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(54) **STAINLESS STEEL PICKLING IN AN OXIDIZING, ELECTROLYTIC ACID BATH**

EDELSTAHLBEIZUNG IN EINEM OXIDIERENDEN UND ELEKTROLYTISCHEN SÄUREBAD

DÉCAPAGE D'ACIER INOXYDABLE DANS UN BAIN ACIDE ÉLECTROLYTIQUE, OXYDANT

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Description

PRIORITY

- 5 [0001] This application claims priority to U.S. Provisional Patent Application Serial No. 61/539,259, filed September 26, 2011, entitled "STAINLESS STEEL PICKLING IN AN OXIDIZING, ELECTROLYTIC ACID BATH,".

BACKGROUND

- 10 [0002] The annealing of a metal strip such as a stainless steel strip may result in the formation of oxides on the surface of the metal strip. These oxides are comprised of, for example, iron, chromium, nickel, and other associated metal oxides, and are removed or reduced prior to utilization of the strip. The oxides of stainless steel, however, can be resistant to the common acid treatments. In addition, these oxides adhere tightly to the base metal, and thus may require mechanical scale cracking such as shot blasting, roll bending, or leveling of the steel strip or electrolytic and/or molten salt bath treatment prior to pickling (removal of the oxides on the surface of the strip) to either loosen these oxides or make the oxide surface more porous before pickling the strip.

- 15 [0003] Traditionally, the oxides on the surface of the stainless steel have been removed, or "pickled off", using nitric acid in combination with hydrofluoric acid; or using a combination of hydrogen peroxide, sulfuric acid, and hydrofluoric acid, such as disclosed in U.S. Patent No. 6,645,306, entitled Hydrogen Peroxide Pickling Scheme for Stainless Steel Grades," issued November 11, 2003. Such acids, particularly hydrofluoric acid, are expensive. Further, nitric acid is not considered environmentally friendly.

- 20 [0004] WO 03/0521165 A1 describes a multi-steps process for the descaling, pickling and finishing/passivating of ferritic or non-ferritic stainless steel strips. The process comprises a two-steps electrolytic rescaling step using in the first step an aqueous solution comprising from 10 to 250 g/l H_2SO_4 with < 80g/l total dissolved Fe and optionally $\text{Fe}^{3+} \geq 15$ g/l and $\text{Fe}^{3+}/\text{Fe}^{2+} \geq 1.0$, and in the second step an aqueous solution comprising from 10 to 250 g/l H_2SO_4 with 80g/l total dissolved Fe and optionally and $\text{Fe}^{3+}/\text{Fe}^{2+} > 1.0$. Said process further comprises a chemical pickling step by means of an aqueous solution comprising H_2SO_4 and HF.

- 25 [0005] WO 02/086199 A2 relates to electrolytic descaling under specified current density conditions in various strong acid solutions.

- 30 [0006] WO 99/32690 A1 does not describe an electrolytic pickling process for a ferritic stainless steel strip using a mixture of H_2SO_4 and an excess of an oxidizing agent such as H_2O_2 , in the absence of HF, nor does it describe an electrolytic pickling process for a stainless strip using a mixture of 10 g/l to 200 g/l H_2SO_4 and an excess of an oxidizing agent such as H_2O_2 .

- 35 [0007] WO 99/32690 A1 does not describe an electrolytic pickling process for a ferritic stainless steel strip using a mixture of H_2SO_4 and an excess of an oxidizing agent such as H_2O_2 , in the absence of HF, nor does it describe an electrolytic pickling process for a stainless strip using a mixture of 10 g/l to 200 g/l H_2SO_4 and an excess of an oxidizing agent such as H_2O_2 .

- 40 [0008] The present application describes a process for pickling stainless steel by preparing a mixture of an acid such as sulfuric acid (H_2SO_4), an excess of hydrogen peroxide (H_2O_2), and at least one electrode set including at least one of a cathode or anode and applying a current to a metal strip (such as a stainless steel strip) running through the mixture. Because of an excess of H_2O_2 , all ferrous sulfate is converted to ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$), which acts as an oxidizing agent itself. The process allows for a reduction of total chemicals consumed in the pickling process from known pickling processes and particularly for a reduction of nitric acid (HNO_3) and/or hydrofluoric acid (HF) over known pickling processes. Further, certain ferritic stainless steels can be pickled without including HF in a pickling process utilizing the above disclosed mixture of an acid such as sulfuric acid (H_2SO_4), an excess of hydrogen peroxide (H_2O_2), and at least one electrode set.

BRIEF DESCRIPTION OF THE DRAWINGS

- 50 [0009] While the specification concludes with claims which particularly point out and distinctly claim the invention, it is believed the present invention will be better understood from the following description of certain examples taken in conjunction with the accompanying drawings, in which like reference numerals identify the same elements and in which:

FIG. 1 depicts a schematic of a three tub arrangement of prior art pickling of a stainless steel strip;

FIG. 2 depicts a schematic for a three tub arrangement of pickling of a steel strip wherein the first tub includes a cathode-anode-cathode electrode set; and

FIG. 3 depicts a schematic for a one tub, electrolytic arrangement of pickling of a stainless steel strip.

[0010] The drawings are not intended to be limiting in any way, and it is contemplated that various embodiments of the invention may be carried out in a variety of other ways, including those not necessarily depicted in the drawings. The accompanying drawings incorporated in and forming a part of the specification illustrate several aspects of the present invention, and together with the description serve to explain the principles of the invention; it being understood, however, that this invention is not limited to the precise arrangements shown.

DETAILED DESCRIPTION

[0011] The following description of certain examples should not be used to limit the scope of the present invention. Other examples, features, aspects, embodiments, and advantages of the new pickling process will become apparent to those skilled in the art from the following description. As will be realized, the invention is capable of other different and obvious aspects, all without departing from the invention. Accordingly, the drawings and descriptions should be regarded as illustrative in nature and not restrictive.

[0012] The present disclosure relates to a process for pickling metal, and in particular to pickling a hot rolled, hot rolled and annealed, or cold rolled and annealed stainless steel strip that is processed in a continuous fashion. The process comprises at least one pickling tank and optionally may include at least one of a pre-pickling tank, a scrubber-brush tank, a de-smutting tank, a filtration unit, or a heat exchanger. For example, the process may comprise a series of pre-pickling steps that are mechanical and/or chemical, one or more pickling tanks, and a posttreatment step to rinse and dry the treated material, all of which are known in the art. A pre-treatment step may include, for example, shot blasting, stretch leveling, a molten bath exposure, or a suitable pre-treatment step as will be apparent to one of ordinary skill in the art in view of the teachings herein. Such pre-treatment steps mechanically crack and/or remove scale and/or chemically reduce a scale layer on a metal strip to prepare the metal strip for more efficient pickling.

[0013] The nature of the oxides and the treatments to remove them from the base metal are dependent on the alloy composition of the base metal. Stainless steels are rich in chromium (Cr) and when heated they form oxides rich in Cr. The Cr rich oxides are relatively resistant/passive to attack by most acids. They typically require use of a combination of acids such as nitric acid (HNO_3) and hydrofluoric acid (HF) to completely remove them. A function of HF is to penetrate the protective Cr rich oxide and then allow for oxidizing acids such as HNO_3 to dissolve Cr depleted base metal and prevent premature passivation of the base metal before the oxide layer is fully removed. HF is an expensive chemical and HNO_3 tends to be disfavored because of environmental concerns.

[0014] The described process reduces the concentrations of acids, particularly HNO_3 and/or HF required without negative impact on production rates by using the additional pickling power of at least one electrode set having a least one cathode and at least one anode, an excess of an oxidizing agent such as H_2O_2 . The excess of the oxidizing agent creates another oxidizing agent, and the power of the another oxidizing agent, such as $\text{Fe}_2(\text{SO}_4)_3$, acts to aggressively attack the rich oxide and thus release/lift the oxide from the base metal. The process allows for a reduction of total chemicals consumed in the pickling process from known pickling processes and for a reduction of nitric acid (HNO_3) and/or hydrofluoric acid (HF) over known pickling processes.

[0015] In known pickling methods, hot rolled metal material, hot rolled and annealed metal material, and/or cold rolled and annealed metal material such as a stainless steel strip are processed in a combination of mixed acids and are exposed to a series of pickling tanks or tubs. In one known process, a first tank may include sulfuric acid (H_2SO_4) and HF. A second tank may include HNO_3 and HF. A final tank may include HNO_3 to passivate the surface of the metal strip, which is then rinsed and dried. FIG. 1 shows a known prior art pickling method having three tanks. First tank 10 includes H_2SO_4 and may additionally include HF. Second tank 12 includes HNO_3 and HF. Third tank 14 includes HNO_3 . Stainless steel strip 16 passes in a continuous manner through each of first tank 10, second tank 12, and third tank 14 in the direction of arrow A.

[0016] A process is disclosed that can reduce or eliminate the need for the HNO_3 and HF bath in the second tank for ferritic stainless steels and reduces the concentrations needed in such a HNO_3 and HF bath for austenitic and martensitic stainless steels.

[0017] The disclosed process follows the pre-treatment step(s) described above in paragraph [0011]. After the pre-treatment step(s), the metal strip is immersed in a first electrolytic pickling bath comprising an acidic composition and an oxidizing agent. The acidic environment may include H_2SO_4 , for example, and may additionally include HF. Certain ferritic stainless steels will not require HF in this step of the process. One of the oxidizing agents may be, for example, ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$), which can be created by continuously injecting another oxidizing agent such as hydrogen peroxide (H_2O_2), and the H_2O_2 may be kept in excess to the dissolved metals such that H_2O_2 would exist at a concentration above what is necessary to convert all ferrous metal to ferric metal. For example, as the scale of oxides on a steel strip is dissolved by a pickling process, ferrous metals dissolve into the pickling mixture as ferrous sulfate. The ferrous sulfate slows the chemical reaction associated with a pickling rate. Ferrous sulfate is able to be converted to ferric sulfate via

an oxidizing agent such as H_2O_2 or HNO_3 , for example. Ferric sulfate advantageously acts as an accelerator to the chemical pickling reaction rate. An excess amount of H_2O_2 ensures that a full conversion of ferrous sulfate to ferric sulfate has been made.

[0018] Electrodes are used to apply a current to the metal strip while the strip is immersed within this bath. An electrode set may include at least one of a cathode or an anode, where a steel strip may act as the other of a cathode or an anode to conduct current. For example, in a batch pickling process, steel wire coils, or steel parts, are submerged as a discrete unit, rather than a continuous strip, into a batch containing a pickling mixture. In such an instance, a cathode may be present in the mixture and the steel part may act as an anode. Additionally or alternatively, for either a batch process or a continuous process, at least one cathode and at least one anode electrode set may be used, for example. The arrangement may be a cathode-anode-cathode electrode set arrangement, though other electrode set arrangements as will be apparent to one of ordinary skill in the art in view of the teachings herein may additionally or alternatively be used. For example, a single electrode set including one cathode and one anode may be used. With the electrolytic pickling bath described above, the control of the ratio of ferric to ferrous ions in the pickling bath is not required.

[0019] Use of such a solution as the first pickling bath described above advantageously de-scales most ferritic stainless steels and significantly reduces a scale layer for austenitic stainless steels that may then need a second pickling bath containing reduced concentrations of acids such as HNO_3 and/or HF, to sufficiently remove any remaining oxide/scale layer. While the disclosed process does not require a third HNO_3 bath to obtain a cleaned and pickled metal strip on ferritic stainless steels, such a third bath may be used to passivate a surface of the treated metal strip.

[0020] FIG. 2 shows an example of the disclosed process using an electrolytic pickling bath after annealing and the molten salt treating of a steel strip 16. First tank 20 includes a H_2SO_4 and HF bath having electrode sets 22, 24, and 26 organized as arrangement 28 through which stainless steel strip 16 runs in a continuous fashion and in the direction of arrow A. First tank 20 may contain, for example, from about 10 g/L to about 200 g/L of H_2SO_4 , or about 30 g/L to about 120 g/L of H_2SO_4 , or about 25 g/L to about 35 g/L of H_2SO_4 , from about 0 g/L to about 100 g/L of HF, from about 0.01 g/L to about 100 g/L of H_2O_2 , or about 1 g/L to about 100 g/L of H_2O_2 , or about 5 g/L to about 100 g/L of H_2O_2 , and at least one cathode and one anode electrode set. The inclusion of HF in the electrolytic bath would necessitate a special compatible material that is resistant to chemical attack, but is still electrically conductive. Electrode set 22 is a cathode electrode set, electrode set 24 is an anode electrode set, and electrode set 26 is a cathode electrode set. Steel strip 16 runs through arrangement 28 and each set 22, 24, 26 applies current to steel strip 16. Current may be applied, for example, in a range of from about 10 to about 200 Coulombs per dm^2 with a current density of from about 1 to about 100 Amps per dm^2 or from about 1 to about 10 Amps per dm^2 . A temperature of from about 21.1 °C (70 °F) to about 54.4 °C (130 °F) or from about 27.7 °C (80 °F) to about 54.4 °C (130 °F) may be maintained to manage breakdown of H_2O_2 when injected into the system. An amount of dissolved metals could be equal to or less than about 80 g/L, in the range of from about 0 to 80 g/L, or in a range of from about 5 to about 40 g/L.

[0021] Second tank 30 includes HNO_3 for use, for example, with ferritic stainless steel processing. Second tank 30 may contain, for example, from about 10 g/L to about 130 g/L of HNO_3 . A second tank is optional for ferritic stainless steel processing unless it is desired to brighten and passivate the steel strip via the pickling process rather than via a later, natural reaction with air, at which point the second tank would be necessary. For austenitic stainless steel grades, a second tank may contain a total amount of HNO_3 and HF reduced from that used in known pickling processes. For example, as described below with respect to Example 1, HF may be reduced by about 50% from a known process such that a total consumption of HNO_3 and HF is reduced in the second tank. The HF may be included in the concentration of, for example, from about 1 g/L to about 100 g/L or about 5 g/L to about 30 g/L or about 5 g/L to about 25 g/L. Third tank 32 may include HNO_3 for use, for example, with ferritic stainless steel processing, or may utilize HF for use, for example, with austenitic stainless steel processing. Third tank 32 may contain, for example, from about 10 g/L to about 130 g/L of HNO_3 . The HF may be included in third tank 32 in the concentration of, for example, from about 1 g/L to about 100 g/L or about 5 g/L to about 30 g/L or about 5 g/L to about 25 g/L. Or the third tank 32 may include no HF and an amount of HNO_3 that is reduced by about 20% from a known process such that a total consumption of acids is reduced over that of prior art processes in the third tank.

[0022] The process of the present application may alternatively only use a single tank, which is shown in FIG. 3 as single tank 40. Such a single tank process may be used particularly for steel strip 16 that is a ferritic stainless steel. Tank 40 includes the bath solution described above for first tank 20 of FIG. 2. After leaving tank 40, steel strip 16 proceeds to a rinsing and drying treatment section as will be apparent to one of ordinary skill in the art in view of the teachings herein.

EXAMPLES

[0023] In the following examples the polarity of the electrolyte was switched at least one time in a manner apparent to one of ordinary skill in the art in view of the teachings herein.

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EXAMPLE 1

[0024] In the first example showing actual data, the electrolytic pickling ("EP") process of the present disclosure was found to consume less total chemicals and operate at a lower temperature while arriving at better results than a pickling process of the prior art (referred to as "Baseline" below).

TABLE 1: TUB 1

	EP	EP	EP		Baseline	Baseline	Baseline
	301 SS	304 SS	316 SS		301 SS	304 SS	316 SS
H ₂ SO ₄ (g/L)	30	30	30		100	100	100
Fe ³⁺ (g/L)	30	30	30		0	0	0
Fe ²⁺ (g/L)	0	0	0		30	30	30
H ₂ O ₂ (g/L)*	>0.1	>0.1	>0.1		0	0	0
C/dm ²	100	100	100		30	30	30
Temp (°C) (Temp (F))	48.9 (120)	48.9 (120)	48.9 (120)		71.1 (160)	71.1 (160)	71.7 (160)
Visual Appearance	Almost Clean	Almost Clean	Same as original		Half Clean	Half Clean	Same as original
*H ₂ O ₂ was not measured in this case, but was theoretically calculated based on the known chemical reaction.							

[0025] Stainless steels of ASTM grades 301, 304, and 316, which grades and associated chemical compositions are known in the art, were tested in both the Baseline process and the EP process. For the Baseline process, a remaining amount of 30 g/L of Fe²⁺ showed that H₂O₂ is not in excess (as does the 0 g/L amount of H₂O₂). For the EP process, an amount of 0 g/L of Fe²⁺ showed that H₂O₂ is in excess (also as shown by the 5 g/L amount of H₂O₂). For the grade 301 stainless steel, the Baseline process used a first tub having 100 g/L of H₂SO₄ and 30 Coulombs/dm² at a temperature of 71.1. °C (160 degrees Fahrenheit), which resulted in a partially cleaned steel surface. The EP process used a first tub having a reduced amount of 30 g/L of H₂SO₄, 30 g/L of Fe³⁺, and an increased 100 Coulombs/dm² at a reduced temperature of 48.9 °C (120 degrees Fahrenheit), which resulted in a substantially fully cleaned steel surface. Similar amounts for the grade 304 stainless steel produced equivalent results. Similar amounts for the grade 316 stainless steel produced results in which the steel surface appeared to be the same as prior to the pickling process, which indicated an unsuccessful cleaning. The materials of this first example may then be fully cleaned in one or more subsequent tubs that included reduced amounts of HNO₃ and HF in comparison to subsequent tubs used in known pickling processes. "Total HF" is described in the following examples and it is the combination of "free HF" and the portion bound to dissolved metals. Depending on the analysis technique, "total HF" or "free HF" can be measured.

[0026] To completely clean the material, subsequent pickling would be expected at the following concentrations for each of tubs 2 and 3 below. The term clean indicates a generally acceptable appearance from a production standpoint as apparent to one of ordinary skill in the art.

TABLE 2: TUB 2

	EP	EP	EP		Baseline	Baseline	Baseline
	301 SS	304 SS	316 SS		301 SS	304 SS	316 SS
HNO ₃ (g/L)	100	100	100		100	100	100
Total HF (g/L)	10	10	20		20	20	40
Fe ³⁺ (g/L)	30	30	30		30	30	30
Temp (°C) (Temp (F))	54.4 (130)	54.4 (130)	54.4 (130)		54.4 (130)	54.4 (130)	65.6 (150)

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TABLE 3: TUB 3

	EP	EP	EP		Baseline	Baseline	Baseline
	301 SS	304 SS	316 SS		301 SS	304 SS	316 SS
HNO ₃ (g/L)	80	80	80		100	100	100
Total HF (g/L)	0	0	0		5	5	5
Fe ³⁺ (g/L)	20	20	20		20	20	20
Temp (°C) (Temp (F))	54.4 (130)	54.4 (130)	54.4 (130)		54.4 (130)	54.4 (130)	54.4 (130)
Appearance	Clean	Clean	Clean		Clean	Clean	Clean

[0027] In the EP process disclosed in the first example, the HF consumed was reduced by more than half of that consumed in the Baseline process in the second tub and removed completely from the mixture in the third tub. The HNO₃ concentration could have been cut by about 20% in the second tub.

EXAMPLE 2

[0028] The following second example is proposed if compatible materials are made for the electrodes. In the second example, a two tub EP process is used where the second tub solely contains HNO₃, and results in a substantially cleaned stainless steel surface. Because no HF is used in the second tub, a reduction in a total consumption of acids occurs from a known process that is known to utilize both HNO₃ and HF in a second tub. As the grade 316 stainless steel is more difficult to pickle, the addition of HF into the second tub is an option.

TABLE 4: TUB 1

	EP	EP	EP	EP
	409 SS	301 SS	304 SS	316 SS
H ₂ SO ₄ (g/L)	30	30	30	30
Total HF (g/L)	5	10	10	20
Fe ³⁺ (g/L)	30	30	30	30
Fe ²⁺ (g/L)	0	0	0	0
C/dm ²	50	100	100	120
Temp (°C) (Temp (F))	48.9 (120)	48.9 (120)	48.9 (120)	48.9 (120)
Expected Results	Clean	Clean	Clean	Half Clean

[0029] For each of the tested grades (301, 304, 316, and 409), 30 g/L of H₂SO₄ and 30 g/L of Fe³⁺ are used at a temperature of 48.9 °C (120 degrees Fahrenheit). For grade 316 stainless steel, a difficult grade to pickle, 20 g/L of HF and 120 Coulombs/dm² are used. For grades 301 and 304 stainless steel, 10 g/L HF and 100 Coulombs/dm² are used. For grade 409 stainless steel, an easier grade to pickle, 5 g/L of HF and 50 Coulombs/dm² are used. To substantially and further completely clean the steel strips of the second example, the second and/or third tubs could include a reduced amount of HF from known pickling processes. For example, the 409 grade stainless steel could eliminate the use of HF in one or more subsequent tubs. The 301 grade stainless steel and the 304 grade stainless steel would utilize between about 0 g/L to about 10 g/L of HF, and the 316 grade stainless steel would utilize about 10 g/L to about 30 g/L of HF. This concentration would have been a reduction of about 20% to about 50% for these grades of stainless steel over known pickling processes.

[0030] EXAMPLE 3

[0031] The third example shown below and derived from actual data highlights that the EP process permits for a reduction in total chemicals used. Here, sodium sulfate (Na₂SO₄) was used in a baseline case and grade 304 and grade 409 stainless steels were tested under the baseline process and the EP process.

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TABLE 5: TUBS 1-3

		409 (baseline)	409 (EP)	304 (baseline)	304 (EP)
5 10	Tub 1				
	Na ₂ SO ₄ (g/L)	175	---	175	---
	H ₂ SO ₄ (g/L)	pH = ~3-5	30	pH=~3-5	30
	Fe ³⁺ (g/L)	1-2	30	1-2	30
	Fe ²⁺ (g/L)	1-2	0	1-2	0
	H ₂ O ₂ (g/L)*	0	5	0	5
	C/dm ²	60	120	120	120
	Temp (°C) (Temp (F))	65.6 (150)	48.9 (120)	65.6 (150)	48.9 (120)
15 20	Tub 2				
	HNO ₃ (g/L)	105	105	120	120
	Total HF (g/L)	8	8	42.3	42.3
	Fe ³⁺ (g/L)	32.5	32.5	27.5	27.5
	Temp °C (Temp (F))	51.7 (125)	51.7 (125)	54.4 (130)	54.4 (130)
25 30	Tub 3				
	HNO ₃ (g/L)	120	105	120	120
	Total HF (g/L)	22.5	8	42.3	42.3
	Fe ³⁺ (g/L)	27.5	27.5	27.5	27.5
	Temp °C (Temp (F))	51.7 (125)	51.7 (125)	54.4 (130)	54.4 (130)
	Appearance	Clean	Clean	Clean	Clean
*H ₂ O ₂ was not measured in this case, but was theoretically calculated based on the known chemical reaction.					

[0032] Notable for tubs 2 and 3, HNO₃ acts as an oxidizing agent that allows for a complete conversion of ferrous ions to ferric ions. For the grade 304 stainless steel, the baseline process used 175 g/L of Na₂SO₄, 1 - 2 g/L of Fe³⁺, 1 - 2 g/L of Fe²⁺, 0 g/L of H₂O₂, 120 Coulombs/dm² and was kept at a temperature of 65.6 °C (150 degrees Fahrenheit) in the first tub. The second and third tubs each included 120 g/L of HNO₃, 42.3 g/L of HF, 27.5 g/L of Fe³⁺ at a temperature of 54.4 °C (130 degrees Fahrenheit). A final clean appearance was visually obtained.

[0033] For the grade 304 stainless steel, the EP process used 30 g/L of H₂SO₄, 30 g/L of Fe³⁺, 0 g/L of Fe²⁺, an excess amount of H₂O₂ (> 0.1 g/L) 120 Coulombs/dm² and was kept at a reduced temperature of 48.9 °C (120 degrees Fahrenheit) in the first tub. The second and third tubs each still included 120 g/L of HNO₃, 42.3 g/L of HF, 27.5 g/L of Fe³⁺ at a temperature of 54.4 °C (130 degrees Fahrenheit). A reduced total amount of chemicals was consumed in the EP process over the baseline process, and a final clean appearance was visually obtained.

[0034] For the grade 409 stainless steel, the baseline process used 175 g/L of Na₂SO₄, 1 - 2 g/L of Fe³⁺, 1-2 g/L of Fe²⁺, 0 g/L of H₂O₂, 60 Coulombs/dm² and was kept at a temperature of 65.6 °C (150 degrees Fahrenheit) in the first tub. The second tub included 105 g/L of HNO₃, 8 g/L of HF, 32.5 g/L of Fe³⁺ at a temperature of 51.7 °C (125 degrees Fahrenheit). The third tub included 120 g/L of HNO₃, 22.5 g/L of HF, 27.5 g/L of Fe³⁺ at a temperature of 51.7 °C (125 degrees Fahrenheit). A final clean appearance was visually obtained.

[0035] For the grade 409 stainless steel, the EP process used 30 g/L of H₂SO₄, 30 g/L of Fe³⁺, 0 g/L of Fe²⁺, 5 g/L of H₂O₂, and 120 Coulombs/dm² and was kept at a reduced temperature of 48.9 °C (120 degrees Fahrenheit) in the first tub. The second tub included 105 g/L of HNO₃, 8 g/L of HF, 32.5 g/L of Fe³⁺ at a temperature of 51.7 °C (125 degrees Fahrenheit). The third tub included, at a temperature of 51.7 °C (125 degrees Fahrenheit), 27.5 g/L of Fe³⁺ and reduced amounts of 105 g/L of HNO₃ and 8 g/L of HF. A reduced total amount of acids were consumed in the EP process over the baseline process. For example, in the third tub of the EP process, HNO₃ was reduced by 15 g/L over the concentration used in the third tub of the baseline process, and HF was reduced by 14.5 g/L over the concentration used in the third tub of the baseline process. This resulted in a total reduced concentration of 29.5 g/L of acids used in the third tub of the EP process over the total concentration of acids used in the baseline process. Further, a final clean appearance was visually obtained.

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EXAMPLE 4

[0036] A fourth example shown below highlights that the EP process permits for a reduction in the expected concentration of the chemicals used. Here, sodium sulfate (Na_2SO_4) is used in a baseline case and grade 304 and grade 409 stainless steels are tested under the baseline process and the EP process.

TABLE 6: TUBS 1-3

		409 (baseline)	409 (EP)	304 (baseline)	304 (EP)
Tub 1	Na_2SO_4 (g/L)	175	---	175	---
	H_2SO_4 (g/L)	pH = ~3-5	30	pH = ~3-5	30
	Fe^{3+} (g/L)	1-2	30	1-2	40
	Fe^{2+} (g/L)	1-2	0	1-2	0
	H_2O_2 (g/L)*	0	5	0	5
	C/dm ²	60	120	120	120
	Temp °C (Temp (F))	65.6 (150)	48.9 (120)	65.6 (150)	48.9 (120)
Tub 2	HNO_3 (g/L)	120	100	120	100
	Total HF (g/L)	20	0	40	20
	Fe^{3+} (g/L)*	30	30	30	30
	Temp °C (Temp (F))	48.9 (120)	48.9 (120)	54.4 (130)	54.4 (130)
Tub 3	HNO_3 (g/L)	80	80	100	80
	Total HF (g/L)	5	0	20	10
	Fe^{3+} (g/L)*	20	20	20	20
	Temp °C (Temp (F))	48.9 (120)	48.9 (120)	54.4 (130)	54.4 (130)
* H_2O_2 would not be measured in this case, but would be theoretically calculated based on the known chemical reaction.					

[0037] For the grade 304 stainless steel, the baseline process uses 175 g/L of Na_2SO_4 , 1 - 2 g/L of Fe^{3+} , 1-2 g/L of Fe^{2+} , 0 g/L of H_2O_2 , 120 Coulombs/dm² and is kept at a temperature of 65.5 °C (150 degrees Fahrenheit) in the first tub. The second tub includes 120 g/L of HNO_3 , 40 g/L of HF, 30 g/L of Fe^{3+} at a temperature of 54.4 °C (130 degrees Fahrenheit) and the third tub includes 100 g/L of HNO_3 , 20 g/L of HF, 20 g/L of Fe^{3+} at a temperature of 54.4 °C (130 degrees Fahrenheit). A final clean appearance is expected to be visually obtained.

[0038] For the grade 304 stainless steel, the EP process uses 30 g/L of H_2SO_4 , 40 g/L of Fe^{3+} , 0 g/L of Fe^{2+} , an excess of H_2O_2 (>0.1 g/L), 120 Coulombs/dm² and is kept at a reduced temperature of 48.9 °C (120 degrees Fahrenheit) in the first tub. The second tub includes 100 g/L of HNO_3 , 20 g/L of HF, 30 g/L of Fe^{3+} at a temperature of 54.4 °C (130 degrees Fahrenheit) and the third tub includes 80 g/L of HNO_3 , 10 g/L of HF, 20 g/L of Fe^{3+} at a temperature of 54.4 °C (130 degrees Fahrenheit). A reduced total amount of acids is consumed in the EP process over the baseline process, as well as a reduction of each of HNO_3 and HF in the second and third tubs. For example, in the second tub of the EP process, HNO_3 was reduced by 20 g/L over the concentration used in the second tub of the baseline process, and HF was reduced by 10 g/L over the concentration used in the second tub of the baseline process. This resulted in a total reduced concentration of 30 g/L of acids used in the second tub of the EP process over the total concentration of acids used in the baseline process. Further, in the third tub of the EP process, HNO_3 was reduced by 20 g/L over the concentration used in the third tub of the baseline process, and HF was reduced by 5 g/L over the concentration used in the third tub of the baseline process. This resulted in a total reduced concentration of 25 g/L of acids used in the third tub of the EP process over the total concentration of acids used in the baseline process. A final clean appearance is expected to be visually obtained.

[0039] For the grade 409 stainless steel, the baseline process uses 175 g/L of Na_2SO_4 , 0 g/L of Fe^{3+} , 40 g/L of Fe^{2+} , 0 g/L of H_2O_2 , 60 Coulombs/dm² and is kept at a temperature of 65.6 °C (150 degrees Fahrenheit) in the first tub. The second tub includes 120 g/L of HNO_3 , 20 g/L of HF, 30 g/L of Fe^{3+} at a temperature of 48.9 °C (120 degrees Fahrenheit).

The third tub includes 80 g/L of HNO_3 , 5 g/L of HF , 20 g/L of Fe^{3+} at a temperature of 48.9°C (120 degrees Fahrenheit). A final clean appearance is expected to be visually obtained.

[0040] For the grade 409 stainless steel, the EP process uses 30 g/L of H_2SO_4 , 30 g/L of Fe^{3+} , 0 g/L of Fe^{2+} , 5 g/L of H_2O_2 , and 120 Coulombs/ dm^2 and is kept at a reduced temperature of 48.9°C (120 degrees Fahrenheit) in the first tub. The second tub includes 100 g/L of HNO_3 , 0 g/L of HF , 30 g/L of Fe^{3+} at a temperature of 48.9°C (120 degrees Fahrenheit). The third tub includes, at a temperature of 48.9°C (120 degrees Fahrenheit), 20 g/L of Fe^{3+} and reduced amounts of 80 g/L of HNO_3 and 0 g/L of HF . A reduced total amount of acids is consumed in the EP process over the baseline process, as well as a reduction of each of HNO_3 and HF in the second tub, and a reduction of HF in the third tub. For example, in the second tub of the EP process, HNO_3 was reduced by 20 g/L over the concentration used in the second tub of the baseline process, and HF was reduced by 20 g/L (to 0 g/L) over the concentration used in the second tub of the baseline process. This resulted in a total reduced concentration of 40 g/L of acids used in the second tub of the EP process over the total concentration of acids used in the baseline process. Further, in the third tub of the EP process, HF was reduced by 5 g/L over the concentration used in the third tub of the baseline process. This resulted in a total reduced concentration of 5 g/L of acids used in the third tub of the EP process over the total concentration of acids used in the baseline process. A final clean appearance is expected to be visually obtained.

[0041] Thus, for the 409 grade stainless steel with the EP process, 100% of the HF may be eliminated. For other ferritic grades and the lower alloyed austenitic grades, like 301 grade stainless steel and 304 grade stainless steel, HF concentration is able to be reduced by 20% or more over baseline processes. For 316 austenitic grade stainless steel, a substantial reduction may not occur. In some cases, the concentration of HNO_3 may be able to be reduced in an EP process by 10 - 20% over a baseline process.

[0042] Having shown and described various embodiments of the present invention, further adaptations of the methods and systems described herein may be accomplished by appropriate modifications by one of ordinary skill in the art without departing from the scope of the present invention as defined in the claims. Several of such potential modifications have been mentioned, and others will be apparent to those skilled in the art. For instance, the examples, embodiments, geometrics, materials, dimensions, ratios, steps, and the like discussed above are illustrative. Accordingly, the scope of the present invention is defined in terms of the following claims and is understood not to be limited to the details of structure and operation shown and described in the specification and drawings.

Claims

1. A process for pickling a strip of ferritic stainless steel comprising:

treating the steel with a first mixture disposed in a first tub, the first mixture comprising H_2SO_4 , an excess of at least one oxidizing agent, wherein the at least one oxidizing agent serves to convert a total amount of ferrous sulfate to ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$), and applying a current to the steel, wherein the first mixture does not include HF .

2. The process of claim 1, wherein the concentration of H_2SO_4 is from 10 g/L to 200 g/L.

3. The process of claim 1, wherein the first tub is the sole tub used in the pickling process.

4. A process for pickling a continuous strip of stainless steel comprising:

treating the steel with a first mixture disposed in a first tub, the first mixture comprising H_2SO_4 an excess of at least one oxidizing agent, wherein the at least one oxidizing agent serves to convert a total amount of ferrous sulfate to ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$), and applying a current to the steel, wherein the concentration of H_2SO_4 is from 10 g/L to 200 g/L.

5. The process of claim 1 or 4, wherein the concentration of $\text{Fe}_2(\text{SO}_4)_3$ is from 5 g/L to 100 g/L.

6. The process of claim 1 or 4, wherein the at least one oxidizing agent is H_2O_2 .

7. The process of claim 4, wherein the first mixture further comprises HF .

8. The process of claim 7, wherein the concentration of H_2SO_4 is from 25 g/L to 35 g/L, and wherein the concentration of HF is from 0 g/L to 100 g/L.

9. The process of claim 1 or 4, wherein the step of applying a current to the steel comprises applying a current via at least one of a cathode or anode.

10. The process of claim 9, wherein the steel comprises one of the cathode or anode.

11. The process of claim 4, further comprising treating the steel with a second mixture disposed in a second tub, wherein the second mixture comprises at least one of HNO_3 and HF, wherein the concentration of HNO_3 is from 10 g/L to 130 g/L, and wherein the concentration of HF is from 0 g/L to 30 g/L.

12. The process of claim 11, wherein the first mixture further comprises HF.

13. The process of claim 12, wherein the stainless steel comprises a ferritic stainless steel and the second mixture comprises HNO_3 .

14. The process of claim 11, wherein the stainless steel comprises an austenitic stainless steel and the second mixture comprises HNO_3 and HF, and wherein the concentration of HF in the second mixture is in the range of from 5 g/L to 25 g/L.

15. The process of claim 11, further comprising treating the steel with a third mixture disposed in a third tub, wherein the third mixture comprises HNO_3 , and wherein the concentration of HNO_3 is from 10 g/L to 130 g/L.

16. The process of claim 1 or 4, wherein the steel is pickled in a continuous fashion.

17. The process of claim 4, where the temperature of the first mixture is in the range of from 21.1 °C (70 °F) to 82.2 °C (180 °F) or in the range of from 27.7 °C (80 °F) to 54.4 °C (130 °F).

18. The process of claim 4, wherein an amount of total dissolved metals in the first mixture after the first mixture treats the strip is equal to or less than 80 g/L.

19. The process of claim 4, wherein step of applying a current to the steel comprises applying a current via electrodes that comprise a cathode-anode-cathode arrangement and are operable to apply a current in the range of from 10 Coulombs/dm² to 200 Coulombs/dm² with a current density in the range of from 1 Amps/dm² to 100 Amps/dm².

Patentansprüche

1. Verfahren zum Beizen eines Bandes aus ferritischem Edelstahl umfassend:

Behandeln des Stahls mit einer ersten, in einer ersten Wanne aufgenommenen Mischung enthaltend H_2SO_4 und einen Überschuss mindestens eines Oxidationsmittels, welches dazu dient, eine Gesamtmenge von Eisen(II)-sulfat in Eisen(III)-sulfat ($\text{Fe}_2(\text{SO}_4)_3$) umzuwandeln, und Anlegen eines elektrischen Stromes an den Stahl, wobei die erste Mischung kein HF enthält.

2. Verfahren nach Anspruch 1, wobei die Konzentration von H_2SO_4 10 g/l bis 200 g/l beträgt.

3. Verfahren nach Anspruch 1, wobei die erste Wanne die einzige Wanne im Beizverfahren ist.

4. Verfahren zum Beizen eines kontinuierlichen Bandes aus Edelstahl umfassend:

Behandeln des Stahls mit einer ersten, in einer ersten Wanne aufgenommenen Mischung enthaltend H_2SO_4 und einen Überschuss mindestens eines Oxidationsmittels, welches dazu dient, eine Gesamtmenge von Eisen(II)-sulfat in Eisen(III)-sulfat ($\text{Fe}_2(\text{SO}_4)_3$) umzuwandeln, und Anlegen eines elektrischen Stromes an den Stahl, wobei die Konzentration von H_2SO_4 10 g/l bis 200 g/l beträgt.

5. Verfahren nach Anspruch 1 oder 4, wobei die Konzentration von $\text{Fe}_2(\text{SO}_4)_3$ 5 g/l bis 100 g/l beträgt.

6. Verfahren nach Anspruch 1 oder 4, wobei das mindestens eine Oxidationsmittel H_2O_2 ist.

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7. Verfahren nach Anspruch 4, wobei die erste Mischung ferner HF enthält.
8. Verfahren nach Anspruch 7, wobei die Konzentration von H_2SO_4 25 g/l bis 35 g/l beträgt und wobei die Konzentration von HF 0 g/l bis 100 g/l beträgt.
- 5 9. Verfahren nach Anspruch 1 oder 4, wobei der Schritt des Anlegens eines elektrischen Stromes an den Stahl das Anlegen eines elektrischen Stroms über mindestens entweder eine Kathode oder Anode umfasst.
- 10 10. Verfahren nach Anspruch 9, wobei der Stahl entweder die Kathode oder die Anode bildet.
11. Verfahren nach Anspruch 4, ferner umfassend das Behandeln des Stahls mit einer zweiten, in einer zweiten Wanne aufgenommenen Mischung, welche mindestens entweder HNO_3 oder HF enthält, wobei die Konzentration von HNO_3 10 g/l bis 130 g/l beträgt und wobei die Konzentration von HF 0 g/l bis 30 g/l beträgt.
- 15 12. Verfahren nach Anspruch 11, wobei die erste Mischung ferner HF enthält.
13. Verfahren nach Anspruch 12, wobei der Edelstahl einen ferritischen Edelstahl umfasst und wobei die zweite Mischung HNO_3 enthält.
- 20 14. Verfahren nach Anspruch 11, wobei der Edelstahl einen austenitischen Edelstahl umfasst und wobei die zweite Mischung HNO_3 und HF enthält und wobei die Konzentration von HF in der zweiten Mischung im Bereich von 5 g/l bis 25 g/l liegt.
- 25 15. Verfahren nach Anspruch 11, ferner umfassend das Behandeln des Stahls mit einer dritten, in einer dritten Wanne aufgenommenen Mischung, wobei die dritte Mischung HNO_3 enthält und wobei die Konzentration von HNO_3 10 g/l bis 130 g/l beträgt.
16. Verfahren nach Anspruch 1 oder 4, wobei der Stahl auf kontinuierliche Weise gebeizt wird.
- 30 17. Verfahren nach Anspruch 4, wobei die Temperatur der ersten Mischung im Bereich von 21,1°C (70°F) bis 82,2°C (180°F) oder im Bereich von 27,7°C (80°F) bis 54,4°C (130°F) liegt.
18. Verfahren nach Anspruch 4, wobei eine Gesamtmenge an gelösten Metallen in der ersten Mischung, nachdem die erste Mischung das Band behandelt hat, gleich oder weniger als 80 g/l ist.
- 35 19. Verfahren nach Anspruch 4, wobei der Schritt des Anlegens eines elektrischen Stroms an den Stahl das Anlegen eines elektrischen Stroms über Elektroden umfasst, welche eine Kathode-Anode-Kathode-Anordnung enthalten und welche derart betreibbar sind, dass ein elektrischer Strom im Bereich von 10 Coulomb/dm² bis 200 Coulomb/dm² mit einer Stromdichte im Bereich von 1 Amps/dm² bis 100 Amps/dm² angelegt wird.
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Revendications

- 45 1. Procédé de décapage d'une bande d'acier inoxydable ferritique comprenant :
- le traitement de l'acier avec un premier mélange disposé dans une première cuve, le premier mélange comprenant du H_2SO_4 , un excès d'au moins un agent oxydant, dans lequel l'au moins un agent oxydant sert à convertir une quantité totale de sulfate ferreux en sulfate ferrique ($\text{Fe}_2(\text{SO}_4)_3$), et l'application d'un courant à l'acier, dans lequel le premier mélange n'inclut pas de HF.
- 50 2. Procédé selon la revendication 1, dans lequel la concentration de H_2SO_4 va de 10 g/L à 200 g/L.
3. Procédé selon la revendication 1, dans lequel la première cuve est la seule cuve utilisée dans le procédé de décapage.
- 55 4. Procédé pour décaper une bande continue d'acier inoxydable comprenant :
- le traitement de l'acier avec un premier mélange disposé dans une première cuve, le premier mélange comprenant du H_2SO_4 un excès d'au moins un agent oxydant, dans lequel l'au moins un agent oxydant sert à

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convertir une quantité totale de sulfate ferreux en sulfate ferrique ($\text{Fe}_2(\text{SO}_4)_3$), et l'application d'un courant à l'acier, dans lequel la concentration de H_2SO_4 va de 10 g/L à 200 g/L.

5 5. Procédé selon la revendication 1 ou 4, dans lequel la concentration de $\text{Fe}_2(\text{SO}_4)_3$ va de 5 g/L à 100 g/L.

6. Procédé selon la revendication 1 ou 4, dans lequel l'au moins un agent oxydant est du H_2O_2 .

7. Procédé selon la revendication 4, dans lequel le premier mélange comprend en outre du HF.

10 8. Procédé selon la revendication 7, dans lequel la concentration de H_2SO_4 va de 25 g/L à 35 g/L, et dans lequel la concentration de HF va de 0 g/L à 100 g/L.

9. Procédé selon la revendication 1 ou 4, dans lequel l'étape d'application d'un courant à l'acier comprend l'application d'un courant via au moins une parmi une cathode ou une anode.

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10. Procédé selon la revendication 9, dans lequel l'acier comprend l'une parmi la cathode ou l'anode.

11. Procédé selon la revendication 4, comprenant en outre le traitement de l'acier avec un deuxième mélange disposé dans une deuxième cuve, dans lequel le deuxième mélange comprend au moins l'un parmi du HNO_3 et du HF, dans lequel la concentration de HNO_3 va de 10 g/L à 130 g/L, et dans lequel la concentration de HF va de 0 g/L à 30 g/L.

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12. Procédé selon la revendication 11, dans lequel le premier mélange comprend en outre du HF.

13. Procédé selon la revendication 12, dans lequel l'acier inoxydable comprend un acier inoxydable ferritique et le deuxième mélange comprend du HNO_3 .

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14. Procédé selon la revendication 11, dans lequel l'acier inoxydable comprend un acier inoxydable austénitique et le deuxième mélange comprend du HNO_3 et du HF, et dans lequel la concentration de HF dans le deuxième mélange se trouve dans la plage de 5 g/L à 25 g/L.

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15. Procédé selon la revendication 11, comprenant en outre le traitement de l'acier avec un troisième mélange disposé dans une troisième cuve, dans lequel le troisième mélange comprend du HNO_3 , et dans lequel la concentration de HNO_3 va de 10 g/L à 130 g/L.

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16. Procédé selon la revendication 1 ou 4, dans lequel l'acier est décapé d'une façon continue.

17. Procédé selon la revendication 4, dans lequel la température du premier mélange se trouve dans la plage de 21,1°C (70 °F) à 82,2 °C (180 °F) ou dans la plage de 27,7 °C (80 °F) à 54,4 °C (130 °F).

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18. Procédé selon la revendication 4, dans lequel une quantité de métaux dissous totaux dans le premier mélange après que le premier mélange a traité la bande est inférieure ou égale à 80 g/L.

19. Procédé selon la revendication 4, dans lequel l'étape d'application d'un courant à l'acier comprend l'application d'un courant via des électrodes qui comprennent un agencement cathode-anode-cathode et permettent d'appliquer un courant dans la plage de 10 Coulombs/dm² à 200 Coulombs/dm² avec une densité de courant dans la plage de 1 Amps/dm² à 100 Amps/dm².

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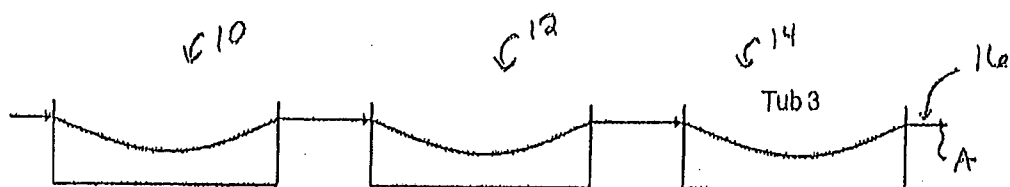


FIG. 1
PRIOR ART

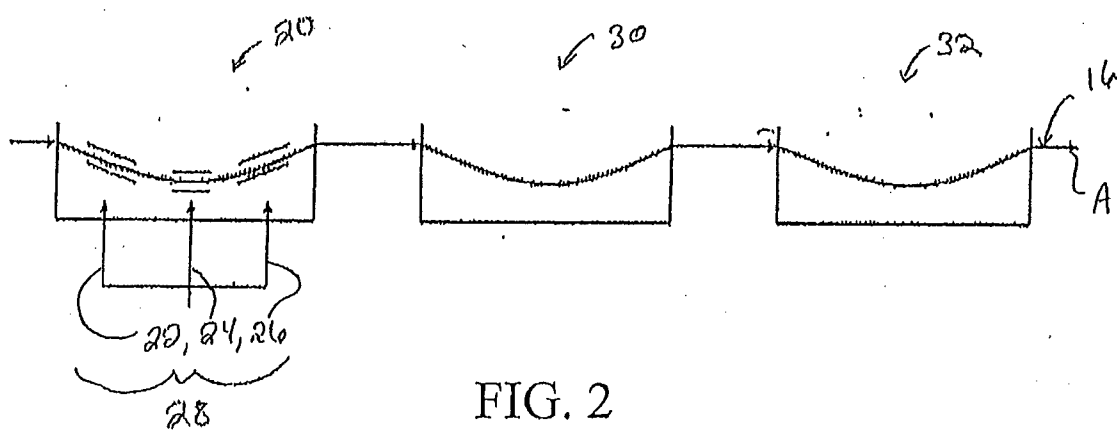


FIG. 2

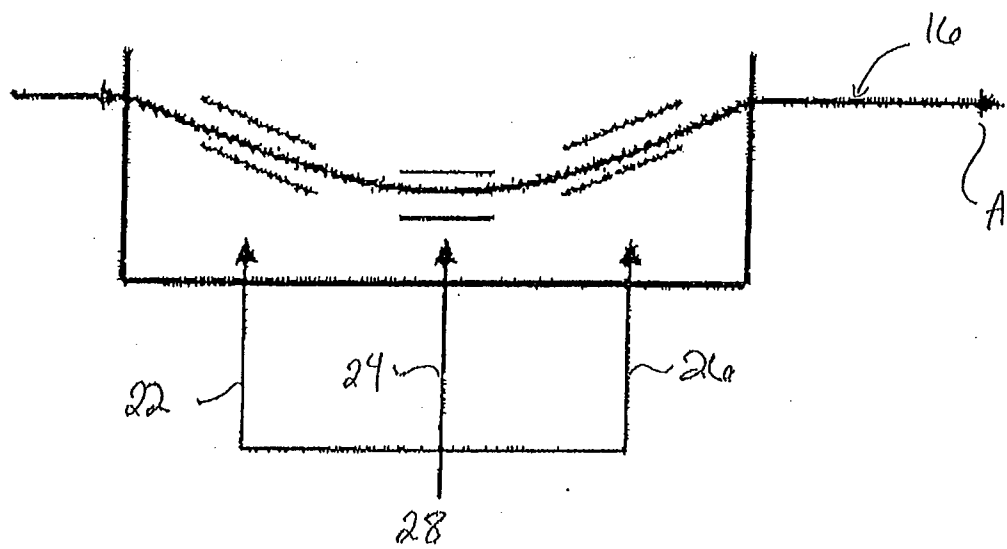


FIG. 3

REFERENCES CITED IN THE DESCRIPTION

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SZABADALMI IGÉNYPONTOK

1. Eljárás ferrites rozsdamentes acél lemez maratására, amely tartalmazza az alábbi lépéseket:
az acélt egy első kádban felvett első keverékkel kezeljük, amely első keverék tartalmaz H_2SO_4 -t, feleslegben legalább egy oxidáló szert, ahol a legalább egy oxidáló szer feladata, hogy a ferro-szulfát teljes mennyiségét ferri-szulfáttá ($\text{Fe}_2(\text{SO}_4)_3$) alakítsa, és az acélra elektromos áramot vezetünk, ahol az első keverék nem tartalmaz HF-t.
2. Az 1. igénypont szerinti eljárás, ahol a H_2SO_4 koncentrációja 10 g/L és 200 g/L közötti.
3. Az 1. igénypont szerinti eljárás, ahol az első kád a maratási eljárásban alkalmazott egyetlen kád.
4. Eljárás folyamatos, rozsdamentes acél lemez maratására, amely tartalmazza az alábbi lépéseket:
az acélt egy első kádban felvett első keverékkel kezeljük, amely első keverék tartalmaz H_2SO_4 -t, feleslegben legalább egy oxidáló szert, ahol a legalább egy oxidáló szer feladata, hogy a ferro-szulfát teljes mennyiségét ferri-szulfáttá ($\text{Fe}_2(\text{SO}_4)_3$) alakítsa, és az acélra elektromos áramot vezetünk, ahol a H_2SO_4 koncentrációja 10 g/L és 200 g/L közötti.
5. Az 1. vagy 4. igénypont szerinti eljárás, a $\text{Fe}_2(\text{SO}_4)_3$ koncentrációja 5 g/L és 100 g/L közötti.
6. Az 1. vagy 4. igénypont szerinti eljárás, ahol a legalább egy oxidáló szer H_2O_2 .
7. A 4. igénypont szerinti eljárás, ahol az első keverék tartalmaz továbbá HF-t.
8. A 7. igénypont szerinti eljárás, ahol a H_2SO_4 koncentrációja 25 g/L és 35 g/L közötti, és ahol a HF koncentrációja 0 g/L és 100 g/L közötti.
9. Az 1. vagy 4. igénypont szerinti eljárás, ahol az elektromos áramnak az acélra történő rávezetésének lépése tartalmazza azt, hogy az áramot legalább egy katódra vagy anódra keresztül alkalmazzuk.
10. A 9. igénypont szerinti eljárás, ahol az acél képezi a katód vagy az anód egyikét.
11. A 4. igénypont szerinti eljárás, amely tartalmazza azt a további lépést, hogy az acélt egy második kádban felvett második keverékkel kezeljük, ahol a második keverék HNO_3 és HF közül legalább egyet tartalmaz, ahol a HNO_3 koncentrációja 10 g/L és 130 g/L közötti, és ahol a HF koncentrációja 0 g/L és 30 g/L közötti.

12. A 11. igénypont szerinti eljárás, ahol az első keverék tartalmaz továbbá HF-t.
13. A 12. igénypont szerinti eljárás, ahol a rozsdamentes acél ferrites acélt tartalmaz, és a második keverék HNO_3 -t tartalmaz.
14. A 11. igénypont szerinti eljárás, ahol a rozsdamentes acél ausztenites acélt tartalmaz, és a második keverék tartalmaz HNO_3 -t and HF-t, és ahol a HF koncentrációja a második keverékben 5 g/L - 25 g/L tartományba esik.
15. A 11. igénypont szerinti eljárás, amely tartalmazza azt a további lépést, hogy az acélt egy harmadig kádban felvett harmadik keverékkel kezeljük, ahol a harmadik keverék tartalmaz HNO_3 -t, és ahol a HNO_3 koncentrációja 10 g/L és 130 g/L közötti.
16. Az 1. vagy 4. igénypont szerinti eljárás, ahol az acélt folyamatos üzemmódban maratjuk.
17. A 4. igénypont szerinti eljárás, ahol az első keverék hőmérséklete $21,1\text{ }^\circ\text{C}$ ($70\text{ }^\circ\text{F}$) - $82,2\text{ }^\circ\text{C}$ ($180\text{ }^\circ\text{F}$) tartományba vagy a $27,7\text{ }^\circ\text{C}$ ($80\text{ }^\circ\text{F}$) - $34,4\text{ }^\circ\text{C}$ ($130\text{ }^\circ\text{F}$) tartományba esik.
18. A 4. igénypont szerinti eljárás, ahol az első keverékben feloldódott fém együttes mennyisége, a lemeznek az első keverékkel történő kezelése után azonos vagy kevesebb, mint 80 g/L.
19. A 4. igénypont szerinti eljárás, ahol az elektromos áramnak az acélra történő rávezetésének lépése tartalmazza azt, hogy az áramot elektródokon keresztül alkalmazzuk, amelyek katód-anód-katód elrendezést tartalmaznak, és 10 Coulomb/dm^2 - 200 Coulomb/dm^2 tartományba eső áram adagolására alkalmas módon működtethetők, ahol az áram sűrűség 1 Amp/dm^2 - 100 Amp/dm^2 tartományba esik.