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METHOD OF ELECTROLYTICALLY DESCALING AND PICKLING STEEL

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3 Claims

ABSTRACT OF THE DISCLOSURE

Two-step process for descaling stainless steel surfaces. The steel article is first electrolytically descaled in an aqueous electrolyte containing at least 2% by weight of the sodium or potassium salt of sulfuric or nitric acid. The article is then pickled with an aqueous solution containing about 6.5–15% of ferric chloride and 5–10%, calculated as NO₃, of nitric acid or an inorganic nitrate. The electrolyte of the first step contains advantageously 0.1–10% of a soluble fluoride and less than 10% of a complex-salt forming substance, such as tartaric or citric acid.

The present invention relates to a novel process for descaling stainless steel surfaces by means of which the scales on the exposed surfaces of stainless steels of various kinds of shapes such as sheets and wires, may be removed very effectively.

Hitherto, as the means of removing the oxide scale formed in rolling, annealing and the like procedures of stainless steel, there has been employed a method which is a combination of an electrolytic treatment in a strong acid, such as nitric acid and sulfuric acid, etc., with an immersion treatment in a liquid mixture of nitric acid and hydrofluoric acid (hereinafter called nitric hydrofluoric acid). This prior art method is generally carried out in a continuous pickling apparatus used in the production of steel web, etc. In performing pickling procedures using strong acid, however, it is generally known that an expensive acid resistant installation has to be provided in conjunction with elaborate and expensive means for the treatment of waste gases and waste liquors because harmful waste gases such as nitrous gases and hydrogen fluoride gas are generated. Further, in the processing of the spent waste acid it must be considered that this waste acid still contains a large amount of free acid as well as acidic and soluble metal salts formed during the pickling. This is so although the pickling effect of the waste acid has been reduced to an extremely low degree. If the waste acid is discarded as such serious sanitation and pollution problems would arise.

It has previously been proposed by the applicants to replace the above-mentioned strong acids by neutral or weakly acidic salts which are safe to handle, and it was found that the descaling may be performed effectively and rapidly when the electrolytic treatment is effected while using an aqueous solution containing the sodium or potassium salt of sulfuric acid or of nitric acid as the solute and containing water-soluble fluorides, such as sodium fluoride, or a complex ion-forming agent such as tartaric acid and citric acid as the additive. Although it has been found that these processes have many advantages over the prior art methods, practice of these prior art processes dissolves the scale layer only but has little effect only on the surface of the metal substrate. In practice, however, it is preferred that the surface of the metal substrate should be dissolved to a slight extent so as to eliminate that various kinds of surface scratches formed

during the rolling. Accordingly it is desirable to impart to the solution such an effect that the surface of the metal substrate can be dissolved to an appropriate degree by means of the solution.

As another process of descaling stainless steel, applicants have further proposed a process which is characterized in that the stainless steel is immersed in, sprayed or applied with an aqueous solution which contains ferric chloride as the main component, to which a specific quantity of a nitric acid salt, such as ferric nitrate, or nitric acid proper is added and which has been adjusted to an appropriate pH value. This process has many advantages and characteristics in that the descaling may be achieved by using salts of weak acidity only and be effecting the scale removal by immersion only. However, the process has the disadvantage that the rate of dissolution of the scale layer in the solution of ferric chloride varies very much depending on the composition of the scale, although the solution of ferric chloride can attack the surface of the metal substrate and effectively dissolve the latter.

The present process is an improvement over the prior art processes referred to. The process according to the present invention is characterized in that, in a first step, the electrolytic treatment is effected by using an aqueous solution containing a neutral salt, such as the sodium and potassium salts of sulfuric acid or nitric acid as the main component while, in a second step, the stainless steel object is immersed in, sprayed with or otherwise contacted by, an aqueous solution containing ferric chloride as the main component. The descaling is mainly effected in the first step although only a neutral or weakly acidic salt, without resorting to a strong acid as in the prior art methods is used. The descaling is effectively and rapidly concluded in the second step by attack on the surface of the metal substrate from which the scale has been removed, and by dissolution of said surface to an appropriate degree in a manner of chemical abrasion.

Hereinafter, as an example of the present invention, a specific detailed embodiment is set forth as follows. As the stainless steel to be descaled, cold-rolled strips of 1.5 mm. thickness were employed as the test objects. The objects were divided into three groups A, B and C, of which group A was subjected to an electrolytic procedure in an aqueous solution containing sodium sulphate as solute (hereinafter called sodium sulphate electrolytic procedure). Group B was subjected to a pickling procedure in an aqueous solution containing ferric chloride as principal component together with a definite amount of ferric nitrate (hereinafter called ferric chloride pickling procedure). Group C was subjected to both the sodium sulphate electrolytic procedure and the ferric chloride pickling procedure successively for each half period of the total processing time, so as to descale the objects. The effects of these procedures were thereafter compared.

As for the processing conditions of the sodium sulphate electrolytic procedure, the electrolysis was conducted with a graphite plate as cathode and a stainless steel as anode, at an electrolyte concentration of 20% Na₂SO₄, at a bath temperature of 70° C. and with a current density of 7 a./dm.². In respect to the ferric chloride pickling procedure, the pickling was conducted by means of a solution containing ferric chloride corresponding to 8% FeCl₃ by weight of the solution and ferric nitrate corresponding to 5% NO₃ by weight of the solution. The solution was adjusted to a pH of 1 and heated to a temperature of 70° C.

The following conditions and effects were compared in respect to the three procedures. The time required for descaling, the loss of weight by dissolution, the roughness of the processed surface and the external appear-

ance. As shown in Table I listing the result, comparison of group A and B, which were treated by prior art procedures, with group C, indicates that the combined procedure of group C results in shorter descaling time and the resulting appearance is remarkably better.

TABLE I

Item	Group A (sodium sulphate electrolytic treatment only)	Group B (ferric chloride pickling treatment only)	Group C (sodium sulphate electrolysis followed by ferric chloride pickling treatment)
Descaling time (second)-----	90	80	60
Dissolution loss (g./cm. ²)-----	0.45	0.93	0.62
Resultant coarseness (μ)-----	0.6	1.7	0.8
Resultant appearance-----	(1)	(2)	(3)

¹ Smooth, but not brilliant.

² Slightly rough.

³ Smooth and polished.

As another example of the present invention, one more embodiment is set forth as follows. As the electrolyte in the sodium sulphate electrolytic procedure of the first step, there were employed a solution containing sodium sulphate and additionally 1% of sodium fluoride, and another solution containing said components together with 1% of tartaric acid heated at a temperature of 70° C., and with a current density of 7 a./cm.². Thereafter, as the second step, the pickling procedure was conducted with a solution containing ferric chloride corresponding to 8% FeCl₃ by weight and ferric nitrate corresponding to 5% NO₃ by weight. The solution was adjusted to a pH of 1 and heated to a temperature of 70° C.

The results according to this procedure were compared with the results obtained by the sole use of the first step only. It was found that the combined procedure is superior in respect to descaling time and resultant appearance.

As for the treatment conditions in the first step and the second step, the scope of conditions described in the said preceding applications gives satisfactory results. As the concentration of sodium sulphate or nitrate in the first step, a concentration of more than 2% thus gives satisfactory results. In respect to the additional soluble fluoride as accelerator, a concentration between 0.1% and 10% thereof is employed with success. With regard to the tartaric acid or citric acid, as complex-salt forming substance, a concentration of less than 10% is suitable.

As the solution employed in the second step, a solution containing ferric chloride of from 6.5% to 15% calculated as FeCl₃, together with nitric acid or nitrates, such as ferric nitrate and sodium nitrate, of from 5% to 10% calculated as NO₃ is employed with complete success.

The process of the present invention is thus characterized in that an electrolytic treatment is conducted with an aqueous solution containing more than 2% of

sodium or potassium sulphate or nitrate as solute together with one or more accelerators such as a soluble fluoride, of a concentration from 0.1% to 10% and a complex-salt forming substance such as tartaric acid or citric acid of a concentration of less than 10%. Thereafter a pickling treatment is effected by contacting the articles with a solution containing ferric chloride at a concentration between 6.5% and 15% calculated as FeCl₃ together with nitric acid or inorganic nitrate at a concentration between 5% and 10% calculated as NO₃, so as to carry out the removal of oxide scales on the surfaces of stainless steels. The descaling may thus be performed very effectively predominantly in the first step by means of a neutral or weakly acidic salt and without resorting to any strong acid as in the prior art methods. The exposed surface of the metal substrate is then dissolved directly and rapidly to an appropriate extent in the second step, so that the process of the present invention is very efficient and economical.

What is claimed is:

1. A two-step process of descaling stainless steel surfaces, comprising:

(1) subjecting, in a first step, a stainless steel article whose surfaces are to be descaled to an electrolytic treatment in an aqueous electrolyte containing at least 2% by weight of at least one of the sodium or potassium salts of sulfuric acid or nitric acid to remove the major amount of scale and from 0.1-10 percent by weight of a soluble fluoride, and

(2) hereafter, in a second step, pickling the steel article in an aqueous solution containing

(a) about 6.5-15% by weight of ferric chloride and and

(b) nitric acid or an inorganic nitrate of a concentration of about 5-10% by weight calculated as NO₃.

2. A process as claimed in claim 1, wherein the electrolyte of step (1) contains less than 10% by weight of a complex-salt forming substance.

3. A process as claimed in claim 2, wherein the complex-salt forming substance is tartaric acid or citric acid.

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