Patented June 23, 1953

2,643,204

UNITED STATES PATENT OFFICE

2,643,204

NITRIC ACID PICKLING

Edgar B. Mancke, Bethlehem, Pa., assignor to Bethlehem Steel Company, a corporation of Pennsylvania

No Drawing. Application October 1, 1948, Serial No. 52,400

5 Claims. (Cl. 134—13)

1

My invention is directed to the pickling of ferrous materials by means of solutions containing nitric acid, and is particularly directed to methods for treating the pickle liquor after it has been used for pickling to remove greater or lesser amounts of iron and to regenerate nitric acid to render the liquor effective for further use as a pickle liquor.

In the pickling of iron and steel the most commonly used material is an aqueous solution of sulphuric acid. Nitric acid solutions are sometimes used as they have certain advantages over sulphuric acid solutions, but heretofore the commercial use of nitric acid solutions has been largely limited to the treatment of alloy steel as nitric acid is expensive in comparison with sulphuric acid and heretofore there has been no adequate process developed for regenerating the wholly or partly spent nitric acid pickling liquor.

In pickling iron and steel, whether it be sulphuric or nitric acid, the acid content of the liquors is being constantly reduced due primarily to the combination of the acid with iron. The acid also combines with other constituents of the steel, this being particularly true in the case of steels containing substantial amounts of alloying constituents, such as nickel and chromium. The efficiency of pickling solutions is reduced not only by the reduction in acid content of the solutions but the increasing amounts of compounds of other substances in the liquors have an inhibiting effect upon the acid which still remains in the solution so that the pickling liquor is rendered practically ineffective long before the acid content is completely exhausted. It is therefore obvious that the absence of an effective method of regenerating pickle liquors containing nitric acid has been a deterrent to more general use of nitric acid for pickling in view of it being an expensive chemical in comparison with sulphuric acid.

I have discovered a method whereby nitric acid may be effectively and economically used in pickling iron and steel. I use a solution of nitric acid to pickle the iron or steel and then submit the solution which has been used for pickling to a temperature comparatively high above the boiling point of water to precipitate iron from the solution and to regenerate the nitric acid thus to restore the activity of the solution for further pickling.

I shall now illustrate my invention by means of a specific example. Hot rolled sheet or ordinary carbon steel, with scale upon its surface, is pickled with an aqueous solution of nitric acid, having an acid content of 10%, until the acid

2

content is reduced to 5% and the solution contains substantial amounts of ferric nitrate. This liquor is then heated to 400° F. under pressure in an autoclave which causes the precipitation of over 80% of the iron with a corresponding regeneration of the nitric acid which has been consumed in forming ferric nitrate. The solution, thus regenerated is then reused for pickling more sheet steel.

The iron precipitated from the pickling solution is in the form of ferric oxide possibly somewhat hydrated and is free from any considerable amounts of impurity except when the liquor has been used in pickling certain high alloy steels or irons and is suitable for use as high grade ore after agglomeration, or for the manufacture of sponge iron, or as a paint pigment.

It is to be understood that the application of my invention is not limited to the specicfic details given above as an illustration of my process. The pickling liquor may be of a considerably wide range of content of nitric acid, the particular content depending more or less upon the kind of iron or steel being pickled and the character of the scale upon its surface. Other pickling agents may be present in the pickling bath in addition to the nitric acid, such for example, as a small amount of hydrofluoric acid which is frequently found to be useful when pickling stainless steel.

The temperature to which the used pickle liquor is to be heated to precipitate iron can vary considerably. For effective use in actual practice it must be considerably above the boiling point of water and usually it is important to employ a temperature not lower than 340° F. The temperatures higher than 340° F. are preferable as I have discovered that the speed with which the iron is precipitated increases with rise in temperature.

I claim:

1. In a process for treating a used nitric acid pickling solution containing ferric nitrate and a substantial amount of free nitric acid, the step of autoclaving the solution at a temperature of not less than 340° F. to produce an insoluble ferric compound and to form and retain free nitric acid in said solution.

2. In a process for treating a used nitric acid pickling solution containing ferric nitrate and a substantial amount of free nitric acid, the step of autoclaving the solution at a temperature of approximately 400° F. to produce an insoluble ferric compound and to form and retain free nitric acid in said solution.

3. In a process of pickling ferrous bodies with

a solution containing nitric acid, the steps of autoclaving the solution after it has been used for pickling ferrous bodies but while it still contains a substantial amount of free nitric acid and contains ferric nitrate at a temperature at least as high as 340° F. to produce an insoluble ferric compound and to form and retain free nitric acid in said solution, and using the solution thus treated to pickle ferrous bodies.

4. In a process of pickling ferrous bodies with a solution containing nitric acid, the steps of autoclaving the solution after it has been used for pickling ferrous bodies but while it still contains a substantial amount of free nitric acid and contains ferric nitrate at a temperature of approximately 400° F. to produce an insoluble ferric compound and to form and retain free nitric acid in said solution, and using the solution thus treated to pickle ferrous bodies.

5. A process for treating an aqueous solution containing a substantial amount of free nitric acid and ferric nitrate, comprising the step of autoclaving the solution at a temperature of not less than 340° F. to produce iron in an insoluble oxide form and to form and retain free nitric acid in said solution.

EDGAR B. MANCKE.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,146,071	Hoffman	July 13, 1915
1,428,521	Bacon	Sept. 12, 1922
1,503,229	Clark	July 29, 1924
1,649,152	Clark	Nov. 15, 1927
2,196,584	Edison	Apr. 9, 1940
2,330,553	Butler	Sept. 28, 1943
2,344,004	Six	Mar. 14, 1944

OTHER REFERENCES

Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," vol. 13, pages 782, 852 (1934); vol. 14, pages 378, 381, 384 (1935) Longmans, Green and Co., N. Y. C.