UNITED STATES PATENT OFFICE.

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PICKLING-BATH AND METHOD OF MAKING THE SAME.

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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 certain new and useful Improvements in Pickling-Baths and Methods of Making the Same, of which the following is a specification.

This invention relates to pickling baths and methods of making the same and utilizing the waste contents thereof, pertaining more particularly to baths adapted to pickle iron and steel, although the bath may be employed for the treatment of copper materials.

Pickling baths heretofore commonly employed have generally consisted of a solution of sulfuric acid (H_2SO_4) or hydro-chloric or muriatic acid (HCl).

In the sulfuric acid bath, the action is principally by dissolving the metal back of the scale or oxid films which form over the metal, causing the scale or film to fall off. Some of the scale is also dissolved by the hot sulfuric acid solution producing ferric sulfate which also has a pickling value, one-third of its acid radical being still available for pickling purposes. The action on the oxid scale is not, however, as active as where muriatic acid solution or one of acid sodium sulfate ($NaHSO_4$) is used, the latter having, in some instances, been used for pickling purposes. The reactions with a sulfuric acid pickling solution are substantially as follows:

$$Fe+H_2SO_4=FeSO_4+H_2;$$

$$Fe_2O_3+3H_2SO_4=Fe_2(SO_4)_3+3H_2O;$$

and

$$Fe_2(SO_4)_3+Fe=3FeSO_4.$$

Where this solution is used in connection with thin plates and light gages of wire, a damaging action thereon frequently occurs, sometimes causing these articles to be eaten through where the pickling is in a strong solution, and especially so when the solution is worked hot, the general operation where speed in the pickling vat is desired. For this and other reasons, among which is the question of economy, the use of strong sulfuric acid solutions for pickling purposes is decreasing at the present day excepting where the material is heavily incrusted with oxids.

The muriatic acid bath is more generally used, it acting somewhat differently in the pickling operation, tending more to dissolve the scale or oxid, and dissolving a very much less amount of metal than the sulfuric bath, producing an increase in finished material output, with a surface condition of the metal equally satisfactory. One of the reasons for this more extensive use is the lower cost of the acid, it being possible to produce it at very low prices.

The use of acid sodium sulfate has also been contemplated, this being the by-product from the manufacture of sulfuric and nitric acids. It has an action somewhat similar to the muriatic acid and has several advantages over the use of sulfuric acid.

The present practice in connection with pickling baths is to discharge the spent waste liquor from the bath into streams or on to the ground where it may reach streams, the result being that the stream is contaminated, making it injurious not only to fish life, but detrimental to human beings; in addition, it causes an enormous industrial damage. This fact has led to attempts to prevent such stream contamination.

While it is possible to reclaim some of the elements of the liquor in the form of by-products, these attempts have not had material application through various causes, among which is the cost of the operation. The extensive demand for sulfate of iron or copperas ($FeSO_4$), a component of the waste liquor of sulfuric acid baths and which enables the liquor to be utilized in the production of this sulfate, tends to reduce the effects of stream contamination by this form of waste liquor, but the increase in the use of pickling solutions in recent years has more than offset the demand for the sulfate, so that an excess of the liquor has been produced, which excess still provides such source of contamination.

The present invention aims more particularly to eliminate these difficulties by the formation of a pickling solution which is not only more effective than either of the baths referred to, but, in addition, is of relatively lower cost and is renewable, thus eliminating the presence of spent or waste liquor, the bath providing a removable precipitate.

The remaining solution is retained in active condition by the addition of the compounds from which the bath is formed. The precipitate can be treated to produce the acids, thus reclaiming elements which enter into the bath formation. The cost of operation when the pickling solution of the present invention is employed is greatly reduced, approximating one-half the cost under present methods, and where the reclamation is had, the cost of the entire operation is approximately one-fourth to one-third of the cost where the sulfuric acid bath is employed.

The solution forming the bath of the present invention is provided by running into the pickling tank or vat a concentrated solution of salt water, either hot or cold, from one tank, and sulfuric acid from another tank. The chemical reaction which takes place in the pickling tank due to the union of these two compounds is as follows:

$$NaCl+H_2SO_4=NaHSO_4+HCl,$$

these substances being employed in the proportion of their molecular weights, the supply being controlled by means of valves, the quantity of each required being dependent upon the strength of the solution, the quantity of metal pickled, and the quantity of each required to satisfy the chemical equations. Salt could be added to the sulfuric acid solution, but salt water has several advantages. This results in the formation of a solution of acid sodium sulfate and hydrochloric acid, each of which is capable of independent use as a pickling solution, the solution formed being one which is a combination of these independent pickling solutions, causing the bath to be more active than with either separately, and obviating the production of poisonous hydrogen gas. H_2SO_4 may also be used in excess.

The muriatic or hydrochloric acid produced by this reaction, in the presence of an abundance of water, remains in solution instead of being driven off as would be the case where the sulfuric acid was poured upon salt. The acid sodium sulfate also remains in solution.

The bath works best when boiling hot. When the pickling operation takes place in connection with iron or steel, the following approximate reactions occur:

$$Fe_2O_3+6NaHSO_4=Fe_2(SO_4)_3+3Na_2SO_4+3H_2O;$$

$$Fe+Fe_2(SO_4)_3=3FeSO_4;$$

and

$$Fe_2O_3+Fe+6HCl=3FeCl_2+3H_2O.$$

These reactions are only illustrative, as the scale on iron and steel is not strictly ferric oxid (Fe_2O_3) but a combination of this with the protoxid (FeO) and the ferroso-ferric oxid (Fe_3O_4) in variant proportions; to show the complete effect, the chemical equations would have to be adjusted to suit the other oxids.

The effect of this bath, in practice, is however, to clean the metallic surface free from scale completely, rapidly, and economically, dissolving only about one-third of the quantity of metal dissolved by a sulfuric acid pickling solution, and is considerably more profitable.

The quantity of pickling liquor formed is under direct control, so that the bath can always be kept of the desired strength. The water required to replace that evaporated can be supplied through the salt solution or by blowing steam into the vat, the latter also keeping up the heat. The greater part of the heat, however, is supplied through the hot material pickled.

The chlorid of iron (ferrous chlorid—$FeCl_2$), the sulfate of iron (ferrous sulfate—$FeSO_4$), and the sulfate of soda (sodium sulfate—Na_2SO_4) which are produced as a result of the reactions, precipitate to the bottom of the tank, probably partly as double salts, when the solution becomes sufficiently concentrated, forming a cake which can be readily removed when desired by means of a suitable rake.

It is not necessary to discharge this pickling solution at intervals, but only to keep it hot, add the necessary chemicals and remove the crystalline mass from the bottom of the tank at intervals, the solution not becoming spent but remaining active for pickling purposes by this treatment.

The crystalline waste thus produced can be treated to form a stimulant fertilizer, gas purifying material, pigment, or be sold as a weed killer.

This waste can also be treated to provide a regenerative action in the production of acids for use in the bath, thus reducing the cost of operation. This action may be provided by a heating or roasting action, employing a retort and a heat ranging from 700° to 900° C., the retort having pipe connection with the pickling tank or a separate tank containing water. Under the heating action, the crystalline waste is separated into oxids and gases, the approximate reactions being as follows:

$$2Na_2SO_4 \leftarrow 2Na_2O \leftarrow \begin{matrix} SO_3 \\ SO_2 \end{matrix}$$

$$2FeSO_4 \leftarrow Fe_2O_3 \leftarrow \begin{matrix} SO_3 \\ SO_2 \end{matrix}$$

$$2FeCl_2 \leftarrow Fe_2O_3 — Cl_4$$

The gases, upon reaching the water of the pickling tank or separate tank, form sulfuric and hydrochloric acids, both of which may be used in the formation of the liquor. The somewhat refractory sulfate of soda can be

decomposed in the retort at comparatively low temperatures by the addition of a little sand or other form of silicate.

In this manner, more than half of the acids can be recovered for further use, thus reducing the amount of chemicals required, obviously reducing the cost of the pickling.

The oxid residue recovered from the retort is also available for commercial use. For instance, if washed, a good quality of iron oxid pigment is recovered.

This bath is also suitable for copper materials.

What I claim is:—

1. A pickling bath formed by the reaction of concentrated salt water and sulfuric acid in the presence of an abundance of water, the salt water and sulfuric acid being proportioned to substantially eliminate free sulfuric acid in the bath.

2. A pickling bath formed from concentrated salt water and sulfuric acid proportioned to substantially satisfy the chemical equation of

$$NaCl+H_2SO_4=NaHSO_4+HCl.$$

3. A pickling bath substantially non-wasting in character and composed of a solution having not less than two acid pickling elements adapted to form precipitates in the presence of the material being pickled, the non-precipitate having the property of continued activity upon the addition of the element-producing chemicals.

4. A pickling bath substantially non-wasting in character and composed of a solution having not less than two pickling elements adapted to form precipitates in the presence of the material being pickled, the precipitates, under the action of heat, forming gases combinable with the non-precipitate of the solution to produce pickling elements.

5. The method of producing a pickling bath which consists in combining not less than two pickling elements in an abundance of water, forming precipitates by the presence of the material being pickled, removing the precipitates and heating them to form gases combinable with the non-precipitate of the solution to produce pickling elements.

6. The method of producing a pickling bath which consists in combining not less than two picking elements in an abundance of water, forming precipitates by the presence of the material being pickled, removing the precipitates and heating them to decompose gases combinable with water to produce pickling elements.

7. The method of pickling iron or steel which consists in subjecting the material to be pickled to the action of a pickling bath containing acid sodium sulfate and hydrochloric acid in solution, whereby precipitation will be provided, and renewing the activity of the bath by the addition of the chemical sources of said pickling elements.

8. The method of pickling iron or steel which consists in subjecting the material to be pickled to the action of a pickling bath containing acid sodium sulfate and hydrochloric acid in solution, whereby precipitation will be provided, removing the precipitate, and renewing the activity of the bath by the addition of the chemical sources of said pickling elements.

9. The method of pickling iron or steel which consists in subjecting the material to be pickled to the action of a pickling bath containing acid sodium sulfate and hydrochloric acid in solution, whereby precipitation will be provided, and renewing the activity of the bath by the addition of the chemical sources of said pickling elements in regulated quantities.

10. The method of pickling iron or steel which consists in subjecting the material to be pickled to the action of a pickling bath formed from regulated quantities of sulfuric acid and of a concentrated solution of salt water in proportions to substantially eliminate free sulfuric acid in the bath, whereby precipitation will be provided, and renewing the activity of the bath by the addition of regulated quantities of the sulfuric acid and salt water solution.

11. The method of pickling iron or steel which consists in subjecting the material to be pickled to the action of a pickling bath formed from regulated quantities of sulfuric acid and of a concentrated solution of salt water in proportions to substantially eliminate free sulfuric acid in the bath, whereby precipitation will be provided, removing the precipitate, and renewing the activity of the bath by the addition of regulated quantities of the sulfuric acid and salt water solution.

12. The method of pickling iron or steel which consists in subjecting the material to be pickled to the action of a pickling bath having the property of producing precipitates of sodium sulfate, ferrous sulfate, and ferrous chlorid in the presence of the material being pickled.

In testimony whereof I affix my signature in presence of two witnesses.

ADDISON F. HOFFMAN.

Witnesses:

MARY MCLAUGHLIN,

W. G. DOOLITTLE.