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(54) **Pickling solution used for removing scales on iron-based alloys**

Beizlösung für die Entzunderung von Legierungen auf Eisenbasis

Solution de décapage pour enlever la rouille sur des alliages à base de fer

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(56) References cited:
EP-A- 0 795 628 **WO-A-93/21362**
DE-A- 2 559 289 **DE-B- 1 161 740**
GB-A- 985 014 **US-A- 4 144 092**

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EP 0 835 333 B9

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Description

[0001] This invention relates to a composition for removing scale and rust (hereinafter referring to as simply 'scale') from a metal surface.

[0002] As is well known, stainless steel is widely used for various industrial uses due to its superiority in properties including corrosion resistance, oxidation resistance, and high temperature strength and etc. Such stainless steels can be classified by their alloy compositions into Cr-Stainless Steel (Cr: 11-27 wt%) and Ni-Stainless Steel (Cr: 15-28 wt%, Ni: 4-22 wt%). Further the Cr-stainless steel can be classified by its metallurgical structure into ferritic stainless steels and martensitic stainless steels, and the Ni-stainless steel can be classified into austenitic stainless steels and dual phase stainless steels having both a ferrite phase and an austenite phase.

[0003] Conventionally the stainless steels and other alloyed steels containing Cr and/or Ni are heat treated for high temperature oxidation after or during hot or cold rolling during production or even during welding operations on finished products.

[0004] During the heat treatment, scales of oxides or carbides having a dense structure, that is difficult to oxidize, are formed on the surface of the stainless steel or the alloyed steel.

[0005] Since stainless steel contains Ni and Cr as essential components and Mo, Ti, Mn, Zr, Nb, N and other elements as additional components, the scales formed during the heat treatment consists mainly of Fe, Fe₃O₄, Fe₂O₃, NiO, Ni₃O₄, Ni₂O₃, CrO₃, and Cr₂O₃.

[0006] As described above, since the scale has dense structures and is hard to oxidize, it is difficult to remove by a conventional pickling process.

[0007] Therefore to easily remove those scales, the stainless steel or other alloyed steels are typically pre-treated using salt bath, shot-blast or neutral salt electrolysis in chemical, physical or electrical methods, respectively, before pickling.

[0008] By the pre-treatment, the scales on the surface can be partially removed to a certain extent and then completely removed by dipping in a conventional pickling solution.

[0009] However each of the pre-treatment processes using shot-blast, salt bath or neutral salt electrolysis has several problems as described below:

[0010] The pre-treatment using shot-blast is brought about by shotting spheroidal particulates of metal or glass onto the surface of metal under high pressure to physically remove the scale formed on substrate to increase the effect of the pickling process to be followed.

[0011] However such pre-treatment using shot-blast may degrade the surface roughness of the substrate and may cause dust formation.

[0012] The pre-treatment using salt bath is brought about by dipping the substrates on which the scales are formed into the salt bath containing sodium hydroxide, sodium nitrate, and sodium chloride in a temperature range from 480 to 520°C to improve the pickling efficiency by softening the scale structure.

[0013] However using the salt bath may produce Cr⁺⁶ which may give rise to environmental problems and requires increased energy consumption.

[0014] The pre-treatment using neutral salt electrolysis is brought about by applying electric power to the solution containing neutral salt such as sodium sulfate to form bubbles to improve the pickling efficiency by softening the scale structure with the formed bubble.

[0015] However the use of this neutral salt also has the disadvantage that energy consumptions are increased.

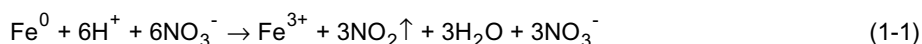
[0016] In addition to the above-described disadvantages of each pre-treatment method, pre-treatment itself increases the length of the process.

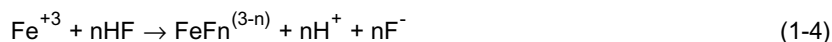
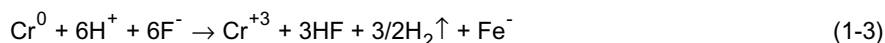
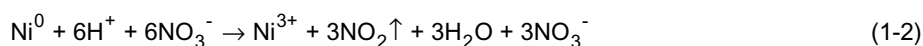
[0017] After conducting such pre-treatment as described above, the substrates covered with scales are treated with pickling solution in order to obtain completely bared surfaces.

[0018] Conventionally aqueous blends containing hydrofluoric acid and nitric acid are used as pickling solutions. Optionally different classes of compounds including hydrochloric acid and sulfuric acid can be added to the pickling solution.

[0019] The components and composition ratios of the pickling solution can be varied depending on the type of substrate and end use.

[0020] During the pickling process using the mixed acid substantially of hydrofluoric acid and nitric acid, the metal ions formed on the substrates are believed to react with the mixed acid as follows;





[0021] As shown in the above, when a pickling process is carried out in a conventional manner noxious and corrosive hydrohalide acid fumes may be liberated into the atmosphere to cause environmental contaminations.

[0022] Specifically the nitric acid reacts with the metal ions of the scale to form the noxious NOx gases representing nitrogen oxide and the NOx gases formed during the pickling process are released into the atmosphere, while unreacted nitric acid and volatile hydrofluoric acid are simultaneously volatilized into the air to give rise to additional environmental problems. (HF: Specific gravity 0.987, Boiling Point 19.4°C, Melting Point -92.3°C, HNO₃: Specific gravity 1.502, Boiling Point 86°C, Melting Point - 42°C).

[0023] Therefore there has been a need for a pickling solution to avoid the disadvantages inherent in the conventional pickling solution, and preferably a pickling solution in which any pre-treatment process could be abbreviated.

[0024] U.S. Patent No. 4,572,743 discloses a method for pickling metallic surfaces especially unalloyed steel surfaces prior to further treatment by phosphating and varnishing in order not only to decrease the workpiece but also to remove rust and scale formed thereon.

[0025] The '743 patent teaches to use a non-aqueous pickling system based on an organic solvent, especially to use homogeneous organic pickling solutions based on low-boiling halogenated hydrocarbons as the basic component to avoid the disadvantages of aqueous pickling system.

[0026] US Patent No. 3,936,316 discloses a process and composition for pickling metals especially iron based metals prior to metal finishing. The '316 patent teaches to use the hydrohalide pickling solution containing urea in order to reduce or completely eliminate the excessive liberation of noxious and corrosive hydrohalide acid fumes.

[0027] WO 93/21 362 discloses a pickling solution comprising nitrate, fluoride and sulphate.

[0028] DE-A-1 161 740 discloses a similar pickling solution.

[0029] EP 0 795 628 A1, state of the art in accordance with article 54(3) EPC, discloses a pickling solution comprising nitrate, fluoride and 0 - 200 g/l sulphuric acid.

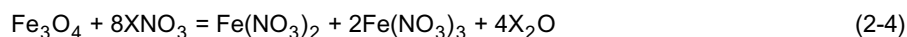
[0030] None of these references discloses or suggests any pickling solutions which could fundamentally eliminate the problems inherent in the conventional pickling solution such as liberation of noxious gases, cost increase, low efficiency of pickling process and necessity of pre-treatment.

[0031] A need therefore exists for an improved pickling solution which could fundamentally avoid the disadvantages of conventional pickling systems.

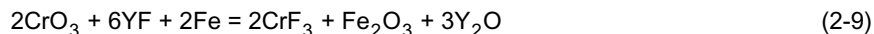
[0032] These objects are achieved by the features of Claim 1.

[0033] We conducted experiments in various ways to find an improved pickling solution which obviates at least one disadvantage, such as those aforementioned in the prior art.

[0034] Using the pickling solution according to the invention, following reactions are proceeded.



EP 0 835 333 B9 (W1B1)



[0035] As shown in the above, the nitrates and fluorides are reacted to form metal compounds which are not detrimental or noxious.

[0036] Examples of nitrates which can be used for the invention may include sodium nitrate, barium nitrate, potassium nitrate, calcium nitrate, and ammonium nitrate.

[0037] And examples of fluorides which can be used for the invention may include ammonium fluorosilicate sodium fluorosilicate, magnesium fluorosilicate, acid potassium fluoride, acid ammonium fluoride acid sodium fluoride, fluoroboric acid, ammonium fluoroborate, potassium fluoroborate, sodium fluoride, barium fluoride, and potassium fluorosilicate.

[0038] Examples of the sulfates may include magnesium sulfate, manganese sulfate, sodium sulfate, potassium sulfate, and ammonium sulfate.

[0039] Phosphoric acid and phosphates serve as inhibitors for protecting the bare metal surface of the substrate from corrosion, specially corrosion by inorganic acid such as sulfuric acid in the pickling solution for ferritic or martensitic stainless steels.

[0040] Examples of the phosphates may include sodium phosphate, ammonium phosphate, sodium pyrophosphate, acid sodium pyrophosphate, calcium phosphate and potassium phosphate.

[0041] Amines or amides can be added to prevent H^+ ion from approaching from the pickling solution to the surface of metal substrate or to prevent Fe^{2+} ion from diffusing from the metal surface to the pickling solution.

[0042] Examples of amines and amides may include hexamethylenediamine, diethylamine, dimethylamine, diethylethanolamine, diethylthiourea, dimethylthiourea, diethylene diamine, cyclohexyl amine, sulfuric aminoguanidine, and ethanol amine.

Brief description of the drawing

[0043] FIG. 1 is a flow sheet of block diagram illustrating an embodiment of the regenerating process of the present invention.

[0044] The stainless steel on which scales have been formed is dipped into pickling bath 1 containing pickling solution 4 to remove the scales on the surface of the stainless steel.

[0045] The spent pickling solution is transferred to the filtration bath 2.

[0046] The solutions transferred to the filtration bath 2 contain not only the separated scale from the substrate in flake form but also iron oxide, metal ions such as Ni and Cr and sludges.

[0047] In the filtration bath 2, the iron oxide and sludges in solid form are recovered through to filtration and the remaining filtrate is transferred to a separation bath 3.

[0048] The filtrate is cooled and the metal ions in salt form 6 are deposited and removed by the difference of solubility.

[0049] Then the regenerated pickling solutions are returned to the pickling bath 1 through conduit 9.

EXAMPLES

[0050] Example 1: Measuring NO_x gas generated during pickling process.

[0051] This example is to measure the amount of nitrogen oxide gas when pickling is proceed with the mixture of nitric acid hydrofluoric acid, and the pickling solution of this invention.

[0052] Comparative pickling solution and pickling solution of this invention were prepared in the 1.21 erlenmeyer flask as below and then temperature of each solution was maintained at 50°C . Inlet of the erlenmeyer flask was equipped gas analysis instrument(Model No. 1MR-3000P, Made in Germany) and specimen was dipped. Kinds and amount of gases generated were measured per one minute for 7 minutes and the results are set forth below in table 1a-1d.

EP 0 835 333 B9 (W1B1)

[0053] 1a, 1b, 1c and 1d show the results of pickling in line heat treated specimen with comparative pickling solution, pickling off line heat treated specimen with comparative pickling solution, pickling in line heat treated specimen with the pickling solution of this invention and off line heat treated specimen treated with the pickling solution of this invention, respectively.

Specimen: SUS-304 pipe heat treated at 900-1200°C

- (1) In Line heat treated pipe, 3.5t, outer diameter 22, length 39mm
- (2) Off Line heat treated pipe, 3.0t, outer diameter 27, length 39mm

Pickling solution:

[0054]

- (1) comparative pickling solution: HNO₃ 16%, HF 4%, residue water
- (2) pickling solution of this invention: nitrate 33g/l, fluorides 33g/l, sulfate 41g/l, sulfuric acid 208g/l, residue water

[Table 1a]

IMR 3000P	03.04.1996	IMR 3000P	03.04.1996.
	14:03:08		14:07:10
fuel oil extra light		fuel oil extra light	
NO --> NO ₂		NO --> NO ₂	
T-Gas 24°C	T-Room 13°C	T-Gas 38°C	T-Room 13°C
CO ₂ 0.0%	O ₂ 20.9%	CO ₂ 0.0%	O ₂ 20.9%
CO 0ppm	SO ₂ 0ppm	CO 0ppm	SO ₂ 0ppm
H ₂ S 0ppm	NO 22ppm	H ₂ S 0ppm	NO 71ppm
NO ₂ 0ppm		NO ₂ 14ppm	
qA ++++%	LAMBDA ++++	qA ++++%	LAMBDA ++++
IMR 3000P	03.04.1996	IMR 3000P	03.04.1996.
	14:04:10		14:08:11
fuel oil extra light		fuel oil extra light	
NO --> NO ₂		NO --> NO ₂	
T-Gas 28°C	T-Room 13°C	T-Gas 36°C	T-Room 13°C
CO ₂ 0.0%	O ₂ 20.9%	CO ₂ 0.0%	O ₂ 20.9%
CO 0ppm	SO ₂ 0ppm	CO 0ppm	SO ₂ 0ppm
H ₂ S 0ppm	NO 36ppm	H ₂ S 0ppm	NO 74ppm

NO₂ 6ppm
qA +++++% LAMBDA +++++

NO₂ 15ppm
qA +++++% LAMBDA +++++

IMR 3000P 03.04.1996
14:05:11

IMR 3000P 03.04.1996.
14:09:11

fuel oil extra light

fuel oil extra light

NO --> NO₂

NO --> NO₂

T-Gas 35°C T-Room 13°C

T-Gas 37°C T-Room 13°C

CO₂ 0.0% O₂ 20.9%

CO₂ 0.0% O₂ 20.9%

CO 0ppm SO₂ 0ppm

CO 0ppm SO₂ 0ppm

H₂S 0ppm NO 85ppm

H₂S 0ppm NO 73ppm

NO₂ 13ppm

NO₂ 17ppm

qA +++++% LAMBDA +++++

qA +++++% LAMBDA +++++

IMR 3000P 03.04.1996
14:06:11

fuel oil extra light

NO --> NO₂

T-Gas 29°C T-Room 13°C

CO₂ 0.0% O₂ 20.9%

CO 0ppm SO₂ 0ppm

H₂S 0ppm NO 62ppm

NO₂ 13ppm

qA +++++% LAMBDA +++++

[Table 1b]

5	IMR 3000P	03.04.1996	IMR 3000P	03.04.1996.
		13:47:08		13:51:08
	fuel oil extra light		fuel oil extra light	
10	NO --> NO ₂		NO --> NO ₂	
	T-Gas 22°C	T-Room 13°C	T-Gas 29°C	T-Room 13°C
	CO ₂ 0.0%	O ₂ 20.9%	CO ₂ 0.0%	O ₂ 20.9%
15	CO 0ppm	SO ₂ 0ppm	CO 0ppm	SO ₂ 0ppm
	H ₂ S 0ppm	NO 57ppm	H ₂ S 0ppm	NO 36ppm

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5	NO ₂ 0ppm	NO ₂ 0ppm
	qA +++++% LAMBDA +++++	qA +++++% LAMBDA +++++
	IMR 3000P 03.04.1996	IMR 3000P 03.04.1996.
	13:48:08	13:52:08
10	fuel oil extra light	fuel oil extra light
	NO --> NO ₂	NO --> NO ₂
	T-Gas 27°C T-Room 13°C	T-Gas 31°C T-Room 13°C
15	CO ₂ 0.0% O ₂ 20.9%	CO ₂ 0.0% O ₂ 20.9%
	CO 0ppm SO ₂ 0ppm	CO 0ppm SO ₂ 0ppm
	H ₂ S 0ppm NO 38ppm	H ₂ S 0ppm NO 43ppm
20	NO ₂ 0ppm	NO ₂ 0ppm
	qA +++++% LAMBDA +++++	qA +++++% LAMBDA +++++
25	IMR 3000P 03.04.1996	IMR 3000P 03.04.1996.
	13:49:08	13:53:08
	fuel oil extra light	fuel oil extra light
30	NO --> NO ₂	NO --> NO ₂
	T-Gas 27°C T-Room 13°C	T-Gas 33°C T-Room 13°C
	CO ₂ 0.0% O ₂ 20.9%	CO ₂ 0.0% O ₂ 20.9%
	CO 0ppm SO ₂ 0ppm	CO 0ppm SO ₂ 0ppm
35	H ₂ S 0ppm NO 39ppm	H ₂ S 0ppm NO 45ppm
	NO ₂ 0ppm	NO ₂ 6ppm
	qA +++++% LAMBDA +++++	qA +++++% LAMBDA +++++
40	IMR 3000P 03.04.1996	
	13:50:08	
45	fuel oil extra light	
	NO --> NO ₂	
	T-Gas 28°C T-Room 13°C	
50	CO ₂ 0.0% O ₂ 20.9%	
	CO 0ppm SO ₂ 0ppm	
	H ₂ S 0ppm NO 36ppm	
55	NO ₂ 0ppm	

EP 0 835 333 B9 (W1B1)

qA +++++& LAMBDA +++++

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[Table 1c]

5	IMR 3000P	03.04.1996	IMR 3000P	03.04.1996.
		14:31:54		14:35:54
	fuel oil extra light		fuel oil extra light	
10	NO --> NO ₂		NO --> NO ₂	
	T-Gas 25°C	T-Room 13°C	T-Gas 31°C	T-Room 13°C
	CO ₂ 0.0%	O ₂ 20.9%	CO ₂ 0.0%	O ₂ 20.9%
15	CO 0ppm	SO ₂ 0ppm	CO 0ppm	SO ₂ 0ppm
	H ₂ S 0ppm	NO 0ppm	H ₂ S 0ppm	NO 0ppm
	NO ₂ 0ppm		NO ₂ 0ppm	
20	qA +++++%	LAMBDA +++++	qA +++++%	LAMBDA +++++
	IMR 3000P 03.04.1996		IMR 3000P 03.04.1996.	
		14:32:54		14:36:54
25	fuel oil extra light		fuel oil extra light	
	NO --> NO ₂		NO --> NO ₂	
	T-Gas 31°C	T-Room 13°C	T-Gas 35°C	T-Room 13°C
30	CO ₂ 0.0%	O ₂ 20.9%	CO ₂ 0.0%	O ₂ 20.9%
	CO 0ppm	SO ₂ 0ppm	CO 0ppm	SO ₂ 0ppm
	H ₂ S 0ppm	NO 0ppm	H ₂ S 0ppm	NO 0ppm
35	NO ₂ 0ppm		NO ₂ 0ppm	
	qA +++++%	LAMBDA +++++	qA +++++%	LAMBDA +++++
40	IMR 3000P 03.04.1996		IMR 3000P 03.04.1996.	
		14:33:54		14:37:54
	fuel oil extra light		fuel oil extra light	
45	NO --> NO ₂		NO --> NO ₂	
	T-Gas 24°C	T-Room 13°C	T-Gas 34°C	T-Room 13°C
	CO ₂ 0.0%	O ₂ 20.9%	CO ₂ 0.0%	O ₂ 20.9%
50	CO 0ppm	SO ₂ 0ppm	CO 0ppm	SO ₂ 0ppm
	H ₂ S 0ppm	NO 0ppm	H ₂ S 0ppm	NO 0ppm
	NO ₂ 0ppm		NO ₂ 0ppm	
55	qA +++++%	LAMBDA +++++	qA +++++%	LAMBDA +++++

IMR 3000P 03.04.1996

14:34:54

fuel oil extra light

NO --> NO₂

T-Gas 30°C T-Room 13°C

CO₂ 0.0% O₂ 20.9%CO 0ppm SO₂ 0ppmH₂S 0ppm NO 0ppmNO₂ 0ppm

qA ++++% LAMBDA ++++

[Table 1d]

IMR 3000P 03.04.1996

14:47:13

fuel oil extra light

NO --> NO₂

T-Gas 12°C T-Room 13°C

CO₂ 0.0% O₂ 20.9%CO 0ppm SO₂ 0ppmH₂S 0ppm NO 0ppmNO₂ 0ppm

qA ++++% LAMBDA ++++

IMR 3000P 03.04.1996.

14:52:00

fuel oil extra light

NO --> NO₂

T-Gas 25°C T-Room 13°C

CO₂ 0.0% O₂ 20.9%CO 0ppm SO₂ 0ppmH₂S 0ppm NO 0ppmNO₂ 0ppm

qA ++++% LAMBDA ++++

IMR 3000P 03.04.1996

14:49:00

fuel oil extra light

NO --> NO₂

T-Gas 12°C T-Room 13°C

CO₂ 0.0% O₂ 20.9%CO 0ppm SO₂ 0ppmH₂S 0ppm NO 0ppmNO₂ 0ppm

qA ++++% LAMBDA ++++

IMR 3000P 03.04.1996.

14:53:00

fuel oil extra light

NO --> NO₂

T-Gas 28°C T-Room 13°C

CO₂ 0.0% O₂ 20.9%CO 0ppm SO₂ 0ppmH₂S 0ppm NO 0ppmNO₂ 0ppm

qA ++++% LAMBDA ++++

IMR 3000P 03.04.1996

14:50:00

fuel oil extra light

NO --> NO₂

T-Gas 24°C T-Room 13°C

CO₂ 0.0% O₂ 20.9%CO 0ppm SO₂ 0ppmH₂S 0ppm NO 0ppmNO₂ 0ppm

qA ++++% LAMBDA ++++

IMR 3000P 03.04.1996.

14:54:00

fuel oil extra light

NO --> NO₂

T-Gas 30°C T-Room 13°C

CO₂ 0.0% O₂ 20.9%CO 0ppm SO₂ 0ppmH₂S 0ppm NO 0ppmNO₂ 0ppm

qA ++++% LAMBDA ++++

IMR 3000P 03.04.1996

14:51:00

fuel oil extra light

NO --> NO₂

T-Gas 24°C T-Room 13°C

CO₂ 0.0% O₂ 20.9%CO 0ppm SO₂ 0ppmH₂S 0ppm NO 0ppmNO₂ 0ppm

qA ++++% LAMBDA ++++

[0055] As shown in the above table 1a-1d, when using the pickling solution of this invention, NO and NO₂ gas were not generated while 22-85ppm of NO gas and 6-17ppm of NO₂ gas were generated when using the comparative pickling solution.

Example 2: Measuring of pickling efficiency depending on the types of steel.

[0056] Various types of steels were pickled with comparative pickling solution containing the mixed acid and acid salt of this invention. Pickling of steels using the comparative mixed acid was conducted after the pretreatment had been proceeded.

[0057] As specimen, SUS-304 was used and the test results are presented in table 2 below. Comparative pickling solution and pickling solution of this invention in Example 1 were used.

[Table 2]

Pickling time of SUS-304 specimen depending on the types of steel (unit: min.)		
type	comparative pickling solution	pickling composition of this invention in Example 1
L type steel	20 - 60	20 - 40
wire rod	15 - 30	15 - 30

[Table 2] (continued)

Pickling time of USU-304 specimen depending on the types of steel (unit: min.)		
type	comparative pickling solution	pickling composition of this invention in Example 1
hot rolled thick sheet	20 - 40	20 - 30
hot rolled sheet	2 - 3	2 - 3
cold rolled sheet	0.5 - 1	0.5 - 1
*Pickling using comparative pickling solution in table 2, pickling time is the consumed time of pickling for specimen which was pretreated such as salt bath, shot blast and neutral salt bath. Pickling time used in pickling by using pickling solution of this invention was same or shorter the time consumed when using comparative pickling solution. **Pickling using pickling solution of this invention of Example in table 2, pickling time is the consumed time for pickling for specimen without pretreated.		

[0058] From the above result, it is understood that oxidation and carbonation scale of stainless steel can be removed only by pickling using the method and pickling solution of this invention without pretreatment.

Example 2

[0059] This example is to decide optimum ratio of nitrate to fluorides in pickling solution.

[0060] Pickling was proceeded by dipping SUS-304 specimen cold rolled coil(C/R) 50 x 50mm, 1.2t sheet which had not been processed pretreatment into the pickling solution at 50°C containing nitrate and fluorides dissolved in industrial water in different ratios. Pickling time was measured and the results are presented in table 4 below.

[Table 3]

Pickling time in various composition of nitrate and fluorides (unit:min)

XNO ₃ (g/l) YF(g/l)							
	10	30	50	70	100	130	150
10	62	58	42	30	30	28	25
30	40	40	30	16	18	20	23
50	42	38	13	12	12	10	10
70	40	36	12	10	10	9	8
100	40	28	12	9	8	8	8
130	34	28	10	8	8	7	7
150	30	28	10	8	7	7	7

[0061] As shown in the table 3, pickling was proceeded rapidly within 7 minutes when each of the amount of nitrate and fluorides was 130g/l, but pickling rate was not directly proportional to the amount of additional components.

[0062] Considering recovery ratio of pickling solution, economical efficiency and pickling time, the most suitable amounts of nitrate and fluoride were 50-70g/l.

[0063] Pickling solution comprising 50-70g/l of nitrate and 50-70g/l of fluorides will be referred to as "Formulation A".

About from 40 seconds to 2 minute was consumed for removing scale when using comparative pickling solution containing nitric acid and hydrofluoric acid, while about from 10 to 13 minute was consumed when using the Formulation A.

Example 3

[0064] Pickling was proceeded for specimen of example 2 using the pickling solution into which sulfuric acid and mixture of 5:1 ratio by weight of sulfuric acid and sulfate were added to Formulation A of example 2 to reduce the pickling time. The results are presented in table 4 below.

[Table 4]

Pickling time when using pickling solution which sulfuric acid and the mixture of sulfuric acid/sulfate were respectively added to formulation A(unit: sec.)							
amount(g/l)	50	100	150	200	250	300	500
sulfuric acid	360	220	100	90	80	60	45
sulfuric acid + sulfate	180	120	90	40	32	30	20

[0065] As shown in the above table 4, when pickling solution which was the mixture of Formulation A and the mixture of 5:1 ratio by weight of sulfuric acid and sulfate was used, pickling time was largely reduced but surface of the specimen became roughened by severe corrosion.

[0066] When pickling using pickling solution comprising 250-300g/l of mixture of 5:1 ratio by weight of sulfuric acid and sulfate, the surface of specimen was not damaged and pickling time was satisfactorily 30-32sec.

[0067] Pickling composition which is formed by the addition of 250-300g/l of mixture of 5:1 ratio by weight of sulfuric acid and sulfate to Formulation A will be referred to as "Formulation B".

Claims

1. A pickling solution used for removing scales formed on iron-based alloys containing chrome and/or nickel essentially consisting of nitrates fluorides each of which is in the amount of 50 - 70 g/l, further consisting of a mixture of sulfuric acid and sulfate in a total amount of 250-300 g/l, the mixture of sulfuric acid and sulfate being in the ratio of 5 : 1, and optionally phosphoric acid and phosphates serving as inhibitors for protecting the base surface of the substrate from corrosion and optionally amines or amides to prevent Fe^{2+} ion from diffusing from the metal surface to the pickling solution.

Patentansprüche

1. Eine Beizlösung, die verwendet wird für das Entfernen von Zunder, welcher auf eisenbasierten Legierungen, welche Chrom und/oder Nickel beinhalten, ausgebildet ist, im wesentlichen bestehend aus Nitraten und Fluoriden, wobei jedes derselben in der Menge von 50 - 70 g/L vorliegt, weiterhin bestehend aus einer Mischung aus Schwefelsäure und Sulfat in einer Gesamtmenge von 250 - 300 g/L, wobei die Mischung aus Schwefelsäure und Sulfat im Verhältnis von 5 : 1 liegt, und optional aus Phosphorsäure und Phosphaten, welche als Hemmstoffe zum Schützen der nackten Oberfläche des Substrats vor Korrosion dienen, und optional aus Aminen oder Amiden, um zu verhindern, daß Fe^{2+} -Ionen aus der Metalloberfläche in die Beizlösung diffundieren.

Revendications

1. Bain de décapage utilisé pour éliminer la calamine sur des alliages à base de fer contenant du chrome et du nickel, consisté essentiellement de nitrates et de fluorures, dont la quantité respective est de 50 - 70 g/l, constitué en outre d'un mélange d'acide sulfurique et de sulfate en quantité totale de 250 à 300 g/l, le mélange d'acide sulfurique et de sulfate présentant un rapport de 5 : 1, et en option l'acide phosphorique et les phosphates servant d'inhibiteurs

EP 0 835 333 B9 (W1B1)

pour protéger de la corrosion la surface de base du substrat et en option des amines ou amides pour éviter que l'ion FE^{2+} ne se diffuse depuis la surface de métal en direction du bain de décapage.

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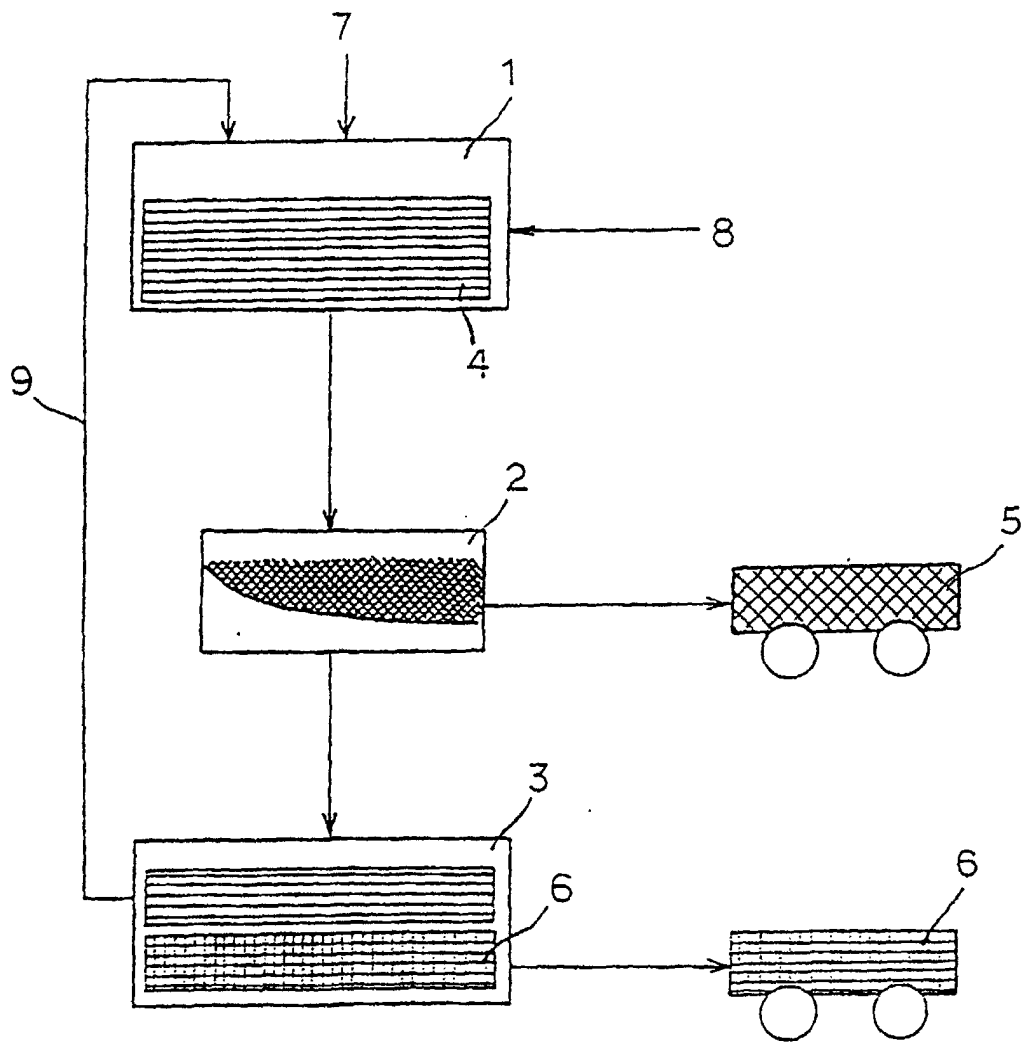


FIG. 1