

Pickling agent for special steelsDescription

5 The invention relates to an aqueous stripper or pickling agent for special steels that is free of wetting agents and emulsifying agents and is based on sulphuric acid, or phosphoric acid, and hydrogen fluoride.

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Generally, it is usual to pickle special steels with various acids or acid mixtures (pickling agents) in order to remove corrosion products and also, for example, layers of scale or tarnishing colours that have resulted during welding. The pickling agents can then be used as pickling baths or otherwise - in particular in the case of large components or local oxide formation - as pickling agents that are applied by spraying or with a brush.

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The acids or acid mixtures which are the most significant for pickling special steels are hydrofluoric acid, hydrofluoric acid/nitric acid, hydrofluoric acid/sulphuric acid with already in the initial phase of the pickling agent to some extent significant additions of iron (III) compounds. To some extent, the pickling agents contain hydrogen peroxide with the aid of which the iron (II) ions that dissolve as a result of the pickling attack are oxidized to form iron (III) ions. Examples of such pickling agents are described in WO 87/01 739, DE-A-38 25 857, DE-A-44 17 284, EP-A-505 605 and EP-A-596 273.

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The greatest variety of disadvantages are attached to the known pickling agents. One disadvantage is often the low pickling speed. A pickling speed that is too

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high can also have disadvantageous effects if cycle times are stipulated in pickling plants. This applies in particular to hydrofluoric acid/nitric acid pickling agents. In addition, with these pickling agents, which
5 have high concentrations of acid, vapours that are injurious to health and which have to be removed by suction and dealt with in a washing plant are given off by the pickling baths. Moreover, on account of the high level of solubility of the nitrates the treatment
10 of the rinsing water and waste water that occurs during the pickling process is difficult. Moreover, attached to low-concentration pickling agents that are based on hydrofluoric acid/nitric acid is the disadvantage that dark, spotted metal surfaces, and not the metallicly
15 bright metal surfaces that are desired per se, result. Pickling agents which already have considerable additions of Fe (III) compound in the initial phase for setting the necessary redox potential are deficient insofar as the absorption capacity of Fe (II) or Fe
20 (III) respectively that originates from the oxide film of the material that is to be pickled is reduced in accordance with the quantity of Fe (III) added.

The methods with pickling agents based on sulphuric
25 acid/hydrofluoric acid/hydrogen peroxide that have dipping applications and in which, as a rule, it is necessary to maintain a certain redox potential are comparatively expensive to conduct so they do not come into consideration in particular for comparatively
30 small pickling establishments. Further disadvantages lie in the fact that the hydrogen peroxide decomposes comparatively easily in the pickling agent and with a small addition of peroxide only slow oxide dissolution results, i.e. the pickling speed is low.

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A further method consists in so-called single-bath

grease-extraction and pickling of objects that contain iron or consist thereof. It operates with solutions which contain acids, wetting agents and/or emulsifying agents and also aromatic water-soluble nitro compounds, such as, for example, nitrobenzenesulphonate (DE-A-25 07 059), as oxidizing agents. The single-bath grease-extraction and pickling automatically results in the entry of oil or grease into the pickling bath, thereby affecting the pickling process in an incalculable manner. In particular, the formation of a uniform pickling picture is prevented. Moreover, the content of wetting and/or emulsifying agents impedes the treatment of the rinsing water and waste water that occurs in the pickling process.

Finally, a method that is indicated as a method for dissolving metals and which operates with aqueous, strong acids that contain an aromatic nitro compound is known from US-Patent Specification 2 698 781. On referring to the examples, this method is intended in the first place to deal with nickel-plated copper and also copper and lead. In one example only is there described the pickling of special steels with a pickling bath that contains sulphuric acid, m-nitrobenzenesulphonic acid and hydrofluoric acid, with the concentration of sulphuric acid amounting in this case to 200 g/l. Pickling baths having such a high concentration of sulphuric acid operate comparatively slowly, however, so that the throughput is low.

An object of the invention is to provide an aqueous pickling agent for special steels that does not have the known disadvantages, and in particular those disadvantages mentioned above, and which can be implemented simply and inexpensively in terms of the method used.

The object is achieved by formulating the pickling agent of the kind mentioned at the beginning in accordance with the invention in such a way that it contains (in each case in relation to 100 % by weight of substance) 1.5 to 16 % by weight sulphuric acid, or 2.0 to 30 % by weight phosphoric acid, and also 0.5 to 14 % by weight hydrogen fluoride and 0.5 to 15.5 % by weight acid-soluble aromatic nitro compound, to which no iron (III) compound is added and to which only in the initial phase can an oxidizing agent oxidizing iron (II) to form iron (III) be added.

The pickling agent in accordance with the invention that is used in order to carry out the pickling process can basically also be employed without an oxidizing agent oxidizing iron (II) to form iron (III) in the initial phase. In order to activate the freshly prepared pickling agent, however, it can be advantageous to add small quantities of oxidizing agent, for example 0.05 % by weight relative to peroxide compounds.

The pickling agent in accordance with the invention can be used as a pickling bath, as a pickle that is applied by spraying or as a pickle that is applied with a brush.

In consequence of the fact that the pickling agent is free of wetting agents and emulsifying agents, it is to be seen that the material that is to be pickled can be completely wetted by the pickling agent. Insofar as oil or grease residues found on the material that is to be pickled impair the possibility of wetting it completely, cleaning or grease-extraction beforehand using the usual cleaners and thorough rinsing with water are to be carried out before the pickling

process.

5 In accordance with a particularly preferred embodiment of the invention, a pickling agent is used that, when applied as a pickling bath, contains 5.0 to 11 % by weight sulphuric acid, or 8.0 to 20 % by weight phosphoric acid, and also 4.0 to 10 % by weight hydrogen fluoride and 4.5 to 11 % by weight acid-soluble aromatic nitro compound. The pickling agent
10 that has the afore-mentioned concentration ranges is distinguished by a sufficiently high pickling speed without the base material being attacked. In addition, it is particularly favourable in terms of costs.

15 When used as a pickle that is applied by spraying or with a brush, the pickling agent preferably contains 2.5 to 5.5 % by weight magnesium compound (calculated as Mg).

20 By adding magnesium in the quantities mentioned, the pickling agent is converted into a thixotropic gel. As a result, the application of a sufficient quantity of the pickling agent, as required for the pickling process, is guaranteed. It is particularly
25 advantageous to add the magnesium in metallic form, as magnesium oxide, magnesium hydroxide, magnesium carbonate or magnesium sulphate.

Accordingly, a preferred embodiment of the invention
30 provides that the pickling agent when used as a pickle that is applied by spraying be used with a content of 9.5 to 15.5 % by weight sulphuric acid, or 15.0 to 30.0 % by weight phosphoric acid, and also 4.0 to 11.0 % by weight hydrogen fluoride, 4.5 to 11.5 % by weight acid-soluble aromatic nitro compound and 2.5 to 4.5 % by
35 weight magnesium compound (calculated as Mg).

In a further preferred embodiment of the invention the pickling agent when used as a pickle that is applied with a brush contains 12.0 to 16.0 % by weight sulphuric acid, or 18.0 to 30.0 % by weight phosphoric acid, and also 4.5 to 12.0 % by weight hydrogen fluoride, 2.5 to 9.5 % by weight acid-soluble aromatic nitro compound and 3.0 to 5.5 % by weight magnesium compound (calculated as Mg).

Suitable acid-soluble aromatic nitro compounds are those which have on the benzene ring at least one nitro and at least one acidic group, in particular a carboxyl or sulphonic acid group. It is particularly advantageous to use m-nitrobenzenesulphonate and/or 3-nitrophthalate as an acid-soluble aromatic nitro compound.

The temperatures, at which the pickling agents in accordance with the invention are used, vary depending upon the type of application. When employed as a pickling bath, they are adjusted to a value in the range of 15 to 80°. The duration of pickling, depending on the degree of scaling or oxide film of the material that is to be pickled, amounts to 5 to 90 minutes, with the shorter pickling times applying to the higher pickling temperatures and the longer pickling times applying to the lower pickling temperatures. When the pickling agent is used as a pickle that is applied by spraying or with a brush, the pickling temperatures are as a rule stipulated by the prevailing room or ambient temperatures. Generally they lie between 15 and 35°C. The pickling time required amounts to approximately 15 to 180 minutes.

With the aid of the pickling agent in accordance with the invention it is possible to carry out a pickling

process which is simpler and less expensive in terms of the method used. In consequence of the moderate removal of material by pickling that is striven for and which is attained by means of the pickling agent in accordance with the invention, bright velvety surfaces are attained. The treatment of the rinsing water and waste water proves to be simple, since the components of the pickling agent can be precipitated and separated with, for example, milk of lime as difficult to dissolve calcium compounds.

The invention is explained in greater detail with reference to the examples which follow.

Example 1

In order to determine the material that is removed and the quality of the surface, metallically pure metal sheets of special steel quality 1.4541 and special steel quality 1.4462 were treated for one hour at 30°C in the pickling-agent systems set out hereinafter in tabular form. The data given in % is understood to be % by weight.

The results, in g/m² with regard to the material that is removed, are compiled in columns two and three and with regard to the quality of the surface in column four.

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No.	Pickling agent	Removal of material		Surface
		1.4541	1.4462	
1.	15% HNO ₃ / 5% HF	55.8	27.1	bright silver, slightly rough
2.	7% H ₂ SO ₄ / 5% HF	18.9	6.9	greyish black coated surface
3.	7% H ₂ SO ₄ / 5% HF 1% H ₂ O ₂	46.3	17.6	bright silver, slightly rough
4.	7% H ₂ SO ₄ / 5% HF 5% H ₂ O ₂	41.1	16.2	bright silver, velvety
5.	7% H ₂ SO ₄ / 5% HBF ₄ 3% Fe (III) sulphate	9.2	0.1	bright, slightly spotted
6.	7% H ₂ SO ₄ / 5% HF 5% m- nitro benzene sulphonic acid	32.8	10.8	bright, velvety

7.	7% H ₂ SO ₄ /5HF 5% m- nitro benzene sulphonic acid 0.05% H ₂ O ₂ in the initial phase	36.4	11.2	bright, velvety
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A comparison of the results shows that - with the exception of pickling agent 4.) - only the pickling agents 6.) and 7.) in accordance with the invention caused the desired bright, velvety surface to develop. All the others resulted in slightly rough surfaces or greyish black coated surfaces or spotted surfaces. The removal of material in the case of pickling agents 6.) and 7.) is moreover comparatively low.

Example 2

In each case two steel metal sheets connected with a longitudinal seam by means of TIG welding, having the dimensions 45 x 140 mm and of special steel quality 1.4541 and special steel quality 1.4462 were dipped into a pickling agent at 30°C that consisted of

5 % by weight hydrogen fluoride
7 % by weight sulphuric acid and
5.4 % by weight m-nitrobenzenesulphonate
(introduced as Na-salt)
remainder water.

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The pairs of metal sheets were inspected visually at

intervals of 2 minutes for descaling of the welded seam and removal of tarnishing colours.

5 The pair of metal sheets made of the material 1.4511 (sic) were clean after 10 minutes; the pair made of the material 1.4462 were clean after 24 minutes.

Example 3

10 A pickle for application by spraying was formulated from

14 % by weight sulphuric acid (96 % by weight)
19 % by weight hydrofluoric acid (50 % by weight)
15 12.1 % by weight MgCO_3 and
9 % by weight Na-m-nitrobenzenesulphonate
remainder water.

20 The clear, viscous liquid that was obtained was sprayed at a pressure of 6 bar onto metal sheets of steel quality 1.4301 that had a welded seam effected by hand. The 1 to 2 mm thick film that was obtained also did not flow away on vertical surfaces in consequence of its thixotropy.

25 After a reaction time of 1 hour, the pickle for application by spraying was rinsed off. The welded seam was descaled clean. The whole sheet-metal surface was uniformly bright and hardly affected by the
30 pickling agent.

Example 4

35 A pickling agent for application with a brush was prepared from

24 % by weight phosphoric acid (85 % by weight)
14 % by weight hydrofluoric acid (70 % by weight)
6.6 % by weight magnesium oxide and
5 % by weight 3-nitrophthalic acid
5 remainder water.

An opaque paste developed that was no longer free-flowing and which was applied with a brush to the welded seam of a metal sheet of special steel quality
10 1.4571 to a thickness of 2 to 3 mm.

After 2 hours the pickling paste was rinsed off and the welded seam sprayed with a strong water jet. The welded seam was bright and clear, the oxide layer had
15 been completely removed and the base material was free from any visible attack by the pickle.

Claims

1. Aqueous pickling agent for special steels that is free of wetting agents and emulsifying agents and is based on sulphuric acid or phosphoric acid and hydrogen fluoride, characterised in that it contains (in each case in relation to 100 % by weight of substance)
1.5 to 16 % by weight sulphuric acid or
2.0 to 30 % by weight phosphoric acid
and also
0.5 to 14 % by weight hydrogen fluoride and
0.5 to 15.5 % by weight acid-soluble aromatic nitro compound,
to which no iron (III) compound is added and to which only in the initial phase an oxidizing agent oxidizing iron (II) to form iron (III) can be added.
2. Pickling agent according to claim 1, characterised in that, when applied as a pickling bath, it contains
5.0 to 11 % by weight sulphuric acid or
8.0 to 20 % by weight phosphoric acid
and also
4.0 to 10 % by weight hydrogen fluoride and
4.5 to 11 % by weight acid-soluble aromatic nitro compound.
3. Pickling agent according to claim 1, characterised in that, when used as a pickle that is applied by spraying or with a brush, it additionally contains
2.5 to 5.5 % by weight magnesium compound
(calculated as Mg).
4. Pickling agent according to claims 1 and 3, characterised in that, when used as a pickle that is applied by spraying, it contains
9.5 to 15.5 % by weight sulphuric acid or



15.0 to 30.0 % by weight phosphoric acid
and also

4.0 to 11.0 % by weight hydrogen fluoride,

4.5 to 11.5 % by weight acid-soluble aromatic

5 nitro compound and

2.5 to 4.5 % by weight magnesium compound

(calculated as Mg).

10 5. Pickling agent according to claims 1 and 3,
characterised in that, when used as a pickle that is
applied with a brush, it contains

12.0 to 16.0 % by weight sulphuric acid or

18.0 to 30.0 % by weight phosphoric acid

and also

15 4.5 to 12.0 % by weight hydrogen fluoride,

2.5 to 9.5 % by weight acid-soluble aromatic

nitro compound and

3.0 to 5.5 % by weight magnesium compound

(calculated as Mg).

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6. Pickling agent according to one or more of claims 1
to 5, characterised in that it contains m-
nitrobenzenesulphonate and/or 3-nitrophthalate as an
acid-soluble aromatic nitro compound.