as follows:

- austenite steels 3-18 s;
- stabilized ferritic steels 3-15 s;
- unstabilized ferritic steels 3-15 s.

The method according to the invention also comprises a finishing and final passivation step (hereafter also just "finishing"). This step, which is generally carried out after having subjected the laminate to careful washing with water to eliminate the residues of sulfuric acid and iron oxides possibly still present on its surface, has the purpose of oxidising the surface of the laminate so as to form a protective layer of chromium oxide.

In general, the finishing step can be carried out according to the prior art. Preferably, according to the method of the present invention the finishing step is carried out by placing the surface of the laminate in contact with an aqueous solution of at least one mineral acid having an oxidation-reduction chemical
potential (measured with respect to a reference electrode Ag/AgCl) comprised between 100 and 800 mV, preferably between 200 mV and 600 mV (finishing solution). Such an oxidation-reduction potential can be obtained, for example, with aqueous solutions comprising one or more acids selected from nitric acid, or sulfuric acid and Fe$^{3+}$ ions possibly in the presence of free hydrofluoric acid.

The concentration of Fe$^{3+}$ ions in the finishing solution varies in the range 5-50 g/1.

As far as the mixture of acids to be used in the finishing solution is concerned, it is selected as a function of the type of steel of the laminate.

In a first preferred embodiment, the mixture of mineral acids used in the finishing step is a mixture of nitric acid and hydrofluoric acid (nitric-hydrofluoric finishing).

The concentration of nitric acid in the finishing solution is preferably comprised in the range 50-150 g/1, whereas that of the free hydrofluoric acid is preferably comprised in the range 5-45 g/1.

In the case of hot rolled austenite steels, the concentration of nitric acid is more preferably comprised in the range 100-150 g/1, whereas that of free hydrofluoric acid is preferably comprised in the range 20-35 g/1.

In the case of hot rolled ferritic and martensitic steels, the concentration of nitric acid is more preferably comprised in the range 75-130 g/1, whereas that of free hydrofluoric acid is preferably comprised in the range 5-20 g/1.

The concentration of Fe$^{3+}$ ions in the finishing
solution is preferably comprised in the range 5-35 g/1.

In the case of cold rolled austenite steels, the concentration of nitric acid is more preferably comprised in the range 60-150 g/1, whereas that of hydrofluoric acid is preferably comprised in the range 10-30 g/1.

In the case of cold rolled martensitic and stabilized ferritic steels, the concentration of nitric acid is more preferably comprised in the range 50-130 g/1, whereas that of hydrofluoric acid is preferably comprised in the range 10-25 g/1.

In a second preferred embodiment, the mixture of mineral acids used in the finishing step is an aqueous solution of sulfuric acid containing, possibly, also free hydrofluoric acid (sulphuric or sulphuric-hydrofluoric finishing) comprising $\text{Fe}^{3+}$ and $\text{Fe}^{2+}$ ions.

The concentration of sulfuric acid in the finishing solution is preferably comprised in the range 20-150 g/1, whereas that of the possible free hydrofluoric acid is preferably comprised in the range 5-30 g/1.

The concentration of $\text{Fe}^{3+}$ ions is preferably comprised in the range 5-80 g/1, whereas the concentration of $\text{Fe}^{2+}$ ions is preferably comprised in the range 5-20 g/1.

In the case of cold rolled austenite steels, the concentration of sulfuric acid is more preferably comprised in the range 60-150 g/1, whereas that of the possible free hydrofluoric acid is preferably comprised in the range 10-30 g/1.

In the case of cold rolled martensitic and stabilized ferritic steels, the concentration of sulfuric acid is more preferably comprised in the range
40-100 g/1, whereas that of the possible free hydrofluoric acid is preferably comprised in the range 5-25 g/1.

In the case of hot rolled austenite steels, the concentration of sulfuric acid is more preferably comprised in the range 40-150 g/1, whereas that of the possible free hydrofluoric acid is preferably comprised in the range 5-30 g/1.

In the case of hot rolled martensitic and stabilized ferritic steels, the concentration of sulfuric acid is more preferably comprised in the range 30-150 g/1, whereas that of the possible free hydrofluoric acid is preferably comprised in the range 5-25 g/1.

In the case of hot rolled austenite steels, the concentration of Fe$^{3+}$ ions is more preferably comprised in the range 45-90 g/1, whereas the concentration of Fe$^{2+}$ ions is more preferably comprised in the range 5-40 g/1.

In the case of hot rolled stabilized ferritic steels, the concentration of Fe$^{3+}$ ions is more preferably comprised in the range 35-80 g/1, whereas the concentration of Fe$^{2+}$ ions is more preferably comprised in the range 5-40 g/1.

In the case of cold rolled austenite steels, the concentration of Fe$^{3+}$ ions is preferably comprised in the range 25-80 g/1, whereas the concentration of Fe$^{2+}$ ions is preferably comprised in the range 5-20 g/1.

In the case of cold rolled martensitic and stabilized ferritic steels, the concentration of Fe$^{3+}$ ions is preferably comprised in the range 20-70 g/1, whereas the concentration of Fe$^{2+}$ ions is preferably
comprised in the range 5-25 g/1.

In a further preferred embodiment, the finishing solution comprises an aqueous solution of nitric acid, as single acid, also comprising Fe$^{3+}$ ions. The concentration of nitric acid in the finishing solution is preferably comprised in the range 20-100 g/1, whereas that of the Fe$^{3+}$ ions is on the other hand comprised in the range 20-50 g/1. This finishing solution is particularly preferred in the case of ferritic cold rolled laminates.

In the case of unstabilized ferritic steels, a further preferred finishing solution comprises nitric acid in a concentration comprised in the range 40-100 g/1 and dissolved metals in a concentration comprised in the range 0-10 g/1 (substantially in the absence of Fe$^{3+}$ ions).

In general, for the purposes of the present invention the finishing solutions that are particularly preferred are those that do not comprise nitric acid, since they allow the environmental impact of the process to be reduced in terms of emissions of polluting gases (NOx) and nitrate and fluorinated compounds in the waste water.

In the finishing step, the finishing solution is kept at a temperature that can vary from 25°C to 65°C.

In the aforementioned conditions, generally the duration of the finishing treatment varies from 10 seconds to 60 seconds.

The finishing step of the pickled laminate can be carried out by placing the laminate in contact with one or more of the aforementioned finishing solutions as a function of the type of steel, of the lamination
process undergone and of the previous pickling steps.

For example, the finishing step can comprise a first treatment with a sulphuric-hydrofluoric solution followed by a second treatment with a nitric-hydrofluoric solution. This embodiment of the finishing step is particularly suitable in the case of cold rolled laminates.

The composition of the scale depends strictly on the type of lamination undergone - hot or cold - and on possible annealing heat treatments to which the laminate has been subjected. As a function of the chemical composition of the steel that forms the laminate and that of the scale, the method according to the invention can comprise one or more further treatment steps. For example, in the case of hot rolled laminates, the treatment method can advantageously also comprise a chemical descaling step to promote the removal of scale in the subsequent electrolytic pickling step.

The chemical descaling step is carried out by placing the laminate in contact with an aqueous solution comprising sulfuric acid and possibly metal ions (descaling solution).

The concentration of sulfuric acid in the descaling solution is selected in the range 150 g/1 - 300 g/1, preferably in the range 200 g/1 - 250 g/1, according to the type of steel and the type of treatments to which the laminate has been subjected.

The concentration of dissolved metals is typically comprised in the range 0-120 g/1.

In a particularly preferred embodiment, the descaling solution comprises 200-280 g/1 of sulfuric
acid and 30–50 g/l of dissolved metals.

The duration of the chemical descaling treatment is typically comprised in the range 15–60 seconds, preferably 25–50 seconds.

The temperature of the descaling solution is preferably kept in the range 70–98°C.

In the case of cold rolled laminates, the chemical descaling step, although possible, is generally omitted, since it is unnecessary.

In the case of cold rolled laminates it has been found that the quality of the pickled surfaces can be improved by also subjecting the laminate to at least one electrolytic treatment in continuous current (DC), using an electrolytic solution having the same composition as the solution used in the treatment in AC current or similar composition.

The electrolytic treatment in DC current is carried out by applying a DC current of density comprised in the range 4–14 A/dm².

For cold rolled laminates, the current density DC is preferably comprised in the range 5–12 A/dm².

The duration of the treatment in DC current is comprised between 3 and 35 seconds, such a duration referring to the period in which a given surface portion of the laminate is anodically polarized.

For cold rolled laminates, the duration of the electrolytic pickling in DC current can vary as a function of the type of steels in the following way:

- austenite steels 4–15 s;
- stabilized and unstabilized ferritic steels 6–35 s.

The treatment in DC current can be carried out
before or after the treatment in AC current, preferably before. The treatment stages in AC and DC current can be carried out in the same tank or in separate tanks, arranged in series in the pickling plant.

The ratio between the duration of the treatment in AC current and the duration of the anodic polarization obtained with the DC treatment is generally comprised between 0.15 and 1, preferably between 0.20 and 0.50.

As happens for electrolytic solutions, also in the other pickling baths the concentration of sulfuric acid and that of dissolved metals varies over time as the treatment of the laminates proceeds. Also in these cases, the concentrations of the different species can be restored through the discharge of the spent solutions, the addition (periodic or in continuous) of fresh reactants, water and for the metals through the addition of oxidants such as hydrogen peroxide, organic and/or inorganic peracids and/or their salts.

The method of the invention can also comprise the conventional steps (intermediate or preliminary) of washing and degreasing the surface of the laminate with suitable aqueous solutions containing surfactants or other additives. In particular, the washing steps (which can be carried out by immersion, spraying with water jets and possibly with the help of metallic brushes) have the purpose of eliminating the residues of the previous treatments from the surface and avoiding contamination of the solutions used in the subsequent steps of the method.

Further steps that can be comprised in the method according to the invention are the steps of mechanical scale removal, through sandblasting or shotblasting, or
stretch levelling of the laminate.

In order to carry out the method of the present invention it is possible to use the apparatuses and the devices commonly used in the field of treatment processes of the surfaces of iron and steel manufactured products, in particular of steel pickling processes.

The electrolytic pickling step, in particular, can be carried out in a tank of the type described in patent application WO 2011/039596.

Figure 1 schematically represents a possible embodiment of an apparatus in which it is possible to carry out the electrolytic pickling step according to the method of the invention.

The apparatus, wholly indicated with 10, comprises a treatment tank 12 suitable for containing the electrolytic solution SE and inside which the laminate 11 is made to pass in continuous along a direction and in the advancing sense indicated by the arrow F. The position of the laminate inside the treatment tank 12 is determined by the rollers 20 and 21 and by the pull applied on the strip.

The apparatus 10 also comprises at least two pairs of electrodes 14 that are opposite one another and between which the laminate 11 is made to pass in continuous.

Each pair of electrodes 14 comprises at least one first electrode 15 facing one of the two faces of the laminate 11 and at least one second electrode 17 facing the other of the two faces of the laminate 11. The electrodes 15, 17, are also substantially equidistant from the laminate 11, each of them being at a distance


Lc from the laminate in general comprised between 50 and 250 mm. The electrodes 15, 17 are arranged in a direction substantially parallel to the faces of the laminate along the path in the tank 12 and they extend substantially for the entire width La of the laminate (the width La is not shown in the figures). The two electrodes 15, 17 of a pair of electrodes 14 are separated by a distance Lg preferably comprised between 100 and 500 mm. Each of the electrodes 15, 17 has a length Le, measured along the movement direction of the laminate, preferably comprised between 300 mm and 2200 mm. Each pair of electrodes 14 is a distance Lx from the next pair, in the movement direction of the laminate, in general comprised between 100 and 800 mm.

The electrodes 15, 17 of each pair of electrodes 14 are immersed in the electrolytic solution SE and can be associated with an electric power supply group (not shown in the figures) capable of delivering a continuous current DC or an alternating current AC at variable frequency. The ways of obtaining an electric power supply group having the aforementioned characteristics are known to the person skilled in the art.

In the case of electrolytic pickling in AC current, a first preferred configuration is that for which the AC current is supplied to the electrodes 15, 17 so that the two electrodes of each pair 14 are with voltage in phase between them, so as to have, at a given moment, on both of the electrodes, a polarization of the same sign. For this purpose, for example, it is possible to connect the electrodes 15 and 17 to a phase of a transformer or of an inverter taking care to arrange a
sufficient distance between pairs of electrodes 14 connected to different phases. Preferably, between pairs of adjacent electrodes 14 there is at least one separator element made of an insulating material, for example in the form of an immersing roller coated in plastic material or of a static separator made from plastic material (not shown in the figures). The separators made from insulating material allow the formation of dispersed currents between electrodes of adjacent pairs that have opposite polarization to be reduced.

A second preferred configuration provides that the electrodes 15 and 17 facing each other are connected to two different phases of the alternating current; in this case it is preferable for successive pairs of electrodes 14, if adjacent and not separated by immersing rollers and other insulating separators, to be connected to the same phases; pairs of electrodes separated by appropriate distance and by immersing rollers and insulating separators, on the other hand, will be connected to different phases so as to minimise the dispersed currents and, at the same time, avoid unbalanced loads on the power supply network.

With the aforementioned second configuration of the electrodes, the resulting electric field has current lines that are substantially vertical and orthogonal to the surface of the laminate, which is thus passed through by the current along the thickness.

In accordance with the method according to the present invention the electrolytic pickling treatment is carried out by applying to the electrodes 15, 17 an alternating current of frequency $f$, variable from 5 Hz
to 150 Hz, said frequency \( f \) being correlated to the forward speed \( v \) (expressed in m/s) of the laminate and to the length \( L_e \) (expressed in metres) of the electrodes 15, 17 by the relation (1)

\[
F(\text{Hz}) \geq \frac{(A-v)}{L_e} \tag{1}
\]

where \( A \) is a rational number greater than 1, preferably greater than 2. Generally, \( A \) does not exceed the value 300.

This provision makes it possible to take into account the geometry of the cell and the evolution phenomena of the electrolysis gases. In this way, moreover, as stated, a given surface portion of the laminate is prevented from being exposed substantially to the same polarization at the pairs of electrodes through which the laminate is made to pass, during the crossing path of the electrolytic bath.

The solution indicated above to improve the efficiency of treatment of the laminate can also be applied to the case in which the apparatus for carrying out the electrolytic treatment comprises electrodes consisting of a plurality of elements (for example plates of the type described in WO 2011/039596). This configuration, schematically illustrated in figure 2, has the advantage of avoiding the accumulation of electrolysis gases and of solid residues (essentially metal oxides) that detach from the surface during the electrolytic process, thus improving the efficiency of the treatment.

The apparatus of figure 2 comprises pairs of electrodes 140 consisting of two groups 150, 170 of elements 160, 180. The elements 160, 180 extend for the entire width of the laminate and have a length \( L_b \).
(measured in the forward direction of the laminate). The elements 160, 180 are arranged substantially parallel with respect to the laminate 11. The distance between two adjacent elements 160, 180 is indicated in figure 2 with reference \( L_d \). Each element 160, 180, in the apparatus 10, performs the function of electrode in the same way as the electrodes 17, 15 of the apparatus 10 described in figure 1.

In figure 2, the elements indicated with the same reference symbols used for figure 1 correspond to the same elements described for figure 1.

Also for the configuration of the apparatus described in figure 2 it has been found that the electrolytic treatment of the laminate 11 could not be uniform over the entire surface for particular geometric arrangements of the electrodes 150, 170, of the elements 160, 180 and of the laminate 11. In particular, non-uniform treatments can be encountered when the distance \( L_d \) between two adjacent elements is close to or greater than the distance \( L_c \) between the element 160, 180 and the laminate 11.

In accordance with the method of the present invention, this drawback can be overcome in the case of an apparatus of the type illustrated in figure 2 by applying to the electrodes an alternating current of frequency \( f \), comprised in the range 5 Hz - 150 Hz, said frequency \( f \) being correlated to the forward speed \( v \) (expressed in m/s) of the laminate and to the length \( L_b \) (expressed in metres) of the element 160, 180 by the relation 

\[
F(\text{Hz}) \geq \left( A' - v \right)/L_b \tag{2}
\]

where \( A' \) is a rational number greater than 1,
preferably comprised between 1 and 25, more preferably comprised between 1 and 10.

In the configuration schematically represented in figure 2, it is suitable for the frequency selected for the AC current of the electrolytic treatment to satisfy one or both of the aforementioned relations (1) and (2).

In particular, when the ratio between the distance $L_g$ between the opposite electrodes 150, 170 and the distance $L_d$ of the elements 160, 180 that form said opposite electrodes 150, 170 is greater than 4, it is preferable for the frequency $f$ to respect at least the relation (1). When, on the other hand, the aforementioned ratio $L_g/L_d$ is equal to or less than 4, it is preferable for the frequency $f$ to respect at least the relation (2).

The method according to the present invention makes it possible to overcome or at least lessen the drawbacks highlighted by the state of the art in the field of pickling treatments of laminates made of stainless steel. The pickling treatments carried out with the method according to the invention have an improved efficacy, making it possible to obtain high-quality pickled surfaces with an overall duration of the treatment that is short.

Thanks to the particular efficacy of the electrolytic treatment and of the subsequent chemical pickling, the method according to the invention, also contemplating carrying out a final finishing and passivation step of the laminates in mixtures containing nitric and hydrofluoric acid, determines a reduction in the environmental impact with respect to
that typically observed in the processes of the prior art. The pickling carried out according to the present invention, indeed, is able to remove – in certain cases – up to 80% by weight of the overall mass of scale and dechromatized steel, thus making it sufficient to have a finishing step in nitric-hydrofluoric acid that is even very short and, consequently, significantly limiting the formation of polluting residues to be disposed of (nitrate, fluorinated compounds and emissions of NOx).

The improved efficacy of the treatment method according to the present invention, moreover, makes it possible to treat the laminates in plants of smaller dimensions with respect to the state of the art, being able to provide for shorter residency times of the laminate in contact with the pickling baths.

A further advantage of the method according to the present invention is the fact that, since at least one electrolytic pickling step is provided, it is possible to adjust the overall speed of the pickling process by acting on the current intensity applied in this step. In the case of slowing down of the pickling line, for example, it is possible to temporarily attenuate the pickling action of the sulfuric acid (decreasing the intensity of the current applied), thus avoiding phenomena of excessive dissolving erosion of the laminate.

The following example embodiments are provided merely to illustrate the present invention and should not be taken to limit the scope of protection defined by the attached claims.

EXAMPLES
The method according to the present invention was applied to treat strips of stainless steel of different chemical composition, obtained through hot or cold rolling processes, possibly accompanied by annealing treatments.

**HOT ROLLED LAMINATES**

In the case of hot rolled laminates, the production and treatment plant comprised the following sections:

- continuous annealing section, of overall length equal to 90 m, capable of heating the strip up to the temperature of 1120°C with a maximum productivity equal to about 133 t/h with strips of width up to 1550 mm;
- cooling section, of overall length equal to 45 m, equipped with cooling means consisting of air blades combined with jets of nebulised water and capable of cooling the laminate up to about 80°C;
- scale-breaker roller for stretch levelling the strip with elongation up to 1% of its original length;
- sandblasting section consisting of 3 cabins equipped with 4 turbines each capable of homogeneously projecting, on both surfaces of the strip, spherical shots of type S110 at speed comprised between 50 m/s and 80 m/s, with flow rate of shots for each turbine comprised between 500 and 1300 kg/min;
- chemical descaling section consisting of 2 immersion tanks of length equal to 15 m each;
- electrolytic pickling section consisting of 2 tanks of length equal to 16 m each, each tank
being equipped with a series of electrodes arranged above and below the strip, in a position substantially parallel to its surface, the overall length of which (taken as the sum of the lengths $L_e$ of all of the electrodes arranged on the same side with respect to the laminate) is equal to 15 m; the electrodes are connected to 5 transformers capable of delivering a current up to 110 kA; the electrolytic section is made according to what is described in document WO 2011/039596 and has the following geometric parameters (with reference to figure 2):

- $L_e = 1.5$ m;
- $L_g = 0.4$ m;
- $L_d = 0.04$
- $L_b = 0.06$ m
- $L_x = 0.5$ m.

- intermediate washing and brushing section equipped with high pressure pumps up to 100 bar;

- finishing and passivation section consisting of 2 tanks of length equal to 14 m each where the strip is immersed in the solution that is continually renewed through a recirculation system having an overall flow rate equal to 800 m$^3$/h.

- washing, final brushing and drying section equipped with high pressure pumps and non-abrasive brushes.

The strips of different dimensions were processed in the aforementioned plant at the speeds given in table 3.

LAMINATES L1-L4
Four different laminates of stainless steel (AISI 304 (L1), AISI 430 (L2), AISI 441 (L3), AISI 409 (L4)).

The concentrations of the different species in the aqueous solutions and the operative conditions adopted in each step of the process together with the dimensional parameters of the laminates L1-L4 are given in Table 3. The efficacy of the method was evaluated by calculating the percentage amount of metal removed from the laminate and/or dissolved during each step with respect to the amount of metal removed and/or dissolved overall.

From the data given in Table 1 it can be seen that for all of the laminates the treatments carried out proved sufficient to obtain a uniformly passivated surface. Such a treatment generated a significantly small amount of polluting products to be disposed of (muds containing nitrate, fluorinated compounds and emissions of NOx), since the amount of metal removed and/or dissolved in the finishing step is reduced to values of 10% by weight (L4) of the mass of steel removed and/or dissolved overall in the entire treatment (chemical descaling, electrolytic pickling and nitric-hydrofluoric finishing). By comparison, in the pickling processes of the prior art, the amount of metal removed and/or dissolved in the nitric and/or hydrofluoric acid baths can reach 80% by weight of the amount pickled overall.
Table 1

<table>
<thead>
<tr>
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<th>L1 (%)</th>
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<td>50</td>
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<td>Finishing</td>
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The method according to the invention, applied to the hot rolled laminates, has resulted in a significant reduction of the polluting substances to be treated.

COLD ROLLED LAMINATES

In the case of cold rolled laminates, the production and treatment plant comprised the following sections:

- continuous annealing section, of overall length equal to 120 m, capable of heating the strip up to the temperature of 1120°C with a maximum productivity equal to about 133 t/h with strips of width up to 1550 mm;

- cooling section, of overall length equal to 65 m, equipped with cooling means consisting of air blades combined with jets of water that intervene on the strip when it reaches temperatures below 200 °C up to a temperature of about 70°C;

- electrolytic pickling section comprising 1 tank of length equal to 55 m to carry out the treatment in DC and AC current; for the treatment in DC current the tank is equipped with a series of horizontal electrodes arranged above and below the strip, in a position substantially parallel to its surface;
the overall length of the electrodes that anodically polarize the strip for the DC treatment (taken as the sum of the lengths of all of the electrodes that anodically polarize arranged on the same side with respect to the laminate) is equal to 24 m; the electrodes are connected to 8 current rectifiers capable of delivering a DC current up to 10 kA (max 40 V) each; for the AC treatment, the tank is equipped with a series of horizontal electrodes, arranged above and below the strip, in a position substantially parallel to its surface, the overall length of which (taken as the sum of the lengths of the electrodes arranged on the same side with respect to the laminate) is equal to 9 m; the electrodes are connected to 3 transformers capable of delivering an AC current up to 10 kA (max 45 V) each; the electrolytic section for the AC treatment is made according to what is described in document WO 2011/039596 and has the following geometric parameters (with reference to figure 2):

- $L_e = 1.5 \text{ m}$,
- $L_b = 0.05 \text{ m}$,
- $L_g = 0.2 \text{ m}$,
- $L_d = 0.05 \text{ m}$
- $L_x = 0.5 \text{ m}$

- washing section equipped with 100 bar pumps;
- finishing section consisting of 2 tanks of overall length equal to 35 m.

- washing, non-abrasive brushing and drying section.

The strips of different dimensions were processed
in the aforementioned plant at the speeds given in Table 4.

**LAMINATES L5-L9**

Four different laminates of stainless steel (AISI 304 (L5), AISI 430 (L6), AISI 441 (L7) and AISI 409 (L8)) obtained through cold rolling and subsequent annealing were subjected to a pickling treatment according to the present invention comprising the following steps in succession: electrolytic pickling in DC current, electrolytic pickling in AC current and finishing in nitric-hydrofluoric mixture.

The same pickling treatment was applied to a fifth laminate (AISI 304 (L9)) obtained through a hot rolling and annealing process.

The concentrations of the different species in the aqueous solutions and the operative conditions adopted in each step of the process together with the dimensional parameter of the laminates L5-L9 are given in Table 4.

The efficacy of the method was evaluated by calculating the percentage amount of metal removed from the laminate and/or dissolved during each step with respect to the amount of metal removed and/or dissolved overall. For all of the laminates the finishing treatments carried out in the conditions given in Table 4 proved sufficient to obtain a uniformly passivated surface. Such a treatment generated a significantly small amount of polluting products to be disposed of (muds containing nitrate, fluorinated compounds and emissions of NOx), since the amount of metal removed and/or dissolved in the finishing step is reduced to values of 20% by weight (L9) of the mass of steel
removed and/or dissolved overall in the entire treatment. By comparison, in the pickling processes of the prior art, the amount of metal removed and/or dissolved in the nitric and/or hydrofluoric acid baths can reach 80% by weight of the amount pickled overall.

The method according to the invention, applied to cold rolled laminates, obtained a significant reduction in polluting substances to be treated.

### Table 2

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### Table 3

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<td>Temperature (°C)</td>
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Note:  
HR = Hot rolled  
CR = Cold rolled

Table 4

<table>
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<tr>
<th>Steel type</th>
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<td>55</td>
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<td>Fe3+ (g/l)</td>
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<td>65</td>
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<td>Dissolved metals (g/l)</td>
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<td>Temperature (°C)</td>
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</tr>
</tbody>
</table>

Note:  
HR = hot rolled  
CR = cold rolled
CLAIMS

1. Method for treating in continuous the surface of a laminate made of stainless steel comprising at least the following steps:

(a) making said laminate (11) pass in continuous in a tank (12) containing an aqueous electrolytic solution (SE) of sulfuric acid, said laminate (11) passing between at least two electrodes (150, 170) immersed in said electrolytic solution (SE) and arranged in a direction substantially parallel to the movement direction of the laminate (11) and having a length $L_e$ measured along said direction, said electrodes (150, 170) facing the opposite faces of said laminate (11) and being arranged in a position facing each other,

(b) subjecting said laminate (11) to an electrolytic pickling treatment by applying an alternating current having a frequency $f$ comprised between 5 Hz and 150 Hz, said frequency $f$ being correlated to said forward velocity $v$ of the laminate (11) and to said length $L_e$ of said electrodes (150, 170) by the relation $F \geq (A - v) / L_e$, where $A$ is a rational number greater than 1, preferably greater than 2;

(c) subjecting said electrolytically pickled laminate (11) to a surface finishing and a surface passivation treatment.

2. Method according to the preceding claim wherein said step (a) is carried out by making said laminate (11) pass in continuous between at least two electrodes (150, 170), each of said electrodes (150, 170) comprising a plurality of elements (160, 180) arranged side by side to each other in a substantially parallel...
manner and arranged transversally to the movement direction of the laminate (11), each of said elements (160, 180) having a length $L_b$ measured along said movement direction of the laminate (11), said electrodes (150, 170) facing the opposite faces of said laminate (11) and being arranged in a position facing each other, and by applying an alternating current having a frequency $f$ comprised between 5 Hz and 150 Hz, said frequency $f$ being correlated to said velocity $v$ and to said length $L_b$ by the relation $f \geq \left(\frac{A'}{v}\right) / L_b$, where $A'$ is a rational number greater than 1, preferably comprised between 1 and 25, more preferably comprised between 1 and 10.

3. Method according to claim 1 or 2 wherein the sulfuric acid is present in said aqueous electrolytic solution in a concentration comprised in the range 40-300 g/l.

4. Method according to one or more of the preceding claims wherein, prior to said step (a), said laminate (11) is subjected to a chemical descaling step (a') in an aqueous solution of sulfuric acid in a concentration comprised in the range 150-300 g/l (descaling solution), said descaling solution optionally comprising metal ions in a concentration comprised in the range 0-120 g/l.

5. Method according to one or more of the preceding claims wherein said electrolytic pickling comprises at least one first and one second stage, said first stage being carried out in continuous current with anodic polarization of said laminate (11) and said second stage being carried out in alternating current.

6. Method according to claim 5 wherein the ratio
between the duration of the treatment in AC current and the duration of the anodic polarization of said laminate (11) in the DC treatment is comprised between 0,15 and 1, preferably between 0,20 and 0,50.

7. Method according to one or more of the preceding claims wherein said electrolytic pickling in alternating current is carried out by applying an alternating current having a frequency \( f \) comprised between 5 Hz and 150 Hz, the current density being comprised between 5 A/dm\(^2\) and 60 A/dm\(^2\), the duration of the treatment being comprised between 3 and 40 s.

8. Method according to claim 5 wherein said electrolytic pickling in continuous current is carried out by applying a continuous current with an anodic polarization density of the strip comprised between 4 A/dm\(^2\) and 14 A/dm\(^2\), the duration of said anodic polarization of the strip being comprised between 3 s and 20 s.

9. Method according to one or more of the preceding claims wherein said step (c) is carried out by putting said laminate into contact with an aqueous solution (finishing and passivation solution) having an oxidation-reduction chemical potential (measured with respect to a reference electrode of the Ag/AgCl type) comprised between 200 and 800 mV, preferably between 200 mV and 400 mV.

10. Method according to one or more of the preceding claims wherein said step (c) comprises a first treatment sub-step with a first finishing and passivation solution and a second treatment sub-step with a second finishing and passivation solution having a different composition from said first solution.
11. Method according to one or more of the preceding claims wherein said finishing and passivation solution is an aqueous solution of nitric acid comprising Fe\(^{3+}\) ions and optionally hydrofluoric acid.

12. Method according to one or more of the claims 1-10 wherein said finishing and passivation solution is an aqueous solution of sulfuric acid and hydrofluoric acid comprising Fe\(^{3+}\) ions and Fe\(^{2+}\) ions.

13. Method according to one or more of the preceding claims wherein said laminate (11) is made to pass in said tank (12) between at least one first and one second pair (140) of electrodes (150, 170) immersed in said electrolytic solution (SE) and arranged in a direction substantially parallel to the movement direction of the laminate (11), between said pairs of electrodes (140) there being interposed a separator element made of an insulating material, in the form of an immersing roller or of a static separator, suitable for reducing the formation of dispersed currents between adjacent electrodes having opposite polarization.
**INTERNATIONAL SEARCH REPORT**

**PCT/IB2014/060230**

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. C25F1/06 C25F7/00

**ADD.**

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)

C25F

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

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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<td>wO 2010/055145 AI (VOESTALPINE STAHG GMBH [AT]; TOMANDL ALEXANDER [AT]; GERPENITCS JOHAN) 20 May 2010 (2010-05-20) page 3 - page 5; figure 1</td>
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**Date of the actual completion of the international search**

23 July 2014

**Date of mailing of the international search report**

01/08/2014

**Name and mailing address of the ISA**

European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel. (+31-70) 340-2040
Fax (+31-70) 340-3016

**Authorized officer**

Hammerstein, G
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