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PROCESS FOR PICKLING IRON, STEEL AND ALLOYS THEREOF

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Fig.1

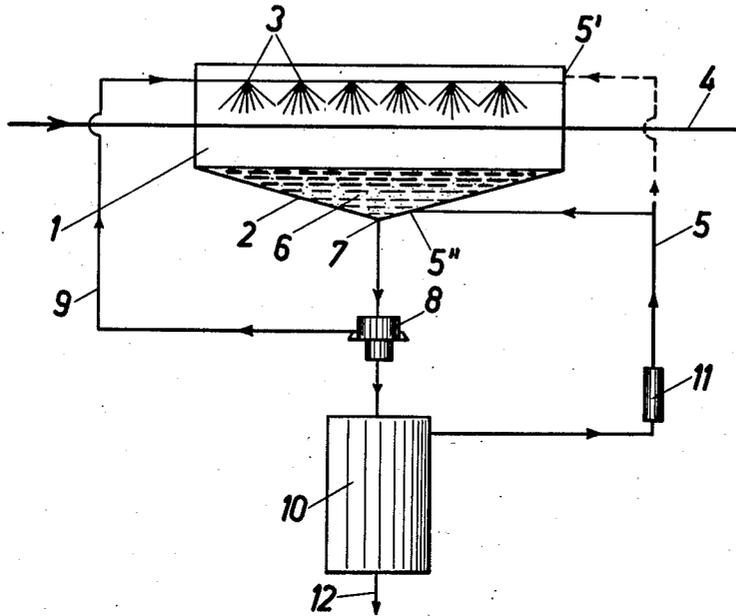
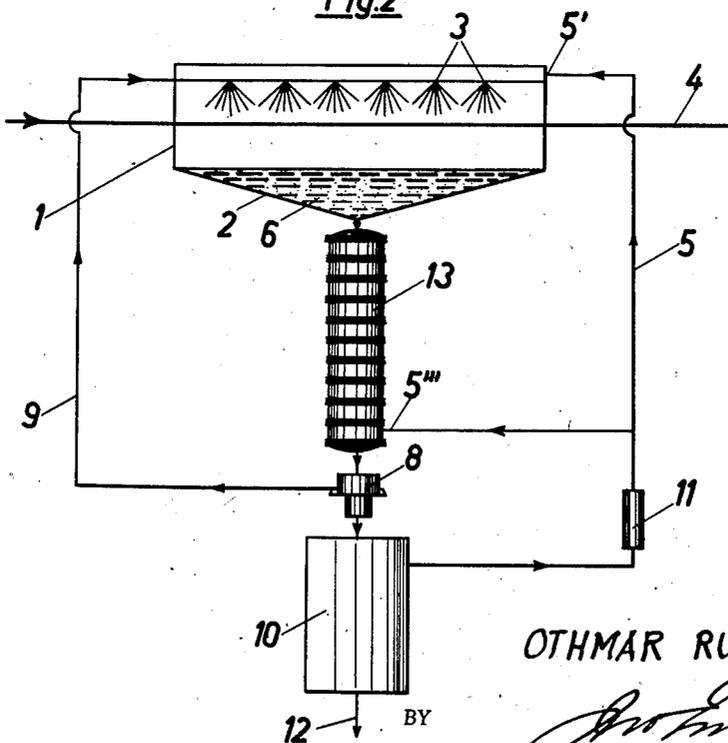


Fig.2



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## PROCESS FOR PICKLING IRON, STEEL AND ALLOYS THEREOF

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Claims priority, application Austria February 16, 1953

15 Claims. (Cl. 134—13)

The present invention relates to the pickling of iron and steel or alloys thereof, and specifically to an improved process for pickling with simultaneous reclamation of the pickling acid.

The increasing industrialization of cold-working plants places increasing requirements upon the pickling plants. Regenerating the spent pickling liquors can no longer be dispensed with today because the provisions governing the purity of industrial sewage no longer tolerate the disposal of the exhausted pickling acid. Various suggestions have been made for the utilization and processing of the pickling acids obtained but said suggestions were governed rather by the regulations on industrial sewage than by technological and economical considerations. The usual procedure was to evaporate the pickling liquor, to roast the depositing iron sulfate crystals, and, if desired, to attempt a reclamation of the gases from roasting.

All known processes are subject to a substantial restriction because the pickling and the regeneration of the pickling acid constitute two operations which are entirely separate from one another. Moreover, a number of additional steps, viz., evaporating, crystallizing, roasting of crystals, etc., must be performed between these two operations. Though that technique has been introduced and is widely used commercially, it is nevertheless unsatisfactory and there is a desire for an improved process, which is simpler from the technological aspect, and more economical.

The main object of the present invention resides in the provision of an improved process for pickling iron, steel or alloys thereof and reclaiming the pickling acid, which process is not subject to the restrictions and disadvantages of the known processes, and in the provision of apparatus to carry out the improved process.

Another object of the invention resides in the provision of a certain composition and certain concentration of the pickling acid and the pickling medium.

Another important object of the invention resides in the continuous operation of the process, by combining the pickling with the regeneration of the pickling acid, all chemicals charged being retained and only the rust or scale introduced into the process being discharged therefrom in the form of oxide of iron.

Further objects of the invention are: To provide apparatus for the continuous operation of the process for pickling and simultaneously reclaiming the pickling acid; to provide a pickling chamber with means for supplying the pickling acid and means for introducing gaseous pickling agents; to provide means for collecting and purifying the pickling liquor, means for separating the pickling liquor from precipitated crystals; to provide a reaction furnace for decomposing the crystals, and to provide means to connect the several parts of the plant.

The above and further objects and the novel features of the invention are apparent from the following description with the accompanying drawing, in which Fig. 1 and Fig. 2 schematically represent two typical arrangements

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of the several steps of the process and construction of the apparatus used.

Essentially the improved process for the pickling of iron, steel or alloys thereof and simultaneous reclamation of the pickling acid resides in the fact that the component steps of the process, to be described in detail hereinafter, are arranged in a novel sequence. As the first component step of the process the material to be pickled, covered with rust or scale, is pickled in a closed pickling chamber by the simultaneous application of liquid sulfuric acid and hydrogen chloride gas. By the action of that combined pickling medium  $\text{FeSO}_4$  and  $\text{FeCl}_2$  are formed beside each other, and dissolve in the pickling liquor. In the pickling chamber an atmosphere is provided which contains HCl so that HCl too is taken up and dissolved in the pickling liquor. It is an essential feature of the process according to the invention that in the first stage of that process more  $\text{Cl}^-$  ions are taken up by the pickling liquor than would correspond stoichiometrically to the  $\text{FeCl}_2$ . According to the law of mass action the solubility product

$$L = [\text{Fe}^{++}] \times [\text{Cl}^-]^2$$

can be influenced by an excess of  $\text{Cl}^-$  ions so that the solubility product is exceeded,  $\text{FeCl}_2$  becoming insoluble and crystallizing out. In the first step of the process of the invention that reaction pattern is worked at and achieved. Whereas under normal conditions of pickling, without an excess of  $\text{Cl}^-$  ions,  $\text{FeSO}_4$  is more difficultly soluble than  $\text{FeCl}_2$  and for this reason crystallizes out earlier, the relations are reversed according to the invention in the case of an excess of  $\text{Cl}^-$  ions in the pickling liquor: From a solution containing beside each other  $\text{Fe}^{++}$ ,  $\text{SO}_4^{--}$ , and  $\text{Cl}^-$  ions, ferrous chloride  $\text{FeCl}_2$  is crystallized out when the solution is supersaturated with HCl.

To carry out that first step of the process according to the invention it is not only necessary to have an excess of  $\text{Cl}^-$  ions, but a certain concentration of sulfuric acid must not be exceeded. It has been found that at room temperature the concentration of sulfuric acid should not exceed 40%  $\text{H}_2\text{SO}_4$ . With a higher content of sulfuric acid, the pickling liquor cannot dissolve enough  $\text{Cl}^-$  ions to influence the solubility of the  $\text{FeCl}_2$  in the desired sense.

Moreover, it was found that the process can be carried out most suitably with a certain concentration of iron in the pickling liquor. When the proportion of



the iron in solution precipitates quantitatively as ferrous chloride. Expressed in grams per liter, a concentration of about 70 grams per liter is preferred. The adjustment of the concentration to the desired range can be effected very simply by an analytical control of the progress of the reaction. Moreover, it has been found that a certain concentration of HCl is preferable in the gas space. Expressed in parts by volume, that preferred ratio of air: HCl is smaller than 4:1. Hence all mixtures from pure hydrogen chloride gas to a mixture of HCl with four times its volume of air can be used as gas atmosphere in the pickling chamber.

After the combined pickling medium described has acted on the material to be pickled, in the first stage of the process, the pickling liquor is supersaturated with HCl in the next step. That second step of the process cannot be separated from the first chronologically because often the supersaturation of the solution occurs simultaneously with the pickling step. The supersaturation with HCl may be effected either directly in the pickling chamber, or in a reaction vessel which is arranged directly behind the pickling chamber and into which additional HCl is fed.  $\text{FeCl}_2$  is crystallized out of the supersaturated solution and is subsequently separated from the pickling acid.

The next stage of the process relates to the separation of

the precipitated ferrous chloride crystals from the pickling acid poor in iron. That separation may be effected in any desired apparatus known for that purpose. A centrifuge is preferred. It has been found that the performance of that step is improved when during the operation a gas atmosphere having a certain HCl content is maintained. A certain concentration of HCl is not essential. The HCl content of the atmosphere during that step prevents a reverse reaction forming  $\text{FeSO}_4$  from  $\text{FeCl}_2$  and  $\text{H}_2\text{SO}_4$ .

To avoid losses of sulfuric acid in that stage of the process, the separated ferrous chloride crystals are preferably washed with concentrated hydrochloric acid. The pickling acid freed from the crystals may be used again for pickling, if desired, and where the process is operated continuously it can be recycled to the pickling chamber. The hydrochloric acid used to wash the ferrous chloride crystals may also be returned to the pickling process.

In the process step following the separation of the  $\text{FeCl}_2$  crystals the same are decomposed thermally to form oxide of iron and HCl. That decomposition may be performed in a manner known per se in a furnace at a temperature of about 400–600 deg. C. The oxide of iron formed is discharged from the process. The reclaimed hydrogen chloride can be fed to the pickling chamber after being cooled, to form again a combined pickling medium in conjunction with sulfuric acid. Part of the HCl reclaimed may be used to form hydrochloric acid, which in the third step of the process serves as a washing liquid for the  $\text{FeCl}_2$  crystals precipitated from the supersaturated pickling acid.

The process according to the invention described may be modified to advantage, either in its individual steps or as a whole.

It has been found that an acceleration of the pickling process can be achieved when in the first stage the hydrogen chloride is introduced into the pickling chamber under a certain superatmospheric pressure. In that case the capacity of the pickling acid is increased and the saturation with HCl is accomplished more effectively.

With reference to the drawing Figs. 1 and 2 represent arrangements for the continuous operation of the process according to the invention.

1 designates a closed pickling chamber with a downwardly tapering conical bottom 2. The upper part of the chamber is provided with injection nozzles 3, by which pickling acid is sprayed onto the material 4 to be pickled. The gas supply line 5 opens into the pickling chamber with two inlets 5' and 5'', through which hydrogen chloride is blown in. The pickling acid trickles over the material to be pickled, dissolves the oxides of iron present in the form of scale and rust, and at the same time is loaded with hydrogen chloride. It collects in the conical bottom of the lower part of the pickling chamber and is supersaturated by the hydrogen chloride entering at 5''. In the lower part of the container a pulp 6 is formed, which consists of pickling acid and crystalline ferrous chloride. That pulp is drawn off into the centrifuge 8 through the bottom outlet 7. In the centrifuge the crystals are separated from the liquid components. The reclaimed pickling acid is returned to the pickling chamber through line 9 and, after having water added thereto, if necessary, is again sprayed into the pickling chamber 1 through the injection nozzles 3.

The ferrous chloride separated in the centrifuge 8 is introduced into the oxide furnace 10 and decomposed into oxide of iron and HCl by heating. The HCl is returned into the pickling chamber after passing through the cooler 11. All reactants being retained, only FeO is discharged from the plant at 12.

Fig. 2 shows an embodiment of a continuous process, which is modified as compared with the arrangement described (Fig. 1). According to Fig. 2 the conical bottom 2 of the reaction vessel 1 passes over into a reaction column 13, into the lower part of which the gas supply

line 5''' discharges. The pickling chamber 1 has only one gas supply line 5' to introduce hydrogen chloride.

The procedure in the process according to Fig. 2 has considerable similarity with that according to Fig. 1. A difference merely resides in the fact that the saturation of the pickling acid with hydrogen chloride is effected not in the pickling chamber, but in the reaction vessel 13, where also  $\text{FeCl}_2$  crystals are obtained. The longer path for the reaction of the acid trickling down in a countercurrent with the rising hydrogen chloride affords advantages. If desired, the upper supply line 5' can be shut off or eliminated entirely and in this case the reaction of the hydrogen chloride gas with the pickling acid and the dissolved iron salts substantially takes place only in the liquid phase and only the excess hydrogen chloride which has not been absorbed by the pickling acid enters the gas space.

The method of working described enables the pickling and regeneration to be carried out within shorter time and at lower temperature than with the known methods. The apparatus requires lower installation costs and less space. Moreover, the process enables substantial economies as regards the expenditure of energy.

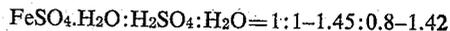
I claim:

1. A process for the pickling of iron and steel or alloys thereof, and for reclaiming the pickling acid, which comprises the successive steps: pickling the metal articles with a pickling medium consisting of liquid sulfuric acid and gaseous HCl in a closed pickling chamber, supersaturating the pickling liquor with HCl to precipitate  $\text{FeCl}_2$  crystals, separating the precipitated crystals from the pickling acid, and finally heating the separated crystals to decompose them into oxide of iron and HCl.

2. A process as set forth in claim 1, in which the concentration of the sulfuric acid at room temperature is less than 40%  $\text{H}_2\text{SO}_4$ .

3. A process for the pickling of iron and steel or alloys thereof, and for reclaiming the pickling acid, which comprises the successive steps: pickling the metal articles with a pickling medium consisting of liquid sulfuric acid and gaseous HCl in a closed pickling chamber until a concentration of about 70 grams Fe per liter has been reached, supersaturating the pickling liquor with HCl to precipitate  $\text{FeCl}_2$  crystals, separating the precipitated crystals from the pickling acid, and finally heating the separated crystals to decompose them into oxide of iron and HCl.

4. A process for the pickling of iron and steel or alloys thereof, and for reclaiming the pickling acid, which comprises the successive steps: pickling the metal articles with a pickling medium consisting of liquid sulfuric acid and gaseous HCl in a closed pickling chamber until a composition of the pickling acid has been reached which corresponds to the proportion



supersaturating the pickling liquor with HCl to precipitate  $\text{FeCl}_2$  crystals, separating the precipitated crystals from the pickling acid, and finally heating the separated crystals to decompose them into oxide of iron and HCl.

5. A process for the pickling of iron and steel or alloys thereof, and for reclaiming the pickling acid, which comprises the successive steps: pickling the metal articles with a pickling medium consisting of liquid sulfuric acid and gaseous HCl in a closed pickling chamber, the pickling acid being injected through injection nozzles in the upper part of the pickling chamber and conducted over the material to be pickled, and hydrogen chloride gas being introduced into the pickling chamber at the same time to precipitate  $\text{FeCl}_2$  crystals, separating the precipitated crystals from the pickling acid, and finally heating the separated crystals to decompose them into oxide of iron and HCl.

6. A process as set forth in claim 5, in which HCl is introduced into the lower part of the pickling chamber

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as well as through the bottom of the pickling chamber.

7. A process as claimed in claim 5 in which HCl is introduced in the upper part of the pickling chamber and through a reaction vessel connected to the bottom of the pickling chamber.

8. A process as claimed in claim 5, in which HCl is introduced under pressure.

9. A process for the pickling of iron and steel or alloys thereof, and for reclaiming the pickling acid, which comprises the successive steps: pickling the metal articles with a pickling medium consisting of liquid sulfuric acid and gaseous HCl in a closed pickling chamber, supersaturating the pickling liquor with HCl to precipitate FeCl<sub>2</sub> crystals, separating the precipitated crystals from the pickling acid below an atmosphere having a certain HCl content, and finally heating the separated crystals to decompose them into oxide of iron and HCl.

10. A process for the pickling of iron and steel or alloys thereof, and for reclaiming the pickling acid, which comprises the successive steps: pickling the metal articles with a pickling medium consisting of liquid sulfuric acid and gaseous HCl in a closed pickling chamber, supersaturating the pickling liquor with HCl to precipitate FeCl<sub>2</sub> crystals, separating the precipitated crystals from the pickling acid, washing the separated crystals with concentrated hydrochloric acid, and finally heating the separated crystals to decompose them into oxide of iron and HCl.

11. A continuous process for the pickling of iron and steel or alloys thereof, and for reclaiming the pickling acid, which comprises the successive steps: pickling the metal articles with a pickling medium consisting of liquid sulfuric acid and gaseous HCl in a closed pickling chamber, supersaturating the pickling liquor with HCl to precipitate FeCl<sub>2</sub> crystals, separating the precipitated crystals from the pickling acid, returning the pickling acid poor in iron into the pickling chamber, heating the separated crystals to decompose them into oxide of iron

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and HCl, cooling said HCl, and finally returning said HCl to the pickling chamber for re-use as a constituent of the pickling medium.

12. A continuous process for the pickling of iron and steel or alloys thereof, and for reclaiming the pickling acid, which comprises the successive steps: pickling the metal articles with a pickling medium consisting of liquid sulfuric acid and gaseous HCl in a closed pickling chamber, until a composition of the pickling acid has been reached which corresponds to the proportion



supersaturating the pickling liquor with HCl to precipitate FeCl<sub>2</sub> crystals, separating the precipitated crystals from the pickling acid, returning the pickling acid poor in iron into the pickling chamber, heating the separated crystals to decompose them into oxide of iron and HCl, cooling said HCl, and finally returning said HCl to the pickling chamber for re-use as a constituent of the pickling medium.

13. In the cleaning of ferrous metals and their alloys in a pickling bath of sulfuric acid solution, the process of maintaining the pickling acid in an atmosphere of gaseous HCl during cleaning of the metal and supersaturating the sulfuric acid solution with HCl to precipitate FeCl<sub>2</sub> crystals separating the crystals from the solution and decomposing them into iron oxide and HCl.

14. A process for pickling ferrous metals and their alloys which comprises immersing the metal articles to be pickled in a sulfuric acid bath maintained in an atmosphere of gaseous HCl, supersaturating the acid bath with HCl during pickling to precipitate FeCl<sub>2</sub> crystals from the bath and maintain the strength of the sulfuric acid in the bath.

15. The process of claim 14 wherein the maximum concentration of sulfuric acid at room temperature is 40%.

No references cited.