PROCESS FOR CONTINUOUS PICKLING OF STEEL STRIP AND REGENERATION OF THE CONTACT ACID

Melville W. Robinson, Jr., Beaver, Pa., Clarence Steelman, Jr., Wintersville, Ohio, and Enoch Perkins, Jr., Pittsburgh, Pa., assignors to Dravo Corporation, Pittsburgh, Pa., a corporation of Pennsylvania

Filed Nov. 18, 1963, Ser. No. 324,479

10 Claims. (Cl. 134—3)

The present invention relates to a process for continuous pickling of iron and steel with hydrochloric acid and treatment of the spent pickle liquor to recover the acid therefrom for economical re-use.

The art of pickling of ferrous materials for removal of scale therefrom is well known. Until recently, the spent pickle liquor was customarily discharged into streams or sewers and thus presented no disposal problems. Pursue stream laws have now prohibited stream pollution and many efforts have been made to treat the spent pickle liquor to conform to such laws. To compensate, in part, for such additional expense for treatment of the spent pickle liquor, prior to discharge into sewers and streams, efforts have been made to recover therefrom the dissolved iron and to regenerate the spent acid for re-use.

Economically such prior efforts have not been satisfactory due to the expense of treatment. Consequently, there is a tendency in industry to continue use of the pickling liquor for long periods, before treatment. It is well known in the art that optimum scale removal is obtained when the acid concentration is high and both efficient scale removal and speed of removal decreases as the acid concentration diminishes, unless otherwise compensated for.

Customarily, sulphuric acid has been employed for such pickling and while hydrochloric acid has been known to be effective, other disadvantages attendant to its use have previously substantially eliminated its use in commercial large scale pickling operations.

One object of the present invention is to provide a novel and highly efficient process for hydrochloric acid pickling of steel strip wherein the acid concentration of the pickling solution is economically maintained at optimum levels.

Another object of the invention is to provide an economical and effective pickle liquor acid regeneration process whereby optimum acid recovery is effected and the iron content of the pickle liquor is recovered for further processing.

The prior art of the invention will be made known from the following description and the schematic drawing of the apparatus and operation of the process, forming a part thereof.

Referring now to the single sheet of drawing; in the preferred form of the invention, the steel strip S to be treated enters a suitable vertical tower 1, which may be of the order of 70 to 150 feet in height and suitably enclosed to restrict escape of acid fumes. Within the tower 1, the steel strip S moves over suitable lower rollers 2 and 2A and upper roller 3 to provide at least one vertically upward and one downward return pass before moving out of the tower over roll 2A and onto rollers 4, 5, 6 for recoiling or further processing.

At the base of tower 1 is provided a suitable tank 7 containing a suitable supply of hydrochloric acid pickling solution. Beneath rolls 4, 5, 6 is another suitable tank 8 wherein the excess acid solution may be rinsed from the strip S before passing to another station where remaining acid thereon may be suitably neutralized before recoiling or passing to any suitable station for further processing, such as cold rolling, etc.

In the present preferred form of the invention, contact between the pickling solution and the metal is obtained by spraying as distinguished from conventional dipping.

Referring again to the drawing, the tank 7 has therein a suitable quantity of the pickling liquor wherein the acid content is maintained at a substantially constant volume by admission of regenerated acid from a suitable storage tank (not shown) connected with tank 7 by a suitable conduit (not shown). Physical losses of acid due to evaporation, carryout on the steel strip, and vent losses from the absorber are made up from time to time by the admission of fresh, concentrated acid. Such losses are a small percentage of the acid entering into the pickling reaction.

A suitable conduit 9, having a connection with the bottom portion of tank 7, leads to a branch conduit 10 having therein a suitable means, such as pump 11, for conveying the pickling solution through conduit 12 into a heat exchanger 13 where the solution is brought to suitable operating temperature, preferably between about 150 to 180° F. From heat exchanger 13 the solution under pressure from pump 11 passes through conduit 14 from which extend branch conduits 15, 16 and 17 leading into tower 1. Each of these latter conduits terminates in suitable spraying devices or nozzles indicated as 15A, 16A and 17A, which direct sprays of the solution upon the exposed inner and outer faces of each up run Su and down run SD of the strip within the tower. The excess solution applied to the strip flows down over both faces of each rim of the strip S back into the tank 7 at the bottom of tower 1. The thus described cycle of solution is continuously maintained during such periods as strip S is moving through the tower 1.

As the strip S issues from tower 1 over rolls 2A, the excess solution thereon may be removed by a suitable means, such as a high velocity air jet indicated generally at 18 and squeegee rolls indicated generally at 19. The issuing strip S then passes over rolls 4, 5 and 6 through the rinse tank 8 which is supplied with rinse water from any suitable source (not shown). The strip issuing from rinse tank 8 passes to further processing or recoiling, as previously described.

Referring again to conduit 9, extending from tank 7, a branch conduit 20 leading therefrom connects with pump 21 which pumps solution from tank 7 through conduit 22 which terminates in a suitable branch conduit 23 spraying the solution into the top portion of a suitable roaster device 24. Adjacent the bottom portions of the roaster device 24 are suitable air and fuel inlets 25 injecting a flame into roaster 24. As the descending spray of pickling solution from conduits 23 contacts the hot combustion gases within roaster 24, the solution is vaporized and the ferrous chloride therein is reacted with the hot combustion gases to provide iron oxide and HCl vapors. The oxide is deposited upon the bottom of roaster 24, from which it may be removed by conduit 26 into a suitable oxide container 27. The roaster just described is countercurrent, but it will be obvious to those versed in the art that a co-current roaster would be equally suitable.

The vapors from the vaporized spray of pickle liquor solution within roaster 24, are withdrawn through a suitable conduit 28 into a suitable gas-solids separating device 29. One such device is known in the art as a cyclone. Here any suspended iron oxides in the vapors are removed through conduit 26a. These vapors, comprising water, HCl and products of combustion, are then removed from 29 through conduit 30 into the bottom portion of absorber 31 and passing upward. The rising HCl vapors, in absorber 31, are condensed and absorbed into the cooler water flowing downwardly therefrom from conduit 32, providing HCl acid. The re-
constituted or regenerated acid is thereafter withdrawn from the absorber 31 through conduit 33 and returned to an acid storage tank as above referred to.

The water supplied to absorber 32 may be obtained from two sources, rinse tank 8 or an outside supply. Referring to Fig. 8, conduit 34 leading from the bottom portion thereof carries a portion of the rinse water therein to pump 35 which passes the rinse water through conduits 36 and 32 into the top portion of the absorber 31. In this manner recovery may be had of acid in the rinse water. Should additional water be necessary, or desirable, it can be supplied to conduit 32 from a suitable outside source, through conduit 37. Such rinse water as is removed from tank 8, must be replaced therein from any suitable source of fresh water.

Initially the acid solution placed in a storage tank for feed to tank 7, and for replenishing the acid solution in the tank 7, is a 20% solution of HCl and water, 20% HCl and 80% water. The regenerated acid returned to the acid solution storage tank is preferably maintained at 20% acid by controlling the rate of feed of water to absorber 31.

After the acid solution contacts the steel strip the solution in the tank is comprised of HCl, FeCl₂ and water. Thus after the pickling operation is established, the solution in the tank 7 will comprise about 11% HCl, about 13% FeCl₂ and about 76% H₂O. Preferably the pickling solution in use will be maintained between about 5% and 18% by weight, acid concentration.

When, for purposes of acid regeneration as discussed hereinbefore, a regulated volume of solution is withdrawn from tank 7 and passed into the roaster 24, the vaporized solution contacting the gaseous products of combustion therein provides the reaction

\[ 2FeCl₂ + 2H₂O \rightarrow Fe₂O₃ + 2HCl \]

During such reaction the ferrous chloride, in the presence of heat and the vapors, provides a solid iron oxide and HCl vapors. These latter vapors along with the other vapors or gases, in the roaster 24, pass therefrom into the bottom of absorber 31.

The rising vapors from the bottom of absorber 31 encountering the descending cooler water, loses much of the HCl vapors by condensation and absorption into the water. Substantially, none of the water vapor is condensed, but heat gained from such water vapor and the hot combustion gas tends to vaporize some of the water flowing downwardly counter current to the rising water vapor and combustion gases. Since the absorber is operating at substantially atmospheric pressure the acid concentration of the bottom product therein will not at any time be in excess of about 20%, the approximate azetrop composition at that pressure, considering the partial pressure of water and HCl vapors.

From the foregoing, the advantages of the herein described process may be summarized as providing optimum pickling efficiency, acid regeneration, oxide recovery and overall economy. To effect these, it will be recognized that certain variables in the process must be compensated for, such as the degree of oxide on the strip and the volume of strip which is passed through the pickling batch during a given period of time.

To maintain the desired solution efficiency in the pickling tank, regenerated or make-up acid should be returned to the pickling tank in amounts to compensate for the acid lost during reaction with the oxide on the strip, plus certain physical losses including carryout on the strip in passage from the pickling tank, evaporation, and vapor loss from the top of the absorber. These can be accomplished by suitable additions of acid solution to the pickling tank from a suitable acid solution storage tank, either periodically or continuously, at substantially the rate at which the pickling solution is withdrawn for regeneration as described.

The acid regeneration by-product, Fe₂O₃, is of significant commercial value since it may be sintered or briquetted and returned to the melting furnaces. Such by-product appears to contain about 70% iron and any trace amounts of chloride. Additionally, any trace metals from the strip pass out with the said oxide and are not returned to the pickling solution.

We claim:

1. A continuous process for pickling ferrous metal strip and for regeneration of the used pickling liquor, comprising the steps of

   (a) providing an initial bath of pickling solution of 20% by weight of hydrochloric acid and water,

   (b) continuously applying said solution to a ferrous metal strip moving through said bath,

   (c) continuously withdrawing a portion of the used solution from said bath during passage of the strip there through,

   (d) confining and heating the withdrawn used solution to vaporize the water and acid therein and to convert the ferrous chloride therein to hydrochloric acid vapor and solid iron oxide,

   (e) continuously collecting the vaporized hydrochloric acid and water from the heating step and condensing the hydrochloric acid vapor by contact with water in amounts to provide a regenerated hydrochloric acid solution of substantially the original content of HCl,

   (f) and returning the regenerated solution to said bath.

2. A continuous process for pickling ferrous metal strip and for regeneration of the used pickle liquor and returning the regenerated liquor to the pickling operation, which comprises the steps of

   (a) conducting the pickling operation with a pickle liquor having from about 15% to 18% by weight of hydrochloric acid concentration and maintaining the pickle liquor at a temperature of about 140°F. to 200°F. for contact with the ferrous strip,

   (b) continuously withdrawing a portion of the used pickling liquor from the pickling step for regeneration,

   (c) confining and roasting the withdrawn pickle liquor in the presence of heat to convert the withdrawn liquor to vapor and chemically react the ferrous chloride therein to solid ferric oxide,

   (d) continuously withdrawing the remaining vapors from the roasting step and passing same into contact with a moving stream of cooling water to absorb the HCl vapors and provide a regenerated liquor of about 20% by weight of hydrochloric acid concentration,

   (e) returning the regenerated liquor to the pickling steps in amounts to maintain the desired acid concentration in the pickling liquor at the pickling step.

3. The method as defined in claim 2 wherein the ferrous strip leaving the pickling step is rinsed with water, and continuously withdrawing a portion of the rinse water from the rinsing step to provide some or all of the cooling water employed in absorbing the HCl vapors in the acid regeneration step.

4. A continuous process for pickling moving ferrous metal strip and for regeneration and returning of the used pickle liquor to the pickling step to maintain a desired acid concentration in the pickle liquor in contact with the moving strip, comprising the steps of

   (a) continuously contacting the moving strip with pickle liquor having an acid content maintained in the range of about 5% to 18% by weight of hydrochloric acid and maintaining the contacting liquor at a temperature of from about 140 to 200°F.,

   (b) continuously withdrawing a measured volume of used pickle liquor from the pickling step and converting it into a spray in the presence of sufficient heat to vaporize all the spray and chemically react the ferrous chloride therein to solid ferric oxide,
(c) continuously collecting the vapors from the heating step and condensing and absorbing the HCl vapors therefrom in a cooling stream of water to provide a solution of hydrochloric acid and water.

(d) regulating the volume of cooling water to the HCl vapors absorbed therein to provide an acid content in the water of about 20% by weight,

(e) then returning the regenerated pickle liquor to the pickling step in amounts to maintain the desired acid content therein.

5. The continuous process as defined in claim 4 wherein

(a) the strip after leaving the pickling step is passed through a rinsing step wherein the pickled strip is rinsed with water, and

(b) a portion of the rinse water is continuously withdrawn from the rinsing step in amounts to provide the cooling water to absorb hydrochloric vapors and provide an acid content in the water of about 20% by weight.

6. The process as defined in claim 4 wherein a storage reservoir of hydrochloric acid and water solution having an acid content of about 20% by weight is provided, from which a measured volume of solution is passed to the pickling step to maintain the desired acid content therein, and the regenerated acid solution is passed to said reservoir.

7. A continuous process for pickling ferrous metal strip and for regeneration of the pickle liquor during use thereof, comprising the steps of

(a) providing a pickling liquor comprised of hydrochloric acid and water having an acid concentration of about 10 to 20% by weight of acid,

(b) maintaining a substantially uniform volume of such pickling liquor within the base of a vertical enclosure within which the strip moves continuously vertically upwardly and vertically downwardly for exposure to the pickling liquor,

(c) continuously withdrawing pickling liquor from the base of said enclosure, heating it to temperatures from about 140° F. to 200° F. and spraying it upon each face of the strip moving within said vertical enclosure,

(d) continuously withdrawing the strip from the enclosure after its downward passage therethrough and passing the strip through a water rinse station before passing the strip to further processing,

(e) continuously withdrawing a portion of the used pickle liquor from the base of said enclosure for regeneration and heating to vaporize the water and hydrochloric acid therein and to chemically convert the ferrous chloride to hydrochloric acid vapor and solid iron oxide,

(f) continuously withdrawing the vapor from the heating step and passing them into contact with a moving stream of cooling water to absorb the HCl vapors and provide a regenerate liquor of about 20% by weight of acid concentration, and

(g) then returning the regenerated acid to the pickling solution for further re-use.

8. A continuous process for pickling ferrous metal strip and regeneration of the pickling liquor, as defined in claim 7, wherein a portion of the rinse water is continuously withdrawn from the rinse step for use as cooling water in regeneration of the pickling solution.

9. A continuous process for pickling ferrous strip metal and for continuous regeneration of the used pickling liquor, comprising

(a) establishing in sequence a pickling area and a water rinse area,

(b) providing the pickling area with a suitable volume of pickle liquor at a temperature from about 140° F. to 200° F. and having a hydrochloric acid content of about 5% to 18% by weight,

(c) continuously passing the said strip successively through the pickling area and rinse area before delivering it for further processing,

(d) continuously withdrawing from the pickling area a preselected volume of the used pickling liquor and passing the withdrawn liquor as a spray into a suitably heated enclosure for volatilization of the liquor and chemical reaction to convert the ferrous chloride therein to solid ferric oxide,

(e) withdrawing the remaining vapor from the heating step and passing them into contact with a moving stream of cooling water to absorb the HCl vapors and provide a regenerated acid solution of about 20% by weight of acid and returning the regenerated solution to the pickling step.

10. The process as defined in claim 9, wherein a preselected volume of rinse water is continuously withdrawn from the rinse area for use as the cooling water for absorption of the HCl vapors in regenerating the pickling solution.

References Cited by the Examiner

UNITED STATES PATENTS

2,386,944 10/1945 Friedman 23—154
2,383,457 11/1945 Pines et al. 23—154
2,402,978 7/1946 Allen et al. 23—154

MORRIS O. WOLK, Primary Examiner.

F. W. BROWN, Assistant Examiner,