A method and a device (13) are disclosed for the electrolytic pickling of flat metal products (2), in particular special steel and/or carbon steel strips. At least one diamond electrode and/or at least one lead/tin electrode, for example a lead 93/tin7 electrode (15) is used. The special characteristic of the diamond electrodes and/or lead/tin electrodes is the form of water replacement. Whereas in electrolysis water is usually split into hydrogen and oxygen, the diamond electrode and/or lead tin electrode provides a working range in which ozone or highly reactive hydroxyl radicals are formed instead of oxygen. As a result the pickling times are significantly reduced in comparison to the conventional chemical descaling, and also in comparison to the conventional electrolytic pickling.
METHOD AND DEVICE FOR PICKING METALS

[0001] The invention relates to a method and a device for the electrolytic pickling of flat metal products, in particular special steel and/or carbon steel strips. The term flat metal products relates primarily to metal strips and plates. However, the invention can also be applied to long metal products (for example, wires, profiles, tubes) or to metal surfaces in general.

[0002] In order to obtain a good level of cleanliness in the case of cold-rolled, rust and acid-resistant strips, their surface must undergo further processing to remove adhering oxide layers, or scale, formed during preceding heat treatment. The removal of scale is still done mechanically in the preproduction phase by means of vortex or sand blasters. Any residual scale remaining, such as the annealing scale resulting from intermediate and final annealing in the further course of production, is dissolved and detached by a chemical process, pickling, as the scale-covered strips pass through multiple acid baths. The pickling agent (=pickling solution=electrolytic fluid=electrolyte) used for special steel is generally a preheated acid mixture (mixed acid) of water-diluted nitric acid and hydrofluoric acid. The temperatures prevailing in the pickling baths continuously give rise during the pickling process to the very unpleasant and also environmentally pollutant reactions of the NO₃ anion forming NOX.

[0003] The pickling of cold-rolled special steel strips using the so-called “neutral electrolyte" method is already known. In this the voltage is indirectly impressed on the strip. This means that there are no points of contact between any current rollers and the strip. A further feature of this method is that the anodes and cathodes are completely covered by electrolyte and are arranged horizontally, that is to say the cells are flooded horizontally.

[0004] AT 406385B describes a method of electrolytic pickling, a vertically fed strip being described as variant of the method. Here the electrodes are arranged vertically. In this case the voltage is impressed indirectly on the strip. The electrolytic fluid (Na₂SO₄) is fed into the gap between the anode and the strip. The advantage of this electrolytic method is that NOX formation occurs, because no nitric acid is used. The disadvantage of this method stems from the narrow sphere of application. This method with this device is used solely in the pickling of cold-rolled special steel.

[0005] The reference manual “Pickling of Metals", by Dr. Rafael Rütpen, (published by Eugen G. Leuze Verlag) describes methods which are concerned exclusively with the electrolytic pickling of metal surfaces. Constant reference is made throughout to the generation of oxygen directly on the anode, which permits the pickling.

[0006] DE 3937438 A1 describes a possible way of pickling metal surfaces, through the combination of Fe³⁺ salts and/or gaseous or liquid oxygen carriers, such as H₂O₂, air and additional oxygen, which is obtained from an anodic oxidation. In this case 0.5 to 1.0 A/dm² are introduced for the electrolysis.

[0007] AT 373922 B furthermore discloses a method for the electrolytic galvanizing of strip. This involves a vertical arrangement of the electrodes. The electrolytic fluid is fed into the gap between the anode and the strip. The voltage is impressed directly onto the strip—the cathodes take the form of current rollers.

[0008] The U.S. Pat. No. 4,363,709 also disclosed the pickling of special steel strip with higher current densities. Current densities of 40 to 60 A/dm² are mentioned without, however, going into the apparatus capable of achieving this within a reasonable range (<40 Volts) in a full-scale plant.

[0009] GB 2140036 further describes a device for electrolytic pickling with vertical strip feed, indirect current supply and an electrolyte gravity-flow in the gap between strip and electrodes. In this case the current must cover long distances in the strip, the risk being that it will be diverted at one of the deflection rollers and will be subsequently no longer available for the pickling process.

[0010] An object of the present invention is to improve existing electrolytic pickling methods and corresponding devices so that the pickling time can be reduced.

[0011] The object is achieved by a method according to claim 1 and by a device according to claim 15. Use is made of at least one diamond electrode and/or at least one lead/tin electrode, for example a lead 93/tin7 electrode. The special characteristic of the diamond electrodes and the lead/tin electrodes is the form of water replacement. Whereas in electrolysis water is usually split into hydrogen and oxygen, the diamond electrode and/or lead/tin electrode provides a working range in which ozone or highly reactive hydroxyl radicals are formed instead of oxygen. One of the outstanding results of this invention is that the pickling times are significantly reduced in comparison to the conventional chemical descaling, and also in comparison to the conventional electrolytic pickling. The reason for this is the formation of highly efficient OH radicals, oxygen in statu nascendi and simultaneous chemical erosion or dissolution of the oxide on the metal surface. Through the use of synthetically produced diamond electrodes and/or lead/tin electrodes, instead of oxygen the extremely efficient OH radicals can be formed here in the electrolysis of the pickling solution. These oxidize all dissolved substances contained in the pickling solution. The diamond electrode and/or lead/tin electrode moreover has a high level of stability in relation to aggressive pickling solutions.

[0012] In one possible development of the invention the current is delivered on the one hand directly to the flat product (for example, via current rollers or current brushes) and on the other to a pair of electrodes. The flat product and one electrode can be connected as anode and the other electrode as cathode. Delivering the electrical current directly to the anode (on the flat product) on the one hand generates oxygen in statu nascendi, whilst the use of the diamond electrode and/or lead/tin electrode as anode at the same time forms OH radicals, which permit the pickling of metal surfaces.

[0013] The generation of oxygen on the anode (steel strip or steel plate) and/or the formation of OH radicals on the anode (electrode) therefore replace the nitric acid HNO₃, the pickling solution forming the metal complexes and therefore being able to remove scale from the surface of the special steel and/or carbon steel. The pickling solution (mineral acids such as HF, H₂SO₄, H₃PO₄, HCl, mixed acid or Na₂SO₄) here serves as carrier medium for the direct electrical current, and at the same time as pickling solution for chemical descaling of the steel surface. Through the direct delivery of current on the anode, which may be the metal strip, oxygen in statu nascendi is generated by the anodic
oxidation. The anode may also comprise a synthetically produced diamond electrode and/or lead/tin electrode, the diamond being applied to a corresponding substrate material and being made conductive by the doping of suitable elements.

[0014] Methods of producing diamond electrodes will be known to the person skilled in the art. The following methods of production will be mentioned as examples:

[0015] 1) by directly producing boron-doped diamond layers on substrate materials (for example, niobium), in particular by chemical vapour deposition (CVD) processes,

[0016] 2) by embedding a powder composed of doped, synthetically produced diamonds into the surface of a metal or a metal alloy, in such a way that an electrically conductive connection is produced between the metal or the metal alloy and the diamond particles (see WO2004005585 A1),

[0017] 3) by embedding a powder composed of doped synthetically produced diamonds into an electrically conductive plastic.

[0018] One advantageous development of the invention is characterized in that the direct current is intermittently impressed, preferably directly, on the flat product (strip) to be pickled and the diamond electrode and/or the lead/tin electrode. However, the direct current may also be delivered continuously, that is to say constantly.

[0019] An advantageous development of this invention is characterized in that the direct current is impressed alternately on the flat product (strip) to be pickled and on the electrode(s), which means that the electrodes can be acted upon by a direct current always changing from a cathodic current to anodic current, then back to a cathodic current again.

[0020] Mineral acids, mixed acid and/or alkaline electrolytes, such as Na₂SO₄, may be used as electrolyte.

[0021] For chemical erosion and/or dissolution of the scale on the surface of the flat metal product (for example, strip) a mixture of mineral acids and water in a concentration of 10 g/l to 250 g/l mineral acid may be used, the concentration of the mineral acids in particular being between 50 to 200 g/l, preferably 150 g/l.

[0022] In particular the electrolyte fluid may be a mixture of water and Na₂SO₄ (sodium sulphate), the composition of the electrolyte being purposely adjusted to the flat product to be pickled and the concentration of Na₂SO₄ being between 100 and 350 g/l, preferably 150 g/l Na₂SO₄. The electrolyte fluid may also use a mixed acid (mixture of HIF and HNO₃), however, and the composition of the mixed acid may be purposely adjusted to the flat product (strip) to be pickled, the concentration of the mixed acid being between 20 and 100 g/l HIF and 50 and 300 g/l HNO₃, preferably 50 g/l HIF and 150 g/l HNO₃. Even where mixed acid is used, only minimal if any NOX is developed, since the oxygen generated, or the OH radicals, causes the NOX produced to be immediately oxidized to HNO₃ again.

[0023] It is also possible, as electrolyte fluid, to use a mixed acid in which the concentration and composition corresponds to that generally used in conventional chemical pickling.

[0024] The use according to the invention of the direct current, which replaces the HNO₃, means that no measures have to be taken to reduce the NOX inevitably produced. The use of urea or hydrogen peroxide can be dispensed with.

[0025] It is in any case possible to provide devices which ensure that the concentration of the pickling bath can be precisely adhered to. This makes it possible to improve the surface quality of the flat product, for example the steel strip.

[0026] The current densities (amperes per unit area) can be purposely adjusted to the flat product to be pickled, the current densities on the electrodes being between 0.5 and 150 A/dm². The electrolyte temperature can be purposely adjusted to the strip to be pickled, the electrolyte temperature being between 20 and 90° C., preferably 75° C.

[0027] An advantageous development of the invention is characterized in that the electrical voltage can be variably adjusted so that the metal surface of the strip can also, if necessary, be polished.

[0028] A beneficial development of the invention is characterized in that the electrolyte feed quantity (quantity of pickling solution) in the gap between the pair of diamond electrodes and/or the pair of lead/tin electrodes and the strip is controlled. The strip can thereby be hydraulically or mechanically positioned precisely in the centre between the pair of electrodes. Thus it is possible to reduce the distance between the diamond electrodes and/or lead/tin electrode and the strip to a minimum.

[0029] An advantageous development of the invention is characterized in that the gap between the diamond electrodes and/or lead/tin electrodes can be varied. This means that the strip can be readily adjusted to the strip undulation.

[0030] A beneficial further development of the invention is characterized in that the strip undulation is determined and the diamond electrodes and/or lead/tin electrodes are distanced from the strip, so that any contact between the strip and the diamond electrodes and/or lead/tin electrodes, which would be bound to lead to short-circuiting, is avoided.

[0031] A device for setting and regulating the distance between the strip and the diamond electrodes and/or lead/tin electrodes can furthermore be provided. The adjustable distance between the strip and the diamond electrodes and/or lead/tin electrodes allows the current flow to be adjusted, thereby reducing the power costs.

[0032] One possible embodiment of a device according to the invention is a pickling cell, in which the direct electrical current is impressed directly onto an electrically conductive contact between the strip and the electrode (cathode and/or anode). In this case guide devices may be provided, by means of which a strip can be guided at an angle to the horizontal, electrodes being arranged at the same angle and devices being provided, by means of which electrolyte fluid can be introduced between the strip and the electrodes. In particular a strip can be led obliquely downwards at an acute angle, in particular an angle of 30 to 45°, and then following at least one deflection roller obliquely upwards at an angle, in particular an angle of 30 to 45°, so that the strip can be easily and efficiently introduced into the pickling cell. The obliquely inclined arrangement makes the cell space-saving. Substantially less space is required compared to conven-
tional chemical pickling plants. A very effective strip guidance is furthermore achieved in that there is no sagging of the strip.

[0033] The position of at least one electrode of a pair of electrodes and the deflection roller may be adjustable perpendicular to the direction of movement of the flat product. The electrodes and the deflection roller can thereby be hydraulically and/or mechanically raised out of the way whilst the strip is being inserted.

[0034] Such an inclined pickling cell may be used both in batch-feed pickling and in so-called continuous pickling, since the introduction of the strip is made substantially easier by the folding up of the diamond electrodes and/or lead/tin electrodes and simultaneous raising of the deflection roller.

[0035] An advantageous variant of the invention is achieved by the provision of a control device for the electrolyte fluid (pickling solution) feed quantity, a separate control device being provided for each fluid inlet between the strip and the diamond electrodes and/or lead/tin electrodes, so that the flow can be adjusted to the strip width and also set to the optimum for strips of different width. The resulting hydraulic or mechanical guidance of the strip means that the position of the strip can be purposely adjusted between the pair of diamond electrodes and/or pair of lead/tin electrodes.

[0036] One advantage of the invention is that the spent pickle, that is to say the used pickling solution, does not contain any nitrates and can thereby be recovered much more easily and cost effectively. The energy costs for the hydropyrolysis of the spent solutions prove to be substantially less than for conventional techniques.

[0037] All metering, monitoring and tank units and pumps for HNO₃ and urea can be dispensed with, resulting in a major cost saving.

[0038] Separators arranged in the strip running direction ensure that the strip can be brought to the electrodes as accurately as possible without permitting any contact between the strip and the electrode. This ensures that the strip does not form an electrical short-circuit with the electrode.

[0039] An advantageous variant of the invention is characterized in that control of the current flow enables the surface of the strip to be pickled rapidly and efficiently and in a manner consistent with the quality grading, without polluting the environment with harmful gases such as NOₓ, or nitrate salts in the spent pickling solution.

[0040] The invention will now be explained with reference to examples in the drawings, in which

[0041] FIG. 1 shows a schematic diagram of a conventional pickling plant with chemical removal by means of mixed acid,

[0042] FIG. 2 shows a plant based on the "neutral electrolyte" method,

[0043] FIG. 3 shows a pickling cell based on the method according to the invention.

[0044] FIG. 4 shows a plant based on the method according to the invention.

[0045] FIG. 1 shows a pickling bath 1 according to the prior art. The metal strip 2 is fed over the take-off reel 44 through the degreasing bath 5, and then cleaned with de-ionized water in the rinser 4 before embarking upon the chemical removal of the scale in the pickling bath 1 using the mixed acid 3 (HF/HNO₃). The mixed acid 3 is fed into the pickling bath 1 by a pump 7 via the pipe 6 and is led off via a pipe 8, for example into an intermediate vessel 9, where the mixed acid 3 is recirculated. The metered addition of a urea solution 10 is performed by a pump 11 directly into the pickling bath 1, and is done for environmental reasons so that the proportion of NOₓ is reduced. After the pickling bath 1, the metal strip 2 has any adhering mixed acid cleaned off by means of de-ionized water in the rinser 12, and the water removed by means of a blower in the drier 16, and is then rolled up on a take-up reel 45.

[0046] FIG. 2 shows a pickling bath 1 according to the prior art. The metal strip 2 is fed through the electrolyte 3, for example Na₂SO₄ between the cathodes 34 and the anodes 35. The distance between the electrodes and the strip is usually approximately 70 to 150 mm, the metal strip 2 having a certain sag, which can be reduced by means of support rollers at the middle of the plant, for example. The electrolyte 3 is led off by a pipe 8 into an intermediate vessel 9, for example, and is returned by a pump 7 via the pipe 6 into the pickling bath 1, from whence the electrolyte 3 is recirculated.

[0047] FIG. 3 shows a pickling cell 13 according to the invention, which fulfills the function of the pickling bath 1. The metal strip 2, for example special steel and/or carbon steel strip, is fed into the gap between the electrodes 15 of a pair of electrodes. One electrode in each pair of electrodes 15 and a current roller 14 (or the metal strip 2) is connected to a rectifier 19 at any time.

[0048] The upper electrodes 15 can in each case be moved in the direction 20, and the deflection roller 14' in the direction 20', so that the distance between the metal strip 2 and the electrodes 15 is adjustable. This permits optimum utilization of the current. The electrolyte or pickling solution 3 is in turn delivered by means of a pump 7 via a pipe 6, pipes 21, 21', 21", 21''' being provided, which feed the electrolyte 3 into the gaps 24, 24', 24", 24''' between the metal strip 2 and the electrodes 15. The delivery of electrolyte or pickling solution can now be adjusted to the required conditions by the control valves 22, 22', 22", 22'''. After passing between the metal strip 2 on the electrodes 15 the electrolyte 3 is collected in the lower part 23 of the electrolytic pickling cell 13 and fed back to the pump 7. The separators 25, 25', 25", 25''' are arranged in the running direction of the strip.

[0049] The lower electrode is in each case connected to the negative output of the rectifier 19, the positive output of the rectifier 19 is connected to the current roller 14. The upper electrode 15 is in each case connected to the negative output of the rectifier 19, the metal strip is connected to the positive output of the rectifier 19. In order for the electrodes 15, which take the form of diamond electrodes or lead/tin electrodes, to be operated as anode, the direct current would have to be impressed alternately.

[0050] A more advantageous development of the invention (which is not limited to the concrete example), is to connect the lower electrode on the inlet side to the positive
output of a rectifier, so that it serves as anode. The metal strip is likewise connected to positive potential. The upper electrode is then connected to the negative output of the rectifier and serves as cathode. On the outlet side the connection of the electrodes is reversed: the lower electrode there serves as cathode, the upper as anode. In this way both the upper side and the underside of the strip comes into the area of the OH radicals formed on the anode. In this development just one rectifier 19 each could be provided both for the inlet side and for the outlet side.

An alternative to the latter possible embodiment (which is not limited to the concrete example) is to connect no current to the metal strip 2, that is to apply current only to the electrode pair serving as cathode and anode ay any one time.

FIG. 4 shows a plant having a take-off reel 44 and a take-up reel 45, which enable the metal strip 2 to be drawn through the processing at a corresponding speed. The treatment comprises a chemical and/or electrolytic degreasing 5, in order to be able to clean the oiled strip, and an electrolytic pickling cell 13. The electrolytic pickling cell 13 is connected to the rectifiers. The pairs of electrodes 15 are arranged so that in only one pair of electrodes 15 is connected to a current roller 14 and to a rectifier at any one time. By means of the rectifier setting, variable electrical voltages, intermittent, alternating and/or continuous can be impressed on the electrodes, which where necessary polish the surface of the metal strip 2. The metal strip 2 is deflected over the current rollers 14 and the deflection roller 14'.

LIST OF REFERENCE NUMERALS

1 Pickling bath
2 Metal strip
3 Electrolyte
4 Rinser
5 Degreasing bath
6 Pipe from pump 6 to pickling bath 1 or pickling cell 13
7 Pump
8 Pipe from pickling bath 1 to intermediate vessel 9
9 Intermediate vessel
10 Urea solution
11 Pump for urea solution 10
12 Rinser
13 Electrolytic pickling cell
14 Current roller
14' Deflection roller
15 Electrodes
16 Drier
19 Rectifier
20 Direction of movement of the electrodes 15
21, 21', 21", Electrolyte delivery pipes 21"
22, 22', 22", Electrolyte delivery control valves 22"
23 Lower part of the pickling cell 13
24, 24', 24", Gap between metal strip 2 and 24" electrode 15
25, 25', 25", Separators
30 Fluid level
34 Cathode
35 Anode
44 Take-off reel
45 Take-up reel

1. Method for the electrolytic pickling of flat metal products (2), in particular special steel and/or carbon steel strips, characterized in that at least one diamond electrode and/or at least one lead/tin electrode, for example a lead 93/tin7 electrode (15) is used.
2. Method according to claim 1, characterized in that the current is delivered on the one hand directly to the flat product (2) and on the other to at least one pair of electrodes.
3. Method according to claim 2, characterized in that one electrode (15) of the pair of electrodes and where necessary the flat product (2) is connected as anode and the other electrode (15) as cathode.
4. Method according to any one of claims 1 to 3, characterized in that the current is delivered intermittently.
5. Method according to any one of claims 1 to 4, characterized in that the current is delivered constantly.
6. Method according to any one of claims 1 to 5, characterized in that direct current is impressed alternately (reverse pulse plating) on the flat product (2) to be pickled and the electrodes (15).
7. Method according to any one of claims 1 to 6, characterized in that a mixture of mineral acids and water in a concentration of 10 g/l to 250 g/l mineral acid, in particular between 50 to 200 g/l, preferably 150 g/l, is used.
8. Method according to any one of claims 1 to 7, characterized in that a mixture of water and Na₂SO₄ (sodium sulphate) is used, the concentration of Na₂SO₄ being set between 100 and 350 g/l, preferably 150 g/l Na₂SO₄, as a function of the flat product to be pickled.
9. Method according to any one of claims 1 to 8, characterized in that mixed acid is used, the concentration being set between 20 and 100 g/l HF and 50 and 300 g/l HNO₃, preferably to 50 g/l HF and 150 g/l HNO₃ as a function of the flat product (2) to be pickled.
10. Method according to any one of claims 1 to 9, characterized in that the current densities on the electrodes are set between 0.5 and 150 A/dm² as a function of the flat product (2) to be pickled.
11. Method according to any one of claims 1 to 10, characterized in that the electrolyte temperature is set between 20 and 90°C, preferably to 75°C, as a function of the flat product (2) to be pickled.
12. Method according to any one of claims 1 to 11, characterized in that the electrical voltage is variably adjusted.

13. Method according to any one of claims 1 to 12, characterized in that the distance between the flat product and the electrode is adjusted with the quantity of electrolyte fluid fed between the flat product (2) and the electrode (15).

14. Method according to any one of claims 2 to 13, characterized in that the distance between the electrodes (15) of a pair of electrodes or between the electrode (15) and the flat product (2) is adjusted to the undulation of the flat product.

15. Device for performing a method according to any one of claims 1 to 14 for the electrolytic pickling of flat metal products (2), in particular special steel and/or carbon steel strips, characterized in that at least one diamond electrode and/or at least one lead/tin electrode, for example a lead/tin electrode (15) is used.

16. Device according to claim 15, characterized in that at least one pair of opposing electrodes (15) is provided, between which a flat product (2) can be fed.

17. Device according to either of claims 15 or 16, characterized in that a device (19) is provided for delivering current on the one hand directly to the flat product (2) and on the other to the electrodes (15), in particular so that one electrode of a pair of electrodes is connected as cathode and the other electrode as anode, and the flat product can if necessary be connected as anode.

18. Device according to any one of claims 15 to 17, characterized in that guide devices (14, 14') are provided, by means of which a strip (2) can be guided at an angle to the horizontal, that electrodes (15) are arranged at the same angle, and that devices (21, 21', 21'', 22, 22', 22'') are provided, by means of which electrolyte fluid can be introduced between the strip (2) and the electrodes (15).

19. Device according to claim 18, characterized in that a strip can be led obliquely downwards at an angle, in particular an angle of 30 to 45°, and then following at least one deflection roller (14') obliquely upwards at an angle, in particular an angle of 30 to 45°.

20. Device according to any one of claims 16 to 19, characterized in that the position of at least one electrode (15) of a pair of electrodes and the deflection roller (14') can be adjusted perpendicular to the direction of movement of the flat product.

21. Device according to any one of claims 16 to 20, characterized in that the gap between the electrodes of a pair of electrodes is adjustable.

22. Device according to any one of claims 15 to 21, characterized in that a control device is provided for regulating the delivery quantity of the electrolyte fluid.

23. Device according to any one of claims 15 to 22, characterized in that at least one separator is fitted on at least one electrode.

24. Device according to any one of claims 15 to 23, characterized in that a control device is provided for controlling the current flow to the electrodes (15).

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