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PICKLING TREATMENT

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1 Claim. (Cl. 134—3)

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In the manufacture of stainless steel into wrought form the material must be rolled at high temperatures, followed by annealing, or normalizing, also at high temperatures, with the attendant formation of a surface film of oxide scale, which must be completely removed in order to render the stainless steel articles corrosion resistant and fit for general use.

My invention relates to the removal of scale from ferrous metals, particularly alloys of the type commonly referred to as "stainless steel," which contain iron, nickel, and chromium as essential ingredients, by a new type of pickling solution which retains its effectiveness during use, since it can be constantly controlled and regenerated and which also has a substantially negligible solvent action on the stainless steel base metal.

To the best of my knowledge, current practice in pickling the stainless steels includes two operations, the first known as the pre-pickling, followed by the second, which includes immersion in a final pickling bath. The pre-pickle usually consists of hot dilute sulphuric acid, or sulphuric acid plus sodium chloride, or sulphuric acid plus ferric sulphate. The function of this first step is to secure preliminary scale attack. The actual pickling, or scale removal, is accomplished in the final pickling bath, which usually consists of a hot solution of nitric, plus hydrofluoric acids.

This final pickle leaves a clean, white surface, but as currently practiced is accompanied by two undesirable features. First, the solution is highly corrosive to the stainless steel base metal, so that its use is accompanied by metal loss, which in the case of thin material such as sheets will constantly run in excess of one per cent. Secondly, the use of this solution results in the evolution of noxious, highly toxic fumes of hydrofluoric acid and nitrogen oxide vapors.

The use of ferric sulphate, plus hydrofluoric acid, has been tried for pickling stainless steel, but although its action is far superior to the nitric-hydrofluoric bath, it is not practicable, since up to the present time, no means have been offered for regenerating this bath, except through addition of increments of ferric sulphate, so that in a space of time far too uneconomical for practical purposes, the bath becomes saturated with iron salts. It is for this reason that this process could not be put into commercial practice.

My invention teaches the use of a soluble oxidizing agent as a regenerative means for control of the ferric sulphate-hydrofluoric acid pickling bath for stainless steel pickling. I have found

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that an oxidizing agent to be of a practical value must be:

1. Easily soluble in the pickling bath,
2. And capable of oxidizing ferrous iron to the ferric condition in hot acid solution, as well as
3. Form reaction products which are highly soluble in the pickling bath, and
4. Form reaction products which are not deleterious to the functional performance of the pickling bath.

In order to successfully utilize ferric sulphate-hydrofluoric baths for the pickling of stainless steel and which are highly desirable for this purpose due to the absence of noxious fumes and saving of valuable stainless steel due to absence of pickling loss, it is essential to accomplish their regeneration by the constant re-oxidation of the ferrous sulphate. The latter is constantly being formed as a decomposition product of the original ferric sulphate as a result of the pickling action of said ferric sulphate. This regeneration must usually be accompanied by adequate additions of hydrofluoric acid.

I have discovered that chlorates, perchlorates, persulphates and chlorites of the alkaline earth and alkali metals and ammonia, in general, offer adequate means for the re-oxidation of ferrous sulphate, although other oxidizing agents having the aforesaid characteristics may be used. The most efficient are the alkali metal compounds notably potassium chlorate. Thus, I have found that a pickling bath for stainless steel composed of effective amounts of ferric sulphate, and hydrofluoric acid to accomplish the pickling action, plus the addition of a suitable oxidizing agent, such as one of those mentioned above, more particularly potassium chlorate, serves to remove scale from stainless steel surfaces in a manner superior to that of any other form of pickling bath in use at the present time.

The following description of the operation of this bath will serve as an example of an embodiment of my invention.

A 35,000 gallon bath was prepared consisting of:

	By weight
Ferric sulphate.....	16.0
Hydrofluoric acid.....	3.0
Potassium chlorate.....	0.3
Balance—water	

and was heated to and maintained at 160°–170° F. Stainless steel sheets of the approximate composition 18-chrome, 8-nickel, balance-iron were pickled in the bath after a pre-pickle in a bath consisting of sulphuric acid, 4%, plus ferric sul-

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phate, 4%. All sheets were immersed in the pickling bath for ten minutes, the bath being constantly stirred by air agitation.

After 700 sheets, having a total surface area of 42,000 sq. ft., and weighing approximately 25,000 lbs., were pickled the bath analyzed as follows:

	Per cent
Ferrous sulphate.....	3.00
Ferric sulphate.....	12.1
Hydrofluoric acid.....	2.8

At this juncture, 20% of hydrofluoric acid was added, and the pickling was continued. However, after 100 additional sheets of the same lot were pickled it became apparent that the bath needed re-oxidizing, since the pickled surfaces, although still commercially satisfactory, were becoming duller in color and starting to show signs of the dulling corrosive action of ferrous sulphate and indicating that an appreciable amount of the latter was present.

In order to ascertain just where this critical point in ferrous iron concentration was, the bath was analyzed as follows:

	Per cent
Ferrous sulphate.....	5.40
Ferric sulphate.....	9.40
Hydrofluoric acid.....	2.91

At this point .3% (100 lbs.) potassium chlorate and .2% hydrofluoric acid were added, and the pickling was continued on a 24 hour basis, the sheets being pickled in racks of 20 sheets at a time, and, as a constant practice, .3% of potassium chlorate, plus .3% of hydrofluoric acid were added after every 35 lifts of 20 sheets each, i. e. after each lot of 700 sheets with a total surface area of 42,000 sq. ft. were pickled.

In this manner, a total of 14,000 sheets, averaging 3' x 10' in size, and weighing approximately 500,000 lbs. were pickled in 12 consecutive working days, or 288 hours.

The control analyses taken each lot of 700 sheets averaged as follows:

	Per cent
Ferrous sulphate.....	3.00
Ferric sulphate.....	12.15
Hydrofluoric acid.....	2.75

and each time at this stage, rectifying additions of .3% potassium chlorate, plus .3% hydrofluoric acid were added, and after each one of these additions the bath was analyzed and at this stage the average analysis of the bath was:

Ferrous sulphate.....	None
Ferric sulphate.....	per cent 16.5
Hydrofluoric acid.....	do 3.00

After a bath life of two weeks, which included 12 working days, the bath was discarded due to accumulation of floatant scale particles which had been removed from the surface of the sheets pickled. Examination of the bath at this point indicated the presence of approximately 7,000 lbs. of scale particles. Analysis of the discarded bath was as follows:

	Per cent
Ferric sulphate.....	16.6
Ferrous sulphate.....	6.8
Hydrofluoric acid.....	2.65
Potassium chloride.....	4.4

Thus, the same bath was maintained with the pickling constituents in effective amounts to carry out the pickling function and operated constantly for two weeks by means of the simple control consisting of regular additions of small increments of potassium chlorate and hydrofluoric acid.

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After the first addition of 16% $\text{Fe}_2(\text{SO}_4)_3$, no more was added, it being constantly regenerated by the KClO_3 additions.

My control system resolved itself into the simple procedure of the addition of .3% potassium chlorate and a .3% hydrofluoric acid for every 42,000 sq. ft. of surface pickled.

There may be instances where addition of hydrofluoric acid is not always necessary, but usually it is required along with the periodic addition of the oxidizing agent.

The present material cost for pickling by the nitric-hydrofluoric acid system is about \$.0019 per pound of steel pickled, and my process represents a saving of about 20% in pickling materials. However, additional advantages were noted incident to the operation of my bath, such as:

1. Elimination of the nitrogen oxide and hydrofluoric fumes.

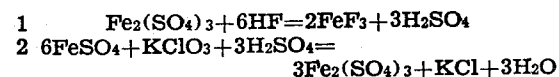
2. Virtual elimination of steel loss due to solution of the underlying metal into the bath.

By actual tests in picking 21 gauge stainless steel sheets of the 18-chrome, 8-nickel variety in the conventional nitric-hydrofluoric bath, a metal loss of 1.25% was encountered, while in tests run in the same manner in my bath, as described above, the actual metal loss was about .10%, this exceptionally low loss being attributable to the virtual absence of ferrous sulphate under operating conditions. Thus, a saving of 23 pounds of stainless steel per ton is effected through the use of my invention.

(Average value: $23 \times \$.30 = \$6.90$ per ton.)

It is generally agreed that the chemical reactions bringing about stainless steel pickling by means of ferric sulphate and hydrofluoric acid are not accurately known. However, it was found that due to the rapid build-up of ferrous sulphate as a reaction product of this pickling in the absence of an oxidizing agent as described herein, baths of ferric sulphate, plus hydrofluoric acid became vitiated and inoperative after six or eight hours' service under conditions identical with those maintained in the 288 hour run described above, except by addition of further $\text{Fe}_2(\text{SO}_4)_3$ as an attempt to regenerate. This latter expedient is impracticable because a limiting amount of added $\text{Fe}_2(\text{SO}_4)_3$ (7.00%) is soon reached.

The reaction in the pickling process of my invention may be described as follows:



in which it is most readily seen that the damaging reaction product of the pickling, viz. FeSO_4 is regenerated by the addition of KClO_3 back and converted to its original form: $\text{Fe}_2(\text{SO}_4)_3$.

The optimum ratio of ferric sulphate to hydrofluoric acid in the practice of my invention is from four to six. Potassium chlorate is the preferred re-energizing or oxidizing agent, and the proper amount of its addition to the bath when pickling stainless steel of the 18-chrome, 8-nickel variety is approximately from two to three pounds of potassium chlorate per 1,000 sq. ft. of stainless steel surface pickled.

Effective amounts of ferric sulphate ($\text{Fe}_2(\text{SO}_4)_3$) and hydrofluoric acid (HF) to satisfactorily accomplish the pickling function, of course, may vary dependent on the composition of the metal or alloy being treated and the condition and amount of the scale.

Generally, an aqueous bath containing about 10% to 20% of ferric sulphate and about 2.0%

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to 5.0% of hydrofluoric acid will be effective to suitably pickle the metal and from about a trace to 2.0% of oxidizing agent (the remainder being water) will be effective to maintain the ferric sulphate continuously in the effective pickling range and the ferrous sulphate present below an amount which would cause appreciable corrosion of the metal base surface.

I claim:

The process of pickling ferrous metal in an aqueous pickling bath consisting essentially of ferric sulfate and hydrofluoric acid comprising subjecting the ferrous metal to an aqueous pickling bath consisting essentially of from about 10 to 20% ferric sulfate and from about 2 to 5% hydrofluoric acid, and an oxidizing agent selected from the group consisting of chlorates, perchlorates, persulfates and chlorites of the alkaline earth and alkali metals and ammonia in amount of from a trace to about 2.0%, the bath having a temperature of about 160° to 170° F., said oxidizing agent continuously oxidizing fer-

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rous sulfate as formed in the bath in the pickling operation to ferric sulfate, and introducing additional oxidizing agent when the amount of ferrous sulfate present is active to appreciably corrode the metal, whereby the ferric sulfate is always maintained in effective amount of about 10 to 20%.

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