STEEL IN

5 PICKLING SECTION

5 MIXING SECTION

5 RINSING SECTION

5 STEEL OUT

VAPOR RECOMPRESSION CONDENSER

2 SPENT ACID LIQUOR PUMP

8 WATER RETURN PUMP

14 OLEUM PUMP

FILTER

FERROUS SULFATE MONOHYDRATE

INVENTOR.

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This invention relates to the pickling of metal and more particularly to apparatus for a continuous process for pickling steel, iron, or ferrous alloys.

As is well known in the art, steel is subjected to a pickling treatment for removal of scale or rust from its surfaces before subjecting it to such subsequent treatments as plating. The pickling treatment is commonly carried out by passing the steel through a bath of sulfuric acid solution whereby the iron oxide on the surface of the steel is removed by conversion to ferrous sulfate.

In the pickling process, the concentration of the pickling acid continuously decreases and the concentration of ferrous sulfate continuously increases until the ability to remove iron oxide from the steel is lost. It has been a common practice to discard the spent pickling liquor into streams or pits, but great disadvantages in this procedure are apparent. The spent liquor contains acid of course, although in low concentration. The value of this acid is lost if the spent solution is discarded and the acid becomes a public nuisance if emptied into public streams. Furthermore, the loss of iron sulfate in the pickling liquor is a waste of iron and sulfur.

The process and apparatus of the present invention are directed to the reclaiming of spent pickling liquor in a continuous manner whereby the waste of unreacted sulfuric acid and of iron sulfate are reduced or avoided.

An understanding of the process and apparatus of the invention can best be gained by reference to the drawing, the sole figure of which shows, in a highly diagrammatic manner, a preferred embodiment of the apparatus of the invention. This apparatus comprises pickling equipment and spent pickling liquor recovery equipment in which the process of the invention can be practiced.

In the drawing numeral 1 designates an elongated tank having a pickling section 2, an acid diluting section 3, and a water rinsing section 4. In picking the steel strip in accordance with the process of my invention, a strip of steel is passed by driven rollers 5, through the pickling section 2, above the acid diluting section 3, and through the water rinsing section 4. Through the pickling section 2 is flowed, countercurrently to the direction of the steel, an aqueous solution of sulfuric acid. In the course of passing through the acid solution of section 2, the iron oxide scale on the steel sheet reacts with the sulfuric acid to form iron sulfate, thus cleaning the surface of the steel. Spent pickling liquor from the pickling section 2, containing iron sulfate and dilute sulfuric acid, is continuously withdrawn by a line 6 at the end of section 2 which is farthest from the rinsing section 4 for passage through spent acid recovery equipment which is illustrated in detail below. Fresh water, preferably from the acid recovery equipment, is continuously introduced to the rinsing section 4 by a line 7. Thus the acid-washed steel strip is passed through the rinse water section 4 to remove adhering acid which would tend to corrode the steel if left on it.

A continuous reconditioning of the acid in section 2 must be carried on to compensate for the continuous loss in acid strength due to the reaction forming iron sulfate. In accordance with my invention the reconditioning of the acid is accomplished by introducing concentrated sulfuric acid from the spent acid recovery equipment via line 8 into the diluting section 3. Section 3 is separated from rinsing section 4 by a barrier or weir 9 and from pickling section 2 by a barrier or weir 10. The water in the rinsing section 4, being continuously introduced by line 7, continuously overflows the weir 9 into section 3. In section 5, a mixing of water flowing from section 4 and acid from line 8 takes place. In accordance with our invention, the flow of the steel sheet bypasses section 3 so that the steel does not contact any of the unmixed concentrated acid from line 8, as would occur if line 8 were introduced directly into the pickling section. Contacting the steel with strong acid from line 8 before the acid is properly diluted with water could result in severe pitting of the steel. This problem is avoided in my process.

The acid solution entering diluting section 3 by line 8 is of high concentration, for example, fifty or sixty per cent by weight sulfuric acid. However, acid of this strength is not effective for pickling and it must be diluted by line 9 as follows.

In diluting section 3, the acid is diluted by water from rinsing section 4 to a concentration of from about ten to twenty per cent by weight. The diluted acid then overflows continuously into the pickling section 2. The acid solution moves continuously across section 2 countercurrently to the direction of flow of the steel strip. In moving through section 2 the pickling solution continuously decreases in acid concentration and increases in iron salt concentration. When the spent solution is withdrawn by line 6, its sulfuric acid concentration is low, for example, about five to ten per cent by weight and its iron sulfate concentration is high, for example, about fifteen to twenty per cent by weight.

It should be noted that throughout the length of elongated tank 1 the flow of steel and liquid are countercurrent to each other. Thus the fresh water is fed to the rinsing section 4 at the farthest point, and is withdrawn from the point at which the steel enters the elongated tank 1 and spent solution is withdrawn from the pickling section 2 at the farthest point from the exit of the steel from the tank 1. This countercurrent flow insures that the strip of steel leaving tank 4 is washed with fresh water and also insures that acid washed from the steel is retained in the tank and passed to the pickling section 2.

Attention can now be shifted to the novel acid recovery equipment of my invention. Spent acid from the end of section 2 farthest from section 4 is continuously introduced by line 6 into the acid recovery equipment. The spent acid passes first into an evaporator 11, of conventional design, wherein the spent acid is heated to drive off water and concentrate the acid and the iron salts of the spent solution. In accordance with the process of my invention, the degree of concentration in evaporator 11 is moderate and insufficient to cause precipitation of substantial amount of the ferrous sulfate carried by the acid solution or at least in an amount sufficient to precipitate all but a small amount of the ferrous sulfate which would be objectionable in the pickling process. Following the addition of make-up acid, the reconditioned solution is passed through the continuous filter 15, of conventional design, wherein precipitated ferrous sulfate is removed. The acid
filtrate then passes via line 8 into acid diluting section 3 as previously explained.

From the foregoing description it can be seen that in accordance with my invention, the make-up acid is added at a highly advantageous point in the spent acid recovery process. It is added to the partially reconditioned spent acid immediately after the evaporation phase. In this way, the make-up acid serves a two-fold purpose: it replenishes the acid lost in the pickling process and it assists in precipitating the iron sulfate from the partially reconditioned pickling solution.

By adding make-up acid to the partially reconditioned pickling solution in accordance with my invention, the evaporation of spent pickling solution can be considerably less complete than if the acid were added directly to the pickling section 2, for then it would be necessary to evaporate the solution sufficiently to precipitate the iron sulfate by evaporation alone. The concentration to which the acid solution is evaporated in evaporator 11 is related to the amount of make-up acid which is added after the evaporation. The evaporation and the addition of make-up acid must together recondition the acid solution to a sulfuric acid concentration at which ferrous sulfate is substantially insoluble or soluble only to an unobjectionable degree, e.g., less than about two percent by weight. In order to maintain a constant acid strength in the pickling section and to use the acid most efficiently, the make-up acid should be added in an amount equivalent to the acid loss in the pickling reaction in forming ferrous sulfate. The make-up acid requirement will remain substantially constant throughout the treatment of any particular batch of steel. Therefore, when the amount of make-up acid to be added is determined, either empirically or by calculation of the amount that will be consumed in the pickling reaction, the concentration to which the solution must be evaporated before addition of make-up acid can also be determined so that precipitation of iron happens only when addition of the determined amount of acid either as oleum or as concentrated sulfuric acid.

It is obvious that the proper concentration to be obtained in the evaporator and the quantity of acid to be added will vary depending on the particular pickling operation and the type of make-up acid used, i.e., oleum, concentrated sulfuric acid solution, and to some extent upon the temperature at which the solution is withdrawn from the evaporator. A typical example is the following: Spent pickling solution is withdrawn from the pickling section at a sulfuric acid concentration of five percent by weight and containing about fifteen percent by weight iron sulfate calculated as FeSO₄. To restore the acid lost in the pickling operation by formation of iron sulfate, it is necessary to add oleum in the amount of about eight percent by weight. Therefore, in order for this amount of oleum to bring the sulfuric acid concentration of the solution to above about sixty percent by weight, i.e., the concentration in which ferrous sulfate is substantially insoluble, the solution is partially evaporated before addition of the acid to raise its acid concentration to about thirty-four percent sulfuric acid. The partially concentrated acid is withdrawn from the vacuum evaporator at a temperature of about 130° F. and to the solution is added the above indicated amount of oleum. Iron sulfate is precipitated and the acid and precipitate are separated by filtration.

The concentration of the solution to only about thirty-four percent by weight sulfuric acid as described for my process compares with the necessity of concentrating the solution to about sixty percent by weight sulfuric acid by evaporation alone as would be the case if my procedure were not followed.

It is clear from the considerably more moderate evaporation which is permitted in my process that important economies in operation are made possible. Thus, since the acid concentration in evaporator 11 in my process is not exceedingly high, the temperature required for the evaporation is low as compared with temperatures which would be required for a stronger concentration of the acid. Also, since the acid concentration is only moderate in my process, it follows that the corrosion problem in the evaporator 11 is reduced as compared with the problem in an evaporator designed to handle highly concentrated acid solutions. The need for expensive corrosion-resistant linings for the evaporator is considerably reduced by my process. Still further, because of the moderate temperatures involved in the evaporation stage of my process, the vaporization and loss of valuable SO₂ in the evaporator is not excessive.

Still another advantage of my process that can be pointed out is the water economy which is made possible by condensing water evaporated in evaporator 11 and returning it to the rinsing section 4 by line 7. As I have indicated above, the preferred procedure in accordance with my invention is to employ oleum as the make-up acid which is introduced into the acid recovery equipment by line 14. While concentrated sulfuric acid solution can also be used with successful results, the advantages of oleum make its use an important element of the preferred embodiment of my invention. Among the important advantages of oleum as the make-up acid are the following: The use of oleum makes it possible to evaporate the spent solution less severely than if sulfuric acid solution were used since the evaporation need not be so complete as to compensate for water which would be added with the acid. Also by using oleum there is actually a net loss of water in the acid recovery system (entrained and combined with iron sulfate) rather than a gain of water as is possible if an aqueous sulfuric acid solution is used as make-up acid. Consequently there is no problem of disposing of acidic waste water, which problem may be serious if a sulfuric acid solution is used. Still further, the use of oleum is advantageous in that it presents a smaller handling problem than a sulfuric acid solution.

While my process and apparatus have been described specifically with reference to the apparatus of the drawing, it should be understood that the invention includes the use of various equivalent elements of the apparatus and process. For example, in lieu of the driven rollers for strip steel as illustrated in the drawing, my apparatus can be provided with means such as a continuous conveyor belt for passing steel or iron articles through the pickling and rinsing sections of the elongated tank 1. An important characteristic of any such conveyor is, however, in accordance with my invention, that it passes the iron or steel through thepickling section and through the water rinsing section but over the acid diluting section.

I claim:

1. A pickling apparatus for iron which comprises an elongated tank having pickling, diluting and rinsing sections, said sections being separated by liquid overflow barriers, the barrier between said rinsing section and said diluting section being higher than the barrier between said diluting section and said pickling section, an evaporating means, a conduit connecting the end of said pickling section farthest from said rinsing section with said evaporating means, a second conduit for delivering concentrated acid from said evaporating means to said diluting section, a means for separating solids from liquid in the line of said second conduit between said evaporating means and said diluting section, means for introducing make-up acid into the said second conduit between said evaporating means and said means for separating solids from liquid, means for condensing steam from said evaporating means into water, and a conduit for delivering said water to the end of said rinsing section farthest from said pickling section.

2. A pickling apparatus for iron which comprises a pickling vessel, a rinsing vessel and means between said
vessels for diluting acid with water flowing from said rinsing vessel to said pickling vessel, an evaporating means, a conduit connecting said pickling vessel with said evaporating means, a second conduit for delivering concentrated acid from said evaporating means to said means for diluting acid with water, means in the line of said second conduit for separating solids from the concentrated acid, means for introducing make-up acid into the second conduit between said evaporating means and said separating means, a condenser connected to said evaporator so as to receive steam therefrom, and a conduit for delivering water from said condenser to the rinsing vessel.

3. A pickling apparatus for iron comprising a pickling section, a diluting section and a rinsing section, means for continuously passing steel through said pickling and rinsing sections and over said diluting section, an evaporating means, a conduit connecting said pickling section with said evaporating means, a second conduit for delivering concentrated acid from said evaporating means to said diluting section, means for separating solids from liquid in the line of said second conduit between said evaporating means and said diluting section, means for introducing make-up acid into the said second conduit between said evaporating means and said separating means, a condenser connected to said evaporator so as to receive steam therefrom, and a conduit for delivering water from said condenser to said rinsing section.

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