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METHOD OF REGENERATING WASTE PICKLE LIQUOR

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ABSTRACT OF THE DISCLOSURE

A process for regenerating aqueous sulfuric acid pickling liquor that contains residual iron-sulfur compounds characterized by the steps of (1) oxidizing the iron-sulfur compounds in at least a portion of the liquor; (2) partially neutralizing the portion of the liquor by raising its pH to at least 2 with the addition of a soluble caustic material, preferably one that contains a cation whose reaction product after the two steps forms a precipitate at a pH of 2 and higher; (3) separating the precipitates from the regenerated pickling liquor; and (4) returning the regenerated pickling liquor to pickling service. Also disclosed are specific preferred materials and processes employing additional steps.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates to a method of regenerating and returning to pickling service the sulfuric acid of a pickling liquor that also contains the iron-sulfur compounds resulting from pickling operations.

(2) Description of the prior art

Disposal of waste pickling liquor has been and still is an expensive and troublesome problem to various industries, particularly those industries concerned with cleaning a surface containing iron or the like preparatory to deposition of another coating thereon, as in galvanizing. Many processes have been proposed that would use or regenerate the waste pickling liquor; but these processes have not been totally satisfactory, being either impractical in operation or economically infeasible in the particular industry. Consequently, mills or the like have had to resort to neutralization before discharge or other disposal methods. With the current emphasis on improving the ecology, the processes for neutralizing the undesirable products have become more expensive, frequently requiring shut-down, pumping and cleaning up to prevent pollution. A good discussion of the prior art pickling practice is to be found in U.S. Pats. Nos. 3,387,927; 2,946,659; 2,739,040; and even back as early as 1,384,974. Related chemical processes are also discussed in U.S. Pats. Nos. 1,636,296; 1,606,470; and 1,047,826. The process of these patents oxidized the iron ions from their lower +2 to a higher +3 oxidation number. A study of these prior art processes indicate that the processes, though theoretically sound, never achieved the full usefulness that they should have. We believed the primary reason for the lack of a totally satisfactory solution was that these processes did not take advantage of the effect of pH on the solubility of reaction products. Specifically, these processes attempted, with logical basis, to keep the pH of the pickling solutions as acid as possible; normally in the range of about 0.5–1.0. Consequently, the prior art processes had to advert to a supplemental operation such as heating or the like to convert the reaction products to a precipitate. The additional conversion step was expensive, time consuming, and not readily adaptable to the oxidation reaction step. It is deemed probable that the prior workers

in this field overlooked the effects of pH on solubility, because conventional solubility data is given at near neutral conditions, not in highly acid conditions.

SUMMARY OF THE INVENTION

Accordingly, it is an object of this invention to provide a process for regenerating waste pickling liquor in which defects of the prior art processes are obviated.

It is a specific object of this invention to provide a process in which the alkalinity of the treated liquor is increased by a factor of at least 10 in order to obtain precipitation of at least the oxidized reaction product of the iron-sulfur compounds that contaminate pickle liquor; thereby enabling the regenerated pickle liquor, without the iron-sulfur compounds that are removed, to be returned to pickling service; and enable cleaning up the pickling solution without polluting a surrounding ambient environment, or otherwise disturbing the ecological conditions that prevail.

These and other objects will become apparent from the following detailed descriptive matter.

In accordance with the invention, contaminated, or degenerated, sulfuric acid pickle liquor is regenerated and restored to service by the following multi-step process. As one of the steps, the iron-sulfur compounds in the degenerated pickle liquor are oxidized by contacting at least a portion of the liquor with an oxidizing agent that is strong enough to oxidize the iron-sulfur compounds. The oxidizing agent is employed in an amount that is at least stoichiometrically equivalent to the iron ions to be removed from the portion of the pickling liquor.

As another step, the portion of the pickling liquor is partially neutralized by adding a soluble caustic material in an amount sufficient to bring the pH of the portion of the liquor to at least 2. A minimum pH of 2 is required in order for the oxidized iron-sulfur compounds to form precipitates that can be separated from the liquor. Preferably, in order to prevent a high concentration of a strong electrolyte in the liquor, the caustic material contains a cation whose reaction product formed after the oxidation and partial neutralization steps also forms a precipitate at a pH of 2 and higher. It can be seen that the pH greater than 2 actually effects a hydroxide ion concentration, or alkalinity, that is more than 10 times that normally attending the pickling liquor. The step of deliberately partially neutralizing a portion of the pickling liquor produces a high degree of precipitate formation and enables separating and returning the regenerated pickling liquor to service. Even we have been surprised by the unexplained and unexpected precipitation of both the oxidized iron-sulfur compounds and the reaction product of the cation of the caustic material.

As a third step, the precipitates, both the oxidized iron-sulfur compounds and the reaction product of the cation of the caustic material, are separated from the portion of the pickling liquor, which then is a regenerated pickling liquor. The separation may be by any of the conventional processes.

As a fourth step, the regenerated pickling liquor is returned to the pickling service.

The described process may be carried out as a batch operation, the steps being carried out in either a separate vat holding a portion of the pickling liquor, or the entire storage tank for small systems. On the other hand, the process may be carried out as a continuous process. The continuous process may be employed to treat either full stream or side stream. For example, it may be carried out as a treatment of about 10 gallons per minute for side stream operation in which an entire pickling operation can have its pickling liquor regenerated by operation of the treatment plant periodically for about 2 to 3 days.

On the other hand, a smaller treatment may be carried out with a smaller side stream operated continuously.

This invention is useful for regenerating, or recovering, waste pickling liquors from steel treating processes as well as other processes which employ pickling liquors; for example, regenerating waste liquors from electroplating processes. The invention has several advantages. For example, impurities such as zinc impurities have frequently required re-running because of the high toxicity thereof. These impurities are also precipitated in the process. The impurities constitute a relatively small percentage of the precipitate, so the precipitate is primarily iron, and it may be sold for recycling to produce iron ingots. Any other constituent; such as, the metal of the cation of the caustic material; may be recovered also, if present in a feasible concentration. The primary benefit of the invention, however, is that it prevents having to shut down the particular operation; for example, having to shut down a large scale galvanizing operation; in order to clean up the pickling liquor and prevent a polluting discharge that will create legal and ecological problems. Moreover, the invention alleviates problems which require separate pumping systems for cleaning up the process, as frequently required in conventional processes.

BRIEF DESCRIPTION OF PREFERRED EMBODIMENTS

In carrying out the invention described briefly hereinbefore, the oxidizing agents that are employed are those which are strong enough to oxidize the iron-sulfur compounds. Satisfactory oxidizing agents include the halogens; derivatives of a halogen, such as bromine water; concentrated nitric acid; and hydrogen peroxide. There may be health hazards associated with employing certain of the oxidizing agents; such as, fluorine, chlorine, and the less stable derivatives like the perchlorates. By their very nature, the strong oxidizing agents present some hazard and require special precautions. The procedures embodying the precautions, however, are well known, have been carefully delineated in safety manuals, and need not be described in detail herein. A particularly preferred oxidizing agent comprises chlorine, since it may be readily contacted with the solution in either a batch process or a continuous process. For example, the chlorine may be first dissolved in water and then reacted with the iron ions in the pickling liquor; or it may be contacted directly wth the pickling liquor in any of the conventional processes. Specifically, the gaseous chlorine can be bubbled through perforated pipe in the bottom of a vessel in a batch process; or flowed into the bottom of a contacting tower for contacting the downcoming liquor in a continuous process. Ordinarily, it is not necessary to employ an expensive bubble tray tower, since a tower that is packed with Berl saddles, Raschig rings, or the like will afford a satisfactory contacting tower. If one of the chemicals that is equivalent to the chlorine; that is, another of the strong oxidizing agens; is employed, the contacting procedures that are conventional for that particular oxidizing agent will be employed in the oxidation step.

The caustic material that is employed to bring the pH of the liquor to at least 2 must be soluble in the liquor such that it will raise the hydroxide ion concentration to the level equivalent to a pH of at least 2. Preferably, the caustic material contains a cation whose reaction product formed after the oxidation and partial neutralization steps forms a precipitate at the pH greater than 2. Ordinarily, this will require a cation which is at least divalent. Typical of such soluble caustic materials are calcium hydroxide and magnesium hydroxide. Particularly preferred is magnesium hydroxide. The reasons for its unusually efficacious performance are not completely understood. The solubility of chemical compounds in highly acidic solutions is still exploratory in nature. The chemical kinetics of the reaction of the magnesium compounds in pickling liquor are uncertain. Chemical

equations are set forth hereinafter in what is believed to be the explanation of the success of the process. Of course, caustic, materials containing the soluble monovalent cations can be employed where a build-up of the monovalent cation can be tolerated.

As indicated hereinbefore, the exact phenomena which explains the efficacy of the process is not clearly understood. The following equations are given by way of tentative explanation, not by way of limiting the process; since the process works, whether or not the equations that are hypothesized are accurate. The iron-sulfur compounds, in soluble form at the low pH have their ions oxidized to the highest valence of the iron; that is, iron ions having a valence of a positive 3, sometimes referred to as iron (III), all in accordance with Equation I (in ionic form):

$$2Fe^{+2}+3(SO_4)^{-2}+Cl_2 \rightarrow Fe_2(SO_4)_3+2Cl^{-1} \quad (I)$$

The addition of the magnesium hydroxide effects precipitation of the iron hydroxide in accordance with Equation II:

$$Fe_2(SO_4)_3+3Mg(OH)_2 \rightarrow 2Fe(OH)_3\downarrow+3MgSO_4 \quad (II)$$

A surprising phenomena that has been observed and that is not as clearly understood is the subsequent precipitation of a major portion of the magnesium that is added. It may be that the precipitation effects a continuing movement of the reaction in accordance with Equation III to the right, even though the predominant reaction rate is to the left side as follows:

$$Mg^{++}SO_4^{--}+H_2O \rightleftarrows Mg(OH)_2\downarrow+H_2SO_4 \quad (III)$$

In any event, the solubility phenomena which result in the precipitating of the iron and magnesium compounds is only experienced at a pH greater than 2; although we have found that magnesium ions alone are removed by the oxidation step at pH's as low as 0.4. Expressed otherwise, a satisfactory proportion of the iron and magnesium compounds are precipitated when the pH is as great as 2. The iron hydroxide can be precipitated substantially quantitatively at a pH of about 4 or higher. In one example, we have found that at a pH of 5 the concentration of iron ions have been lowered from about 17,000 parts per million (p.p.m.) to about 1 p.p.m.

The oxidizing agent is employed in an amount that is at least stoichiometrically equivalent to the iron ions to be removed. Preferably, an excess of the oxidizing agent is employed, particularly, where the efficiency of contacting the liquor is such that it effects less than 100 percent contact.

The soluble caustic material is employed in an amount sufficient to bring the pH of the portion of the liquor to a pH that is at least 2. If the maximum precipitation is desired, an amount of soluble caustic material is employed that will raise the pH to a level of about 5.

The steps of separating the precipitates from the regenerated pickling liquor and returning the regenerated pickling liquor to the pickling service may be carried out by any of the conventional separation processes. For example, a settling basin, with or without additives, may be provided such that the heavy salt precipitates will settle to the bottom and the supernatant liquid drawn from a quiescent zone. On the other hand, the iron compounds may form floc-like precipitates such that separation will be more nearly complete if a filtering operation is done. In such an event, the supernatant liquid from a quiescent zone of a treatment, or settling, vessel is flowed through a filter where the precipitate is removed. The filtrate is regenerated liquor that is returned to pickling service. That portion of the precipitate which is trapped by the filter may be subsequently removed by backwashing the filter. Ordinarily, a settling vessel will also have a concentrated slurry of precipitate which

can be "blown down," or sent to a recovery pit, to recover the precipitate without clogging the filter. If desired, centrifugation, with or without additives, may be employed to separate the precipitates from the pickling liquor.

The process may be carried out in any order of steps desired. For example, the soluble caustic material may be added first to raise the pH of the portion of the liquor to be treated and thereafter the portion of the liquor contacted with the oxidizing agent to oxidize the iron-sulfur compounds. On the other hand, the oxidation of the iron-sulfur compounds may be carried out first, as by bubbling the chlorine through the liquor; and subsequently, the soluble caustic material added to raise the pH. If desired, the process may be carried out by simultaneously carrying out both steps; that is, adding the soluble caustic material while simultaneously contacting the liquor with the oxidizing agent, as by bubbling the chlorine therethrough.

In the event that the liquor is contacted with the oxidizing agent first and the soluble caustic material added thereafter, an additional step of contacting the effluent from the partial neutralization step with the oxidizing agent may be carried out to further precipitate the cation reaction product; that is, the reaction product formed by reaction of the cation of the soluble caustic material during the oxidation and partial neutralization steps. For example, an additional chlorinator may be employed, or the additional step of chlorinating the supernatant liquid employed, to effect further precipitation of the cation reaction product; such as, magnesium hydroxide, as in accordance with Equation III.

The process of the invention is enhanced in its efficacy by periodically concentrating the sulfuric acid by removal of the water therefrom. The water may be removed from the sulfuric acid by any of the conventional processes; for example, by evaporating the water from the dilute sulfuric acid to form a more concentrated solution. The water that is removed does not, of course, pollute the atmosphere or the environment, and does not require special handling, as did the waste liquor that had to be disposed of previously. As indicated hereinbefore, the precipitate, or sludge, containing the precipitates is a desirable commercial product and does not present disposal problems.

Having thus described the invention, it will be understood that such description has been given by way of illustration and example and not by way of limitation.

What is claimed is:

1. A method of regenerating aqueous sulfuric acid pickling liquor that contains residual iron-sulfur compounds comprising ferrous sulfate comprising the steps of:

(a) oxidizing said iron-sulfur compounds comprising ferrous sulfate to ferric sulfate by contacting at least a portion of the liquor with an oxidizing agent selected from the group consisting of the halogens, concentrated nitric acid and hydrogen peroxide; said oxidizing agent being present in an amount that is at least stoichiometrically equivalent to the iron ions to removed; then

(b) adding to said portion of said liquor a soluble caustic material selected from the group consisting of calcium hydroxide and magnesium hydroxide in an amount sufficient to bring the pH of the portion of the liquor to at least 2 to form precipitates comprising ferric hydroxide and said caustic material;

(c) separating the precipitates from the regenerated pickling liquor; and

(d) returning the regenerated pickling liquor, sans the removed iron-sulfur compounds, to pickling service.

2. The method of claim 1 wherein said oxidizing agent is employed in an amount that is in excess of the stoichiometric equivalent of the iron ions to be removed.

3. The method of claim 1 wherein said soluble caustic material is added in an amount sufficient to bring the pH of the portion of the liquor to at least 4.

4. The method of claim 3 wherein said pH is brought to at least 5.

5. The method of claim 1 wherein said oxidizing agent is selected from a group consisting of chlorine, bromine water, concentrated nitric acid and hydrogen peroxide.

6. The method of claim 5 wherein said oxidizing agent is chlorine.

7. The method of claim 1 wherein said caustic material is magnesium hydroxide.

8. The method of claim 1 wherein an additional step of chlorinating said portion of said liquor is employed subsequently to step(b) to further precipitate the caustic material.

9. The method of claim 1 wherein said oxidizing agent is chlorine and said caustic material is magnesium hydroxide.

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