

UNITED STATES PATENT OFFICE.

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PICKLING FERROUS ARTICLES AND ELECTRICALLY REGENERATING THE PICKLING-BATH.

1,305,213.

Specification of Letters Patent.

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To all whom it may concern:

Be it known that I, ADDISON F. HOFFMAN, a citizen of the United States, residing at Pittsburgh, in the county of Allegheny and State of Pennsylvania, have invented new and useful Improvements in Pickling Ferrous Articles and Electrically Regenerating the Pickling-Bath, of which the following is a specification.

The invention of the present application relates to a pickling process and bath used therein, and particular reference to that type of processes in which the bath or pickle liquor, after being used for treating the iron or steel articles, or similar articles to be pickled, is revived by being subjected to an oxidation treatment, whereby the ferrous salts therein are either partially or entirely converted into ferric salts, as in my prior Patent 1,146,071.

In operating the process of my prior patent referred to, I have found that the oxidation of the ferrous salts to ferric salts is in some instances rather difficult, particularly when the liquor is rather strongly impregnated with ferrous compounds. I have, however, found that this objection can be overcome by electrolytically oxidizing the solution preferably in the presence of an oxygen-transferring catalyst, by the oxygen given off at the anode from which an electric current is passed through the liquor.

As the starting material for the bath for pickling iron and the like, I can employ either dilute sulfuric acid or dilute muriatic acid, or in some cases a solution of niter cake or other acid salt. The iron article is (according to one modification of the process) pickled in this solution in the usual manner, after which it is preferred to withdraw the pickle liquor, when the same has accumulated a considerable quantity of ferrous sulfate or other ferrous salts. The liquor is then subjected to electrolysis, whereby the oxygen given off at the anode acts as a powerful oxidizing agent, to oxidize ferrous compounds to ferric. This treatment may be effected in the presence of a manganese compound, or other compound capable of serving as an oxygenating catalyst.

In some instances it is not necessary to withdraw the waste pickle liquor from the pickling tank, but the liquor may be electrically treated in the tank in which the pickling operation is or has been carried out,

preferably with the addition of a catalyzing agent such as the manganese salts above referred to, the ferrous salt in solution being oxidized during such treatment by the nascent oxygen given off at the anode.

When oxidizing the liquor by electrolysis, in the presence of manganese compounds, I preferably stop the electrolysis some little time before drawing off the liquid from the bath, and in this manner, any manganese dioxid compounds precipitated (e. g. hydrated manganese dioxid, basic sulfate, etc.) will be redissolved by the liquor, replacing an equivalent amount of iron in the solution.

In the electrolytic treatment, there may be a considerable amount of the iron precipitated, thereby forming a valuable by-product.

In some instances the electric current may be so arranged as to not only regenerate the liquor, but also may be used to produce a pacifying effect upon the metal, this being accomplished by the generation and location of the hydrogen bubbles. This effect may be produced by connecting the articles to be cleaned, in the circuit, the iron article being made the cathode, and an insoluble anode being used. During this treatment, the pickling bath will preferably be agitated to prevent polarization. During this step, the nascent hydrogen will act, to some extent, to reduce the scale. This however in some instances is not to be recommended, on account of increased resistance and hence the use of considerably larger quantities of electricity. However, in some instances the loss of electricity is more than compensated for by the saving in acid.

In the step of oxidizing the ferrous to ferric salt, by electrolysis, it is preferable to maintain the solution at or near its boiling point, under which conditions a considerably larger quantity of ferric hydrate or partially hydrated ferric oxid will be precipitated than would occur at ordinary room temperature, perhaps since the free acid at ordinary room temperature is considerably more active in dissolving basic ferric hydrate, and basic ferric salts, than at or near the boiling point.

The pickling process is started with an acid liquor, but after the formation of ferric salts, the pickling is also in part effected by the chemical action of the said ferric salts. For this purpose, the solution, when in con-

