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METHOD OF PICKLING

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This invention relates to the cleaning of metallic surfaces by chemical treatment with acid, and has for its objects the pickling of ferrous metal parts, the reclaiming of acid in the spent pickling solution for further use, and the recovery of ferrous sulphate.

Heretofore, it was the practice in pickling ferrous metal articles to use a pickling bath of sulphuric acid having a concentration of from 3% to 8%, and heating the bath to about 160° F. to 190° F. When the specific gravity of the bath reached about 1.2 to 1.26 by the depletion of acid and by the increased content of soluble ferrous sulphate ($FeSO_4.7H_2O$), it was spent, and the solution was treated to reclaim some of its constituents. In treating the solutions the concentration of the ferrous sulphate was increased by exhausting the residue of acid with scrap iron or by evaporating the water so that a saturated solution would be produced, or the solution would be cooled by refrigeration to temperatures which approximate the freezing point of water in order to crystallize the copperas. When the treatment was such that the acid had not been exhausted, the mother liquor was sometimes utilized for pickling, but in such processes the treatment by refrigeration or evaporation required much time, the attention of operators, the expenditure of power, and the use of costly apparatus which adversely affected the economy of the processes. Furthermore, the use of a bath in which the acid concentration decreased with use required great skill on the part of workmen to avoid embrittlement, staining, and incomplete pickling of the articles.

According to the present invention, ferrous metal articles are pickled by immersing them in a particular, constant strength solution of sulphuric acid. The pickling bath is run at comparatively low temperatures and is used until its ferrous sulphate content is higher than that which has been used heretofore. It is then cooled to about normal atmospheric temperature or lower to crystallize the copperas. The copperas is separated from the mother liquor, and the mother liquor with its unspent acid is returned to the pickling vat. Additions of water and fresh acid are made to maintain the predetermined volume and acidity of the bath.

The invention is illustrated by the following specific embodiment, but it is to be understood that modifications thereof can be made.

A pickling bath comprising water and 5% by weight of sulphuric acid is maintained at about 135° F. The bath has a specific gravity of about 1.04. As the ferrous articles are pickled, the acid concentration of about 5% by weight is maintained substantially constant by frequent additions of sulphuric acid. Pickling is continued until the specific gravity of the bath reaches approximately 1.4 at which time all of the bath is removed and cooled to approximately 68° F. About 65% of the copperas in solution crystallizes and settles to the bottom of the mother liquor.

The copperas is separated by filtration, decantation, centrifuging or any combination of these. The mother liquor is combined with water and fresh acid to make fresh pickling solutions of the original volume and strength. The specific gravity of this fresh pickling solution is about 1.16 and contains about 5% H_2SO_4, 25% $FeSO_4.7H_2O$ and remainder H_2O. This pickling solution, or bath, is heated to about 135° F. and used until its specific gravity is about 1.4—the temperature and acidity of the bath being maintained constant at their starting values. It is then treated to recover its acid and copperas as was done with the initial solution as described above. This process is continued indefinitely.

The time required for pickling as the specific gravity of the bath increases from 1.16 to 1.4 gradually increases. But if the acidity of the bath is maintained constant, the rate of pickling is high enough to be economical and otherwise satisfactory up to a specific gravity of 1.4. The final specific gravity may vary from about 1.35 to about 1.4.

The crystallized ferrous sulphate which is recovered is washed with a small amount of cold water, which reduces the free acid in the crystals to below .1%. The slight amount of free acid which remains in the crystals is advantageous because it aids in preventing oxidation and discoloration of the crystals.

The temperature of the pickling bath may vary between 130° F. and 145° F. without disadvantageously affecting the operation. The temperature should not materially exceed 147° F. since at and above this temperature a monohydrate of ferrous sulphate ($FeSO_4.H_2O$) is likely to be precipitated. The presence of solid monohydrate of ferrous sulphate in the bath is detrimental because it tends to settle about the articles and shields them from the acid.

If the temperatures below 130° F. are used, the rate of pickling becomes too low to be economical, and the capacity of the bath for holding the ferrous sulphate in solution is decreased.

While the acidity of the bath should be maintained preferably at about 5%, it may be varied slightly. Values lower than 5% cause a slower rate of pickling and an increased capacity of the bath to hold the sulphate in solution when it is cooled. Values higher than 5% tend to make the ferrous sulphate less soluble and cause a precipitation thereof at the specific gravities used. The acidity should never be lower than

2% nor exceed 8%. When the spent pickle liquor containing 5% H_2SO_4 is cooled, a greater yield of crystals is obtained than if there were little or no acid present. Thus, besides the fact that no acid is wasted, maintaining the acidity at about 5% results in two advantages; namely, a larger crop of crystals in cooling and less slowing down in the rate of pickling.

The spent pickle liquor should be cooled to atmospheric temperatures and preferably to about 68° F. A lower temperature than 68° F. does not result in much increased crystallization, although, of course, lower temperatures may be used. About 85% as much copperas is crystallized out at 68° F. as can be crystallized out at 40° F. The cooling temperature should never exceed 90° F. Cooling to a temperature of 68° F. can be conveniently and economically effected through the agency of water from wells, rivers, or municipal mains, thus avoiding the use of expensive refrigerating apparatus. For instance, municipal water is available to applicant at an average yearly temperature of about 59° F. and the variations from this value are slight throughout the season. The water used for cooling purposes undergoes but a few degrees change in temperature and, consequently, can be used immediately for other process purposes where the increased temperature is not detrimental. The high acid concentration and the high specific gravity used in this method particularly adapt the spent pickling liquor for cooling at atmospheric temperatures to yield a large crop of crystals and hence provide an economical and convenient method of reclaiming the spent pickling liquor without waste.

The invention provides means of regulating the pickle liquor within limits which uniformly produce excellent pickling of ferrous articles. All of the copperas is recovered and all of the acid is utilized. These results are accomplished according to the invention within temperature levels which do not require extraordinary expenditures of energy for heating or cooling.

What I claim is:

1. The method of treating ferrous metal articles which comprises immersing the articles in a sulphuric acid bath having a temperature of about 130° F. to 145° F. and an acid concentration of about 5%, maintaining the temperature and acid concentration of the bath substantially constant by the addition of sulphuric acid until the specific gravity reaches about 1.4, and cooling the bath to crystallize metal sulphates.

2. The method of treating ferrous articles which comprises immersing the articles in a bath of sulphuric acid of about 5% concentration, said bath being heated to temperatures of about 130° F. to 145° F., maintaining the acid concentration substantially constant by adding sulphuric acid, maintaining the temperature substantially constant within the above range until the specific gravity of the bath reaches about 1.4, and cooling the bath to atmospheric temperature to crystallize copperas.

3. The method of pickling ferrous metal articles which comprises immersing them in a sulphuric acid bath having a temperature of approximately 130° to 145° F. and an acid concentration of about 5%, maintaining the temperature of the bath and the acid concentration substantially constant within the above range, removing the liquor from the bath when a specific gravity of 1.35 to 1.4 is attained, cooling this liquor to about 68° F., and separating crystallized copperas from the cooled liquor.

4. The method of continuously pickling ferrous metal parts which comprises successively immersing them in a sulphuric acid bath having a 5% concentration and a temperature of about 135° F., maintaining the temperature of the bath substantially constant by adding heat thereto, maintaining said concentration of acid in the bath during pickling, removing a portion of the bath, or liquor, when its specific gravity attains about 1.4, cooling this liquor to about 68° F., separating the crystallized copperas from the cooled liquor, then returning the cooled liquor to the pickling bath and adding sufficient fresh acid and water to preserve the original acidity and volume of the bath.

5. The method of pickling sheets of steel which comprises immersing the sheets in a sulphuric acid bath having a temperature of about 130° to 145° F. and an acid concentration of about 5%, maintaining the acid concentration and temperature substantially constant, cooling the bath to about 68° F. when its specific gravity attains 1.35 to 1.4, separating crystallized ferrous sulphate from the cooled bath, then adding water to this recovered liquor to dilute it to its original acid concentration, and heating this diluted liquor to about 130° F. to 145° F., whereby it is again in condition to be used as a pickling bath.

6. The method of pickling ferrous metal articles which comprises immersing the articles in a bath having a temperature between about 130° and 145° F. and an acid concentration of about 5% of sulphuric acid, maintaining said acid concentration and the temperature within said range during pickling until the specific gravity of the liquor increases to about 1.35 to 1.4 by the addition of ferrous sulphate which results from the action of the acid on the articles which are being pickled, cooling the liquor to precipitate and crystallize about 65% of the ferrous sulphate, separating the crystals, heating the liquor to about 130° to 145° F., and adding acid and water to restore the liquor to a specific gravity of about 1.16 and an acid concentration of about 5%.

7. The method of pickling ferrous metal articles which comprises immersing the articles in a bath having a temperature between about 130° and 145° F. and an acid concentration of about 5% of sulphuric acid, maintaining said acid concentration and the temperature within said range during pickling until the specific gravity of the liquor increases to about 1.35 to 1.4 by the addition of ferrous sulphate which results from the action of the acid on the articles which are being pickled, cooling the liquor to precipitate and crystallize about 65% of the ferrous sulphate, separating the crystals, heating the liquor to about 130° to 145° F., and adding acid and water to restore the liquor to a specific gravity between about 1.16 and a value of less than 1.4.

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