

UNITED STATES PATENT OFFICE.

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PICKLING PROCESS AND BATH.

1,269,443.

Specification of Letters Patent. Patented June 11, 1918.

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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 Processes and Baths, of which the following is a specification.

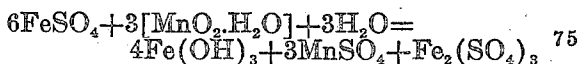
The present invention relates to a pickling process and bath used therein, and particular reference to that type of processes in which the bath or pickle liquor, after being used for treating the iron or steel articles, or similar articles to be pickled, is revived by being subjected to an oxidation 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 addition to the liquid of a suitable catalytic or other agent, of which class of bodies manganese compounds have been found to give excellent results in practice.

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 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. To this I add manganese dioxid or a salt of manganese such as manganese sulfate, or chlorid, and I then oxidize the liquor, which can be conveniently done as in my prior patent, namely by allowing the same to trickle down through a tower against a counter current of air or oxygen or other oxidizing gas. The manganese compounds can be added at any desired stage of the process. In some cases it is feasible to employ ozonized air for this step. The oxidation in many cases will convert a considerable portion of the ferrous salts in solution into ferric sulfate which when acted upon by heat in the presence of water is in part hydrolyzed, producing ferric hydroxid com-

pounds or perhaps basic ferric salts which are precipitated and can be removed from the bath before adding a further amount of sulfuric acid and bringing the same back into the pickling tank. In some instances the precipitated material may contain a considerable amount of the total amount of manganese compounds present, either manganese dioxid (hydrated) or compounds of this material or basic manganous compounds. Allowing the liquor to stand in contact with this, however, the manganese goes into solution again, precipitating a further quantity of iron from the liquor, in the form of iron hydroxid.

The following is one of the possible reactions, although other reactions much more complicated are involved:



In some instances it is not necessary to withdraw the waste pickle liquor from the pickling tank, but the liquor may be treated in the tank in which the pickling operation has been carried out, with the addition of a catalyzing agent such as the manganese salts above referred to, by oxidation, the ferrous salt in solution being oxidized.

In the oxidation of the solution by oxygen from any source, a considerable portion of the iron in solution may be precipitated, which by calcination yields an excellent variety of ferric oxid suitable for use as a pigment or polishing material.

In the step of oxidizing the ferrous to ferric salt, by the action of air or other oxidizing gas, 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 salt. For this purpose, the solution, when in contact with ferrous articles being pickled is preferably maintained at a temperature of about 100° C.

In this specification, and in the claims, I have referred to the use of "an oxygenating catalyst." This term is well understood in the art of catalysis to refer to such catalysts as promote reactions in which oxygen (such as free oxygen contained in air) is caused to react with other materials.

My experiments show that various compounds of manganese, besides the dioxid, such as the sulfate, chlorid or hydroxid, whether containing the manganese in the form of compounds of MnO or compounds MnO_2 , are suitable for the purpose.

What I claim is:

1. A process of pickling which comprises subjecting the article to be pickled to the action of a pickling solution and restoring the bath to an active condition by subjecting the same to oxidation by treating the same with an oxidizing agent in the presence of an oxygenating catalyst.

2. A process of pickling which comprises subjecting the article to be pickled to the action of a pickling solution and restoring the bath to an active condition by subjecting the same to oxidation by treating the same with an oxidizing agent in the presence of a manganese compound capable of serving as an oxygenating catalyst.

3. A process of pickling which comprises subjecting the article to be pickled to the action of a pickling solution containing a ferric salt and a free acid, and subsequently

restoring the bath to an active condition by subjecting the same to oxidation by treating the same with an oxidizing agent in the presence of an oxygenating catalyst.

4. The process which comprises pickling ferrous articles in an acid solution of a ferric salt, and regenerating the said solution by oxidation by treating the same with an oxidizing agent in the presence of a catalytically acting manganese compound.

5. A bath suitable for pickling ferrous metal articles, said bath comprising an acid solution of a ferric salt, containing an oxygenating catalyst.

6. A pickling bath comprising an aqueous vehicle containing sulfuric acid, ferric sulfate, and a manganese salt.

7. A process of pickling which comprises subjecting the article to be pickled to the action of a pickling solution and restoring the bath to an active condition by subjecting the same to oxidation in the presence of a catalyzer.

8. A process of pickling which comprises subjecting the article to be pickled to the action of a pickling solution and restoring the bath to an active condition by subjecting the same to oxidation by treating the same with an oxidizing agent in the presence of a catalyzer, while the solution is at a boiling temperature.

In testimony whereof I affix my signature.
ADDISON F. HOFFMAN.