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PROCESS OF ELECTROLYTICALLY PICKLING ALLOY STEELS

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The present invention relates to the cleaning of metallic surfaces, particularly to the removal of scale and deposits from the surface of alloy steels by an electrolytic pickling treatment.

It is known to subject the scaled workpieces to electrolytic pickling in order to remove scale and deposits from the surfaces of alloy steel. In the previously known processes the articles are arranged as an anode, cathode, or intermediate conductor in acid baths and are treated until scale-free surfaces have been obtained.

In the known processes the baths in which the workpieces are electrolytically treated consist of mineral acids such as sulfuric acid, hydrochloric acid, nitric acid, or of mixtures of such acids. Small amounts of hydrofluoric acid may be added to the bath.

According to other known processes the workpieces are alternatingly arranged as a cathode and as an anode in the electrolyte in which they are pickled and descaled.

In many of the known processes the electrolytic treatment is followed by an immersion treatment of the workpieces in nitric acid, or nitric acid and hydrofluoric acid, in order to brighten the electrolytically treated metal surfaces.

The known processes in which the electrolytic treatment of the metal pieces to be descaled and cleaned was effected in baths consisting of a mineral acid or of mixtures of mineral acids have a number of serious disadvantages. The most essential disadvantage resides in that the surfaces of the electrolytically treated articles are roughened because the acids do not only attack the scale and impurities but also the metallic surface itself.

To avoid these disadvantages it has already been proposed to carry out the electrolytic treatment for removing scale and deposit in baths which consist of aqueous solutions of neutral salts of mineral acids such as sulfuric acid, nitric acid, and hydrochloric acid. This known process also failed to give the desired results because a difficultly removable deposit remains on the workpieces after the electrolytic treatment and because the treatment times and current densities required are so long and high, respectively, that this process cannot be carried out economically.

It is an object of the present invention to provide a process for an electrolytic pickling treatment for removing scale and impurities from surfaces of workpieces of alloy steel, which process is free of the described disadvantages of the known processes.

More particularly, the present invention relates to a process of the type described, in which the articles to be pickled are arranged as an anode or as an intermediate conductor in electrolytic baths which consist essentially of aqueous solutions of at least one neutral salt of the alkalies, including ammonium, and of mineral salts, e.g., sulfuric, nitric and hydrochloric acids, particularly of aqueous solutions of neutral sodium sulfate or sodium nitrate, the pH of the electrolyte being permanently maintained preferably between 1.0 and 7.0, and in which the oxides which represent the scale to be removed, which have been loosened up or only chemically changed by such electrolytic treatment, are completely detached from the metallic surface by a short immersion treatment in a mineral acid such as sulfuric acid, nitric acid or a mixture of nitric acid and hydrofluoric acid following the electrolytic treatment.

In this way, pure metallic, bright, almost glossy surfaces are obtained. As contrasted with the known processes the surfaces are virtually not roughened to any appreciable extent.

It has also been found that the pickling bath used in the process according to the invention is self-regenerating under the action of the electric current. Whereas the exact nature of the mechanism taking place in the process according to the invention has not been entirely clarified, my thorough investigations suggest the following mechanism although the following explanation is given without engagement and not to be considered to constrict the invention.

During the electrolytic process, acid is formed at the anode and alkali is formed in an equivalent amount at the cathode. The pickling action of the acid formed at the anode causes the scale on the surface of the treated metal to enter into solution as a salt of the acid formed. From this salt the metal is precipitated as a hydroxide by the alkali formed at the cathode, whereby the neutral salt of the alkali and of the mineral acid is re-formed.

The presumable reaction mechanism will be explained hereinafter with reference to an example of carrying out the electrolytic pickling process of the invention using an aqueous solution of neutral sodium sulfate as an electrolyte.

TABLE I

Electrolyte: Aqueous solution of Na_2SO_4.

Process at the anode: Formation of H_2SO_4; Fe (and the alloying constituents of the steel such as Ni, Cr) is transformed into the sulfate.

Process at the cathode: Free Na is formed first, which forms NaOH with the H_2O present.

$$FeSO_4+2NaOH=Fe(OH)_2+Na_2SO_4$$

At the same time:

$$2Na_2SO_4+\tfrac{1}{2}O_2+H_2O=Na_2S_2O_8+2NaOH$$

It is seen that persulfate is formed during the electrolysis. This persulfate is believed to oxidize the primarily dissolved $FeSO_4$ to form $Fe_2(SO_4)_3$ so that $Fe(OH)_3$ rather than $Fe(OH)_2$ is precipitated during the process.

Thus, the process according to the invention has an additional advantage over the known processes. The per-compounds formed have a strong oxidizing activity. For this reason they passivate the steel articles treated and protect them from overpickling. As a result the steel itself is not attacked and the above-described advantage residing in the formation of satisfactory, almost glossy surfaces is obtained.

It is pointed out that the persulfate-forming reaction represented by the formula in Table 1 is an equilibrium reaction. For this reason care must be taken that the reaction does not only proceed from left to right, to form persulfate, because in this case the electrolyte would assume an undesired alkalinity owing to the increasing production of NaOH. This can be avoided by carrying out the electrolysis at elevated temperatures in a range in which a decomposition of the persulfate in the sense of the reverse reaction

$$Na_2S_2O_8+2NaOH=2Na_2SO_4+\tfrac{1}{2}O_2+H_2O$$

can be expected with certainty so that the required pH-range of 1.0–7.0 is maintained also in continuous operation.

It has also been found according to the invention that the formation of persulfuric acid in the electrolyte can be further promoted by adding small amounts of at least one compound of the class consisting of the fluorides,

chlorides, perchlorates, chromates, nitrites, sulfites, and nitrates.

The pH-value to be maintained according to the invention can be controlled, if desired, by an addition of small amounts of an acid, alkali or ammonium salt of a mineral acid, e.g., a bisulfate, or by an addition of small amounts of a free mineral acid.

The process according to the invention will be further explained more fully by the following examples.

Example 1

Using 200 grams technically pure Epsom salts (magnesium sulfate) per liter, pH 7.0, a satisfactory pickling of a ferritic material was obtained within ten seconds by an anodic treatment at 76° C. and 6.0 amperes per square decimeter. A 25-second dip in 10% nitric acid at 40° C. was employed for brightening and passivating.

Example 2

Using 165 grams technically pure Epsom salts per liter, pH 3.0, cathodic and anodic treatments at 25 seconds each at 85° C. and 9 amperes per square decimeter of austenitic strip material continuously fed as an intermediate conductor gave a loosely adherent scale, which had been entirely changed chemically and the major part of which was removed in the washing brush machine whereas the residue was easily detached in a usual mixed acid consisting of nitric acid and hydrofluoric acid. The surface of the strip was not only entirely free of scale and clean white but showed a fine silky gloss, which cannot be obtained by any chemical or electrolytic acid pickle .

Example 3

The same result was obtained on austenitic and ferritic materials when the Epsom salts were replaced by an equivalent amount of ammonium sulfate or potassium sulfate in processes analogous to Example 1 or 2.

Example 4

Using 200 grams Epsom salts+10 grams sodium fluoride, pH 3.0–7.0, cathodic and anodic treatments of 45 seconds each, at 90° C. and 10 amperes per square decimeter, of austenitic hot strip arranged as an intermediate conductor, caused the scale oxides to be sufficiently loosened up and to be chemically changed so that they dissolved spontaneously in the usual mixed acid. The surface was absolutely satisfactory microscopically and macroscopically.

Sodium fluoride was added to promote the formation of persulfates, or, at the anode, of persulfuric acid. As is apparent from the book by W. Machu, "Das Wasserstoffperoxyd und die Perverbindungen," Springer Verlag, 1951, page 134, fluorides, chlorides, perchlorates, and bichromates, which are per compound-forming agents, as well as reducing agents such as sulfite, bisulfite, or nitrite promote even in small quantities the formation of persulfates or of persulfuric acid, which is considered the effective pickling agent in the examples given. The amounts added are relatively so small, varying between 0.1 and 50 grams per liter, that they cannot be considered to intensify the pickling action at the anode to any significant degree.

Example 5

Using 250 grams common salt per liter at 90° C., alloy steels were satisfactorily pickled by a cathodic treatment of 10–40 seconds and an anodic treatment of 10–60 seconds at current densities of 3–10 amperes, depending on the degree of scaling. A subsequent immersion in HNO_3 or mixed acid brightens the treated surfaces. The chlorides of ammonium and potassium act like common salt. The precipitated iron hydroxide is green ferrous hydroxide.

Example 6

Using 200 grams ammonium chloride and 200 grams ammonium sulfate per liter, pH 3.0, the pickling is carried out as in Example 5 with the difference that brown ferric hydroxide is obtained. To avoid ammonia losses it is suitable to maintain the electrolyte at a weakly acid reaction between pH 1.0 and 4.0. This can be accomplished simply by a continual dropwise addition of sulfuric acid during the pickling operation.

It is apparent from the foregoing that another advantage of the process according to the invention resides in that the less acid medium of the pickling bath treated according to the invention facilitates the corrosion problem of the equipment. Further, the disposal of the effluent is obviously less critical where the process according to the invention is used than with the much more highly acid effluents obtained in the known processes.

It is also apparent from the foregoing explanations given in connection with the examples that the current densities and treatment times required according to the invention are much lower and shorter, respectively, than with the known processes of electrolytic pickling in solutions of free acid.

In view of the foregoing disclosure a number of changes, variations and modifications of the process described will be obvious to a man skilled in the art without departing from the invention. It is also apparent that the examples of the invention given hereinbefore are considered only to illustrate the invention and are not intended to restrict the invention except as defined in the following claims.

What I claim is:

1. Process for electrolytically pickling a stainless steel article which comprises the steps of subjecting said article as the anode to the action of a direct electric current in an electrolyte consisting essentially of an aqueous solution of at least one neutral salt selected from the group consisting of the chloride, sulfate and nitrate of an alkali metal including ammonium, at a current density between about 6 and about 10 amperes per square decimeter for a period of about 10 to 60 seconds, the pH of said electrolyte being maintained between 1.0 and 7.0, and then dipping said article in a solution of a mineral acid selected from the group consisting of sulfuric, nitric, and hydrofluoric acid, and mixtures of nitric and hydrofluoric acids.

2. The process of claim 1 in which the bath additionally contains from about 0.1 to about 50 grams per liter of a compound selected from the group consisting of an alkali metal fluoride, chloride, perchlorate, chromate, nitrite, sulfite and nitrate.

3. The process of claim 1 in which the temperature of the electrolyte is maintained between about 75° and about 90° C.

4. The process of claim 2 in which the added compound is sodium fluoride.

5. A process as set forth in claim 1, wherein the neutral alkali metal salt is neutral sodium nitrate.

6. A process as set forth in claim 1, wherein the neutral alkali metal salt is neutral sodium sulfate.

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