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(54) METHOD FOR PICKLING IRON OR STEEL OBJECTS.

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EP-A-0 032 886 SE-B- 440 239
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Patent Abstracts of Japan, abstract of JP, 58-73 778, published 4 May 1983

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Description

This invention relates to methods for pickling iron or steel objects, before a subsequent surface treatment or a mechanical processing.

5 Before the mechanical processing of objects of iron or steel, e.g. by drawing, milling or pressing, or before application of any anti-corrosive film, the surface coating usually must be removed. This coating can comprise various oxides, e.g. rust, being formed by chemical corrosion. Other coatings can consist of scale from a preliminary heat treatment or rolling skin from a preliminary rolling. These different coatings are normally removed by pickling in acid baths.

10 Normally, either sulphuric acid or hydrochloric acid is used for pickling carbon steel or cast iron. The former is less expensive to buy, but the hydrochloric acid presents several technical advantages, often making the total economy for this acid the most profitable.

A pickling bath intended for pickling with hydrochloric acid normally comprise about 200 g HCl per liter. During pickling, normally performed at a temperature of about 20°C, iron is solved as Fe^{2+} . The proportion of iron in the pickling bath rises gradually until it, after some use, reaches about 80—85 g per liter pickling solution. The proportion of acid in the pickling bath is now about 80—100 g per liter pickling solution. The pickling continues very slowly during these circumstances making it necessary to exchange the pickling solution for regenerating or dumping. In total, 7—8 kg of hydrochloric acid is used per kg of dissolved iron.

20 The depositing or regenerating of used pickling solution is very important from various points of view. Partly because these pickling baths constitute a dangerous waste, which has to be destructed before deposition. Partly because the pickling bath has a significant value with respect to the content of remaining free acid, solved iron and a corresponding amount of negative ions.

The hydrochloric solution can be regenerated through a roasting process within an oil-burning oven. Thereby the solved iron forms iron oxide and hydrogen chlorine. The latter is absorbed while the pickling acid is recovered. One disadvantage with this process is that a certain amount of hydrogen chlorine is lost because also the remaining free acid goes into the oven.

It is also possible to regenerate the pickling solution through electrolysis. The iron in the solution will be deposited at the cathode of the electrolytic cell. The electrolyte (the pickling solution) must form an almost neutral solution of ferrous chloride in order to enable the electrolysis. Since the pickling solution, however, contains a comparatively large proportion of remaining acid, there will mainly be development of hydrogen gas at the cathode, i.e. the deposition of metal will be small in relation to used electric energy.

The solution can be neutralized by evaporation and crystallization of iron chloride and separation of remaining surplus acid, which can be returned to the pickling process.

35 Because of the solubility of iron chloride, the evaporation of the bath must be complete to enable crystallization. Furthermore, the subsequent electrolysis will consume a lot of electric energy, since a great deal of the chloride is used up by the development of gas, while oxidation of ferrous chloride to ferric chloride takes place at the anode. The gradual increase of Fe III changes the polarity leading to the forming of basic salts, while the electrolytic efficiency declines steeply.

40 From this, an electrolytic cell for recovery of pickling acid must have a ion-exchange membranes as a partition between anode and cathode, so that the acid formed at the anode will not prevent the deposition of metal at the cathode.

A useful pickling solution may comprise between 100—200 g free hydrochloric acid per liter solution with between 0—80 g Fe^{2+} and usually attacks the base metal furiously. When objects of iron or steel with scales, normally comprising $\text{Fe}_2\text{O}_3 \cdot \text{FeO}$ -oxides, are pickled, pittings occur. This happens because the surface of the base metal usually is rather small compared to the oxide surface, i.e. the cathode, wherein the oxide has the high electric potential in relation to the iron within said solution and is cathodic in relation to the base metal, which becomes the dissolving electrode, because of its anodic potential. Therefore, the scales are not dissolved in the acid, but rather "explodes" away from its surface, because the acid penetrates below the scale and lifts it away. The consequence is severe pittings on the base metal, because of the anodic current density (corrosive current) is very high. While the proportion of acid in the solution declines, the difference of potential also declines and thereby the pickling effect of the solution. The Fe_3O_4 -oxide is deposited as a sludge on the bottom of the pickling bath. The proportion of iron rises during conventional pickling, while the proportion of acid declines. At the beginning of the process the difference of potential between the iron oxides is at least 1000 mV. The base metal Fe then acts as anode, meaning that the iron oxides form $\text{Fe}^0 \rightarrow \text{Fe}^{2+}$. The surface of the metal is therefore pitted when it is exposed by fractures and pores in the oxide coating. It is normal to use an inhibitor or restrainer in the pickling bath to reduce the pitting damage on the base metal.

DE—3 141 949 discloses a method for regeneration of an etch bath which is used for etching of a metal foil. Such methods are used in the industry for manufacture of printed circuit cards. The dissolved copper has a substantial metal value which allows for the use of energy consuming regeneration methods. Thus the regeneration takes place in an electrolytic cell having diaphragms, at a temperature of between 50 and 95°C, and with a current density of between 20 and 60 A/dm². For a current of 8 volts, the energy consumption will then be between 160 and 480 Watt/dm². This prior art method is not applicable for large scale pickling processes.

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The object of the present invention is to provide a method for pickling objects of iron and steel, which enables a continuous regenerating of the pickling solution, at a high level of electrolytic efficiency, wherein the pickling can be performed in a closed process having as residual products pickled objects of iron and steel and pure electrolytic iron corresponding to the amount of dissolved iron.

5 The method according to the present invention is characterized in that the objects are transported into a pickling solution having a temperature above 25°C and containing ferrous chloride and a low proportion of free hydrochloride acid, and that said solution is continuously regenerated in a circulation system with electrolytic cells, which are connected to a source of direct-current, in order to deposit iron electrolytically and recover free acid.

10 Preferably, the pickling fluid contains at least 300 g FeCl₂ per liter and no more than 50 g of free acid reckoned as HCl per liter.

Preferably the electrolytic cells are electrically connected in series with the source of direct-current and in parallel with the flow of pickling solution in said circulation system.

15 Preferably, the proportion of ferrous chloride sinks no more than 10 g per liter solution during its passage through any of the electrolytic cells, and the current intensity at each of their respective cathode is especially between 0.2—10 A per dm² of cathodic surface.

A solution for pickling objects of iron or steel, before a subsequent surface treatment or mechanical processing, comprising: FeCl₂, Fe₂ and HCl, preferably contains the following proportions: FeCl₂ between 250 and 450 g/l, Fe₂ between 110 and 200 g/l and HCl between 5 and 50 g/l.

20 Since the pickling is carried through at a high proportion of iron and therefore at a low proportion of free acid and also at rised temperature, the oxides are dissolved efficiently, without any pitting of the base metal. This very favourable pickling effect, in spite of the high proportion of iron in the solution, is a result of the ability of chloride to form large complexes. That is, a large proportion of the iron in the pickling solution is bound in anion form as:

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This complex ion is in balance with other ions in the solution tanks to the rised temperature, which results in an increased proportion of free hydrogen ions.

30 Since the ionization energy is comparatively low in a solution of ferrous chloride with a low proportion of free acid it is possible to electrolytically deposit the iron with a high electrolytic efficiency, and cathodically within a simple electrolytic cell, without any partitioning ion-exchanging membrane between anode and cathode.

35 The invention will now be described in further detail, with reference to the accompanying drawing, which represents a schematic elevation of a pickling plant for using the method according to the invention with continuous regenerating of the pickling solution in a closed circuit.

The figure shows a pilot plant for pickling of cast iron and hot rolled objects before hot zinc coating. A tank containing pickling solution is generally denoted 10. Objects represented by the arrow 11 are transported down into the solution after a preliminary degreasing and rinsing. Pickled objects are represented by the arrow 12.

40 The pickling solution is continuously pumped, by means of a pump 13, from the tank 10, into five electrolytic cells 14, connected in parallel with the flow from the pump 13, and returns to the tank 10 by means of a return pump 15. The electrolytic cells are electrically connected in series to the positive and negative terminals 16 and 17, respectively, of a direct-current source. Each electrolytic cell 14 conventionally comprises one anode 18 and one cathode 19.

45 These conditions prevail:

In the pickling solution

50	Volume:	10 m ³
	Flow of objects:	2 tons/h
	Dissolved iron:	10 kg/h
	Theoretical amount of acid used per hour ≈ 15 kg HCl at 100% ≈ 50 kg acid at	
55	30% Concentrations:	FeCl ₂ 340 g/l Fe 150 g/l free HCl 20 g/l
	Temperature:	40°C

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Among others, the following chemical reactions take place in the solution: $\text{Fe}^0 \rightarrow \text{Fe}^{2+}$, $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$.

In the regenerating section

5	Dimensions:	1500 × 1000 × 1200 mm
	Electrode system:	5 cells with bipolar electrodes anode: graphite cathode: stainless, acid resistant
	Voltage drop per cell:	2.5 V
	Current density:	2 A/dm ²
10	Static current changer:	16 V, 1000 A
	Amperage per cell:	900 A
	Total quantity of current:	4500 Ah
	Theoretical amount of dissolved Fe:	4680 g
15	Real amount of dissolved Fe:	4300 g
	Estimated electrolytic efficiency:	91%
20	Amount of recovered acid:	22 kg at 30%

The following reactions take place in the electrolytic cells: Cathode: $\text{Fe}^{2+} \rightarrow \text{Fe}^0$, Anode: $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$.

The cathode plates 19 are made of 0.1 mm thin stainless, acid resistant sheet. The cathodes are changed regularly in the cells 14. By bending the sheets, the electrolytic iron can easily be removed from said sheets.

The pickling solution circulates through the cell system during the electrolysis at a rate of about 30 liter per minute. This implies that the difference in concentration of iron in the solution leaving vs. entering the tank is between 2.0—2.5 g/l. In the present case, when the dissolving rate of iron in the pickling solution is 10 kg/h, 40% of the acid is recovered.

In order to get a full recovery of acid, a cell system with a total current of 10000 A is therefore required. This means that the static current changer must be rated at, e.g. 16 V and 200 A or 24 V and 1000—1500 A. The latter alternative is preferable, since the cost of a static current exchanger mainly depends on current capacity and not on output or voltage.

The above described method radically alters the properties of the pickling solution. The iron oxides Fe_3O_4 becomes the dissolving electrode and the base metal is not attacked by pitting. The sludge of iron oxides is completely dissolved leaving no remains at the bottom of the tank. At the same time the objects are cleaned with no trace of dirt film. The surrounding pickling solution is strongly reducing at the conditions according to the invention.

The very high electrolytic efficiency during the process according to the invention results from the relation between the overpotential of the hydrogen towards the cathode and the dissolving potential of the iron. The overpotential of hydrogen is preferably as high as possible, since the electrolytic efficiency declines with a rising proportion of free acid in the solution.

The regenerating cells can be built as a modular system, which can be adapted to most existing pickling plants, while changing from a conventional process to the pickling process according to the invention.

The above mentioned dimensions, rates and values can obviously be varied within the scope of the following claims. The method according to the invention can be used in combination with conventional pickling methods. An activator can be added to the above described pickling solution, comprising a surface active agent with a high affinity to the base metal surface, to facilitate the penetration of the pickling fluid beneath the scales. Further, the electrolytic current between terminals 16, 17 can be pulsed at low frequency, giving a lower electrolytic polarization and therefore a higher electrolytic efficiency.

The pickling effect of the solution according to the invention can be even more improved by addition of any of the salts: magnesium chloride, calcium chloride or aluminium chloride. This increases the overpotential at any given proportion of free acid and therefore the electrolytic efficiency. An additive of 50 g/l MgCl_2 reduces tensile stress at the iron deposited at the cathode, so that a ductile film of iron is formed. The iron can be plated to form any desired thickness. The growth is about 1 $\mu\text{m}/\text{min}$ at a current density of 5 A/dm² and 90% electrolytic efficiency. This addition of magnesium chloride also improves the pickling process.

60 Claims

1. A method for pickling iron or steel objects before a subsequent surface treatment or a mechanical processing, characterized in, that the objects (11) are transported into a pickling solution having a temperature above 25°C and containing ferrous chloride FeCl_2 , Fe and a free hydrochloric acid HCl, wherein the proportion of FeCl_2 is between 250 and 450 g/l, the proportion of Fe is between 110 and 200 g/l and the

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proportion of HCl is between 5 and 50 g/l, that said solution is continuously regenerated in a circulation system with electrolytic cells (14), which are electrically connected in series with a source of direct-current (16, 17), in order to deposit iron electrolytically and recover free acid, without the presence of any diaphragm, and that the electrolytic cells (14) are connected in parallel with the flow of pickling solution in said circulation system.

2. A method according to claim 1, characterized in, that the pickling solution contains at least 300 g ferrous chloride per liter.

3. A method according to any of claims 1 or 2, characterized in, that the proportion of ferrous chloride is brought down no more than 10 g per liter solution, during its passing through any of the electrolytic cells.

4. A method according to any of the preceding claims, characterized in, that the amperage at each cathode (109) in the electrolytic cells (14) is between 0.2—10 A per dm² cathodic surface.

5. A solution for pickling of iron or steel objects before a subsequent surface treatment or a mechanical processing, containing: FeCl₂, Fe and HCl, characterized in, that the proportion of FeCl₂ in the solution is between 250 and 450 g/l, that the proportion of Fe₂ in the solution is between 110 and 200 g/l and that the proportion of free acid, HCl is between 5 and 50 g/l.

6. A solution according to claim 5, characterized in, that it contains a magnesium or calcium chloride, in order to improve the pickling process, increase the electrolytic efficiency and reduce the tensile stress at the iron deposited on the cathode.

20 Patentansprüche

1. Verfahren zum Beizen von Eisen- oder Strahlgegenständen vor einer nachfolgenden Oberflächenbehandlung oder einer mechanischen Bearbeitung, dadurch gekennzeichnet, daß die Gegenstände (11) in eine Beizlösung transportiert werden, die eine Temperatur oberhalb von 25°C besitzt und Ferrochlorid FeCl₂, Fe und einen freien Chlorwasserstoff HCl enthält, wobei der Anteil an FeCl₂ zwischen 250 und 450 g/l liegt, wobei der Anteil an Fe zwischen 110 und 200 g/l beträgt, und wobei der Anteil an HCl zwischen 5 und 50 g/l liegt, daß die Lösung kontinuierlich in einem Umlaufsystem mit elektrolytischen Zellen (14) regeneriert wird, welche elektrisch in Reihe mit einer Gleichstromquelle (16, 17) geschaltet sind, um elektrolytisch Eisen niederzuschlagen und freie Salzsäure ohne das Vorhandensein irgendeines Diaphragmas zu gewinnen, und daß die elektrolytischen Zellen (14) parallel zu der Strömung der Beizlösung in dem Umwälzsystem geschaltet sind.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Beizlösung wenigstens 300 g Eisenchlorid pro Liter enthält.

3. Verfahren nach einem der Ansprüche 1 oder 2, dadurch gekennzeichnet, daß der Anteil an Eisenchlorid auf nicht mehr als 10 g/l Lösung während dessen Durchtritt durch irgendeine der elektrolytischen Zellen verringert wird.

4. Verfahren nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, daß die Stromstärke an jeder Kathode (19) in den elektrolytischen Zellen (14) zwischen 0,2—10 A pro dm² Kathodenfläche beträgt.

5. Lösung zum Beizen von Eisen- oder Stahlgegenständen vor einer nachfolgenden Oberflächenwandlung oder einer mechanischen Bearbeitung, bestehend aus: FeCl₂, Fe und HCl, dadurch gekennzeichnet, daß der Anteil an FeCl₂ in der Lösung zwischen 250 und 450 g/l liegt, daß der Anteil an Fe in der Lösung zwischen 110 und 200 g/l beträgt, und daß der Anteil an freier Säure, HCl, zwischen 5 und 50 g/l liegt.

6. Lösung nach Anspruch 5, dadurch gekennzeichnet, daß sie ein Magnesium- oder Calciumchlorid enthält, um den Beizvorgang zu verbessern, die elektrolytische Effizienz zu erhöhen und die Zugspannung bei dem auf der Kathode niedergeschlagenen Eisen zu verringern.

Revendications

1. Procédé de décapage d'objets en fer ou en acier avant un traitement de surface ou un traitement mécanique ultérieur, caractérisé en ce que les objets (11) sont transportés dans une solution de décapage présentant une température supérieure à 25°C et contenant du chlorure ferreux FeCl₂, Fe et de l'acide chlorhydrique libre HCl, dans laquelle la proportion de FeCl₂ est comprise entre 250 et 450 g/l, la proportion de Fe est comprise entre 110 et 200 g/l et la proportion de HCl est comprise entre 5 et 50 g/l, en ce que ladite solution est régénérée en continu dans un système de circulation avec des cellules électrolytiques (14), qui sont reliées électriquement en série à une source de courant continu (16, 17) afin de précipiter le fer par voie électrolytique et de récupérer l'acide libre, en l'absence de tout diaphragme, et en ce que les cellules électrolytiques (14) sont reliées en parallèle au courant de solution de décapage dans ledit système de circulation.

2. Procédé selon la revendication 1, caractérisé en ce que la solution de décapage contient au moins 300 g de chlorure ferreux par litre.

3. Procédé selon l'une des revendications 1 et 2, caractérisé en ce que la proportion de chlorure ferreux est abaissée jusqu'à une valeur non supérieure à 10 g par litre de solution au cours de son passage à travers l'une quelconque des cellules électrolytiques.

4. Procédé selon l'une des revendications précédentes, caractérisé en ce que l'intensité de courant au

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niveau de chaque cathode (19) des cellules électrolytiques (14) est comprise entre 0,22 et 10 A par dm^2 de surface cathodique.

5. Solution de décapage pour des objets en fer ou en acier avant un traitement de surface ou un traitement mécanique ultérieur, contenant: FeCl_2 , Fe et HCl, caractérisée en ce que:

5 la proportion de FeCl_2 dans la solution est comprise entre 250 et 450 g/l,

la proportion de Fe dans la solution est comprise entre 110 et 200 g/l et

la proportion d'acide libre HCl est comprise entre 5 et 50 g/l.

6. Solution selon la revendication 5, caractérisée en ce qu'elle contient un chlorure de magnésium ou de calcium afin d'améliorer le processus de décapage, d'augmenter le rendement électrolytique et de
10 réduire les contraintes de traction au niveau du fer déposé à la cathode.

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