May 24, 1955 C. B. FRANCIS ET AL 2,709,143

METHOD AND APPARATUS FOR PICKLING AND FOR RECOVERING SPENT ACID SOLUTIONS

Filed Aug. 13, 1948

2 Sheets-Sheet 1

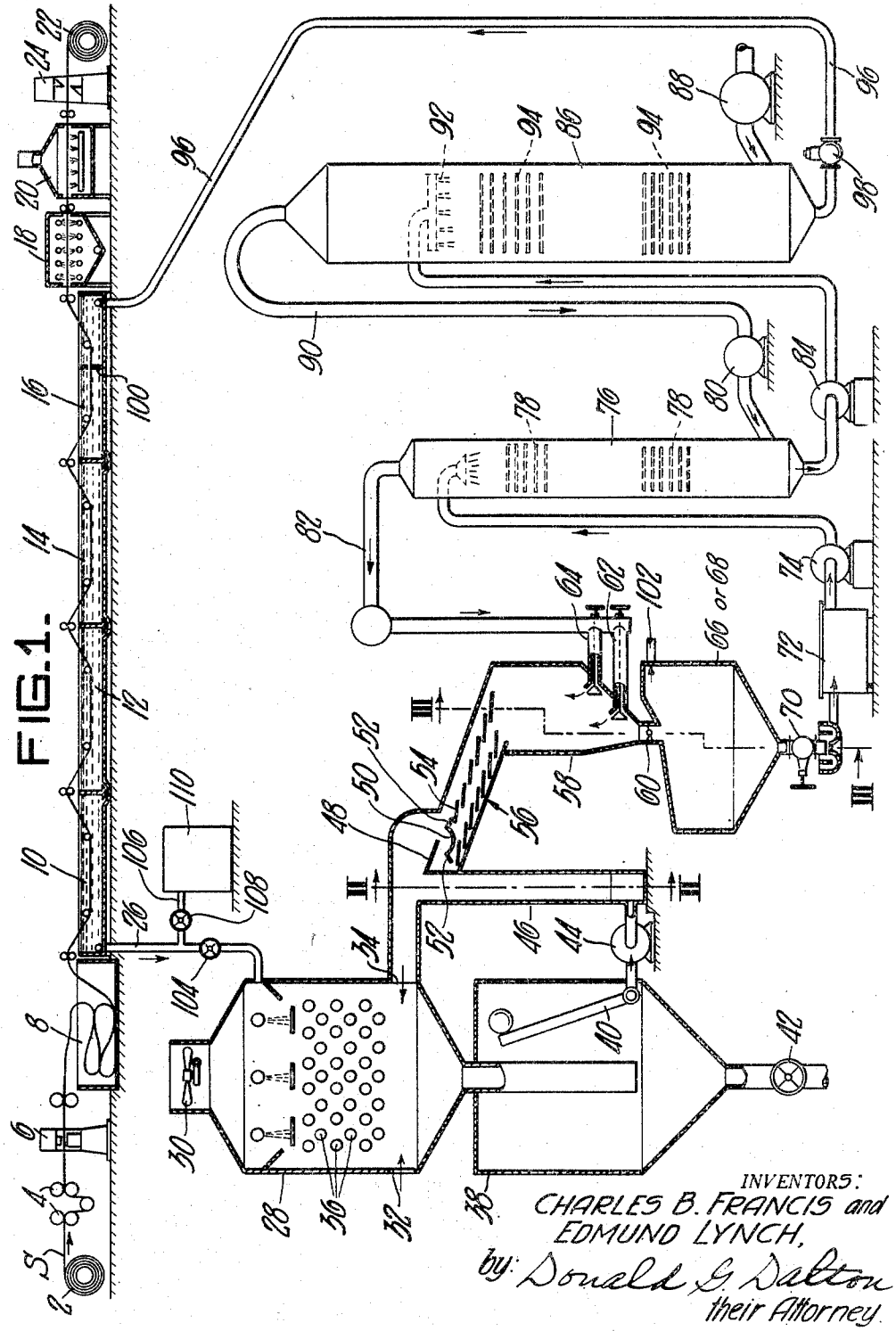


FIG. 1.

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FIG. 4.

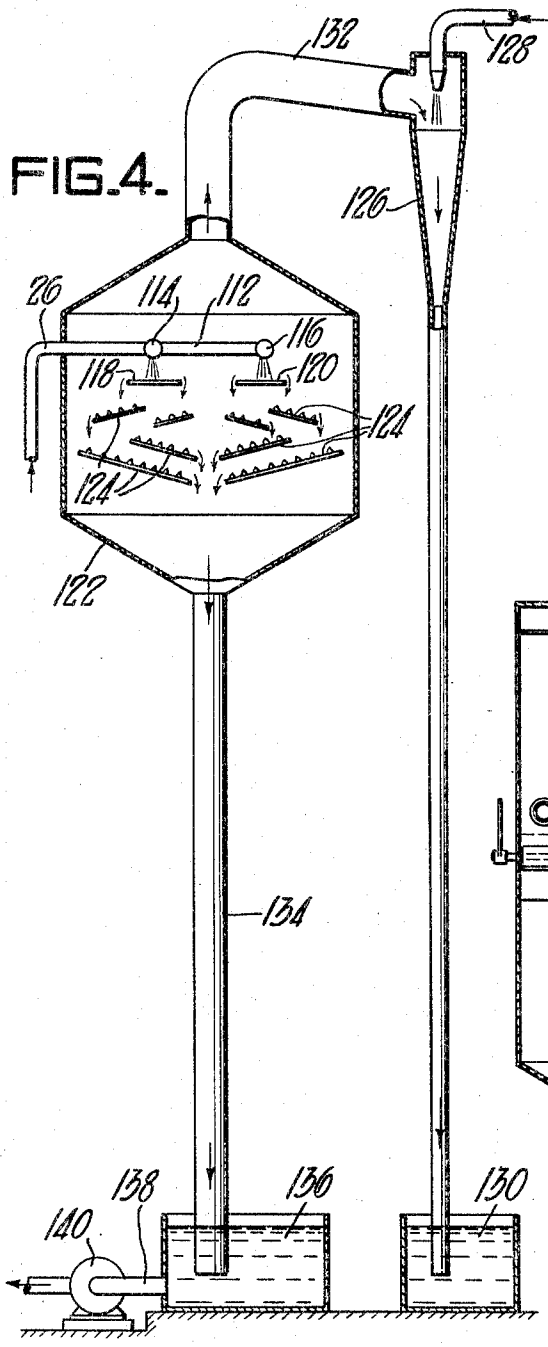


FIG. 2.

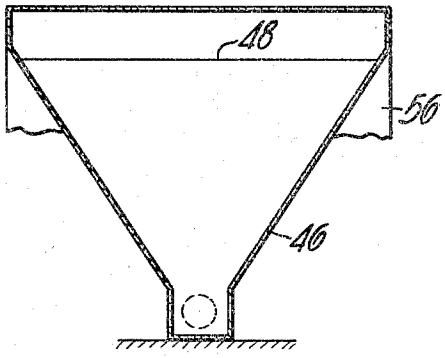
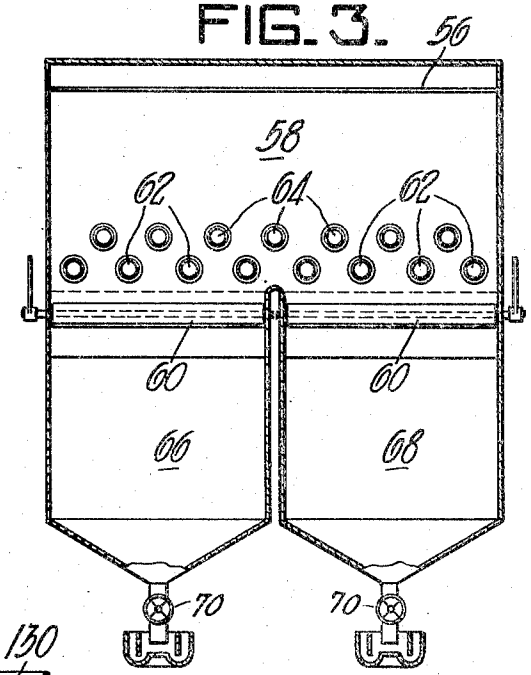


FIG. 3.



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METHOD AND APPARATUS FOR PICKLING AND FOR RECOVERING SPENT ACID SOLUTIONS

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Application August 13, 1948, Serial No. 44,108

14 Claims. (Cl. 134—13)

This invention relates to a method and apparatus for treating spent acid solutions and more particularly to the treatment of spent solutions of sulphuric acid used in the continuous pickling of steel. In the continuous pickling of steel, the acid concentration is ordinarily maintained above 10%. In order to maintain this concentration fresh acid is added to the last tank and the spent solution is removed from the first tank. The spent acid solution consists of 18 to 20% by weight of ferrous sulphate, 5 to 6% of free sulphuric acid, other sulphates of metals which are alloyed with iron in the steel, such as manganese, in about the proportions they occur in the metal, and the remainder of water. Such a solution has the specific gravity of about 1.2, 25° Bé., and weighs approximately 10 pounds per gal. at 4° C. This waste pickle liquor must be disposed of as a waste product, and in the past, most of the waste pickle liquor has been dumped into streams, thus polluting them. More and more States are passing laws preventing this dumping of waste pickle liquor and therefore various processes have been proposed for disposing of the waste pickle liquor. In most instances, no profit is made from such processes and in many instances, the net cost is greater than the cost of dumping it into streams. It has been proposed to cool the waste pickle liquor to remove some of the ferrous sulphate, but the methods proposed have not been successful in practice.

It is an object of our invention to provide a method of pickling steel in which the waste pickle liquor is purified and returned to the pickling line.

Another object is to provide a method of recovering free acid and the salt thereof from waste pickle liquor.

Still another object is to provide apparatus for continuous pickling.

A further object is to provide apparatus for cooling a liquid.

These and other objects will be more apparent after referring to the following specification and attached drawings, in which:

Figure 1 is a schematic diagram of our invention as applied to a continuous pickling line;

Figure 2 is a sectional view taken on the line II—II of Figure 1;

Figure 3 is a sectional view taken on the line III—III of Figure 1; and

Figure 4 is a view, partly in section, of a modification.

Referring more particularly to the drawings, the reference numeral 2 indicates an uncoiler from which a strip S to be pickled is uncoiled prior to the pickling thereof. Adjacent the uncoiler 2 are the bridle rolls 4 which feed the strip S to a welding machine 6 where the trailing end of one strip is fastened to the leading end of a following strip. From here the strip passes to a looper pit 8 and thence through a series of pickling tanks 10, 12, 14 and 16. Acid is washed from the strip in the rinse tank 18 and the strip is then dried in the drier 20 prior to recoiling on the coiler 22. A shear 24 is provided between the drier 20 and coiler 22 to cut the strip into the

desired length. The apparatus so far described is that commonly used for continuously pickling strip. The acid flows from the tank 16 to tank 10 with fresh acid being introduced into tank 16. The waste pickle liquor is removed from the tank 10 through a conduit 26 and is delivered into the upper end of a cooling tower 28, which may be of either the atmospheric or forced draft type. As shown, a fan 30 is provided at the upper end thereof to provide draft. Air inlets 32 and 34 are provided at the lower end of the cooling tower 28 which contains the usual baffles 36. Below the cooling tower 28 is a surge tank 38. The waste pickle liquor is introduced into the bottom of the surge tank 38 and is withdrawn therefrom through the floating outlet of a tube 40 made of rubber or other suitable acid resistant material. A valve 42 is provided at the lower end of tank 38. The acid leaving tank 10 is at a temperature within the range of 180° F. to 205° F. In tower 28 and tank 38 the waste pickle liquor is cooled to a temperature within 10° of the wet bulb temperature of the air. In temperature zones this means that the temperature of the waste pickle liquor will be between 50 and 80° F. in the winter, 60 and 70° F. in the spring and fall, and between 70 and 100° F. in the summer. Since ferrous sulphate begins to crystallize at 70° F. from spent acid solutions containing as much as 20% of the salt, it is desirable during cold seasons to regulate the cooling to prevent lowering the temperature of the solution below 70° F. in the tank 38.

From the tube 40 the solution is pumped by means of a pump 44 to a V-shaped feed tank 46 whose top is open to the air conduit 34. A weir and liquid apron 48 is provided at the top of feed tank 46 and the waste pickle liquor flows over the weir into a distributing trough 50. This trough has aprons 52 on both sides thereof over which the waste pickle liquor flows in a thin sheet approximately 1/16 to 1/8 of an inch thick. The top edges of the trough are in a horizontal plane a few inches below the top edge of the weir 48. From the aprons 52 the spent acid drops upon the top two boards 54 of a sloping double louver 56, which forms the top section of a novel apparatus for cooling liquids. These boards may be made of any acid resistant material from 6 to 8 inches wide and may vary in thickness up to 1 inch. The boards are supported one above the other a few inches apart with the top surface of the boards sloping to form an angle of 3 to 5 degrees from the horizontal so that the waste pickle liquor flows slowly across their surface. The number of boards and the length and width of the louvers are determined by the volume of spent acid to be treated per unit of time and are adjusted so that the depth of the liquid flowing over the surface thereof does not exceed 1/8 inch. For example, to treat 50,000 gallons of spent acid per day, it is necessary to provide a louver 20 feet long, 10 feet wide and about 2 feet deep. In a louver with a frame of these dimensions, the number of boards depends upon their width, at least 20 in each row being required when using boards 8 inches wide. When the waste pickle liquor is flowing slowly over the louver boards, a current of cool air passes thereover so that the liquid is rapidly cooled due to the exchange of sensible heat from the liquid to the air. The air entering the louver is saturated with moisture so that the total heat transferred from the liquid depends largely upon the difference in temperature between the liquid and the air, the relative weight of the liquid and air, and the area of the exposed surfaces of the air and liquid. With the relative masses and temperatures fixed, the rate of heat transfer is controlled by the areas exposed. Thus, by regulating the flow of liquid and spreading it over a large surface, the rate of heat transfer is increased to a maximum and it is

possible to cool the spent acid from 190° F. to 100° F., from 100° F. to 60° F., or from 60° F. to 40° F. in 20 to 30 seconds when the air is introduced at 0° F. In the particular example given, the liquid will flow from the end of the louver at a temperature no higher than 70° F. into a vertical tank **58**. A pair of butterfly valves **60** are provided in the bottom of the tank **58** and are kept closed until the waste pickle liquor rises to a level some distance below the bottom edge of the louver, which distance in a commercial installation may be approximately 4 or 5 feet. Air which has been compressed to 100 pounds pressure and cooled to below minus 100° F. is then admitted into the tank **58** through two rows of trumpet-shaped nozzles **62** and **64**. By admitting the air at this temperature and pressure through nozzles submerged in the liquid, violent agitation and rapid cooling of the spent acid is effected because the air expands forcing the liquid from the region of the nozzle and absorbing heat equivalent to that extracted after compression. Since the agitation of the liquid is violent, it causes intimate admixture of the air and waste pickle liquor so that the latter is cooled very rapidly at a temperature which may be assumed to be 20° F. at a particular concentration. At this temperature a large part of the ferrous sulphate will separate from the solution in the form of very small crystals. If the weight of the air necessary to cool the waste pickle liquor from 70° F. to 20° F. in tank **58** is equal to the weight of the liquor passing through tank **38** it will lower the temperature of spent acid on the louver **56** from about 110° F. to 75° F., the reduction being effected through an exchange of sensible heat sufficient to raise the temperature of the air from 0° F. to 75° F. and the evaporation of about 35 pounds of water per ton of air or liquid. Therefore, it is desirable to have the temperature of the solution entering the louver approximately 100° F. so that it may leave at a temperature of about 70° F. Under these conditions the amount of ferrous sulphate remaining in the solution will vary from 5% to about 8% according to the season of the year. Better control of the final temperature of the liquid leaving the tank **58** can be obtained in cold weather by using the fan **30**. In hot weather the desired temperature control can best be obtained by increasing the amount of air compressed.

Below the cooler **58** is a pair of tanks **66** and **68**. As soon as the liquid in the cooler **58** is cooled to the desired temperature, one of the valves **60** is opened so as to permit the liquid to flow into one of the two tanks **66** or **68**. When the first tank is full the valve **60** for the other tank is opened slightly until it is filled. Thereafter the valves over both of the tanks may be left wide open and valves **70** at the bottom of the tank adjusted to permit the liquid to flow from the tanks at the same rate as it flows into the tanks. The tanks **66** and **68** are preferably made of steel and lined with acid resistant material on the inside in the same manner as the rest of the equipment, this being necessary to prevent attack by the acid. The tanks are insulated on the outside to avoid transfer of heat to the surrounding air, and are preferably large enough to contain all the liquor treated during a period of 4 to 6 hours. It is preferred to withdraw the solution from the two tanks alternately so as to allow time for crystal growth and to permit the crystals to settle to the bottom, but not sufficient time for the crystals to consolidate into a solid mass. The liquid and crystals withdrawn from the bottom of the tanks are passed alternately into two centrifugal type driers **72**, which serve to separate the crystals from the cold mother liquor. The cold mother liquor is pumped from the drier **72** by means of the pump **74** to the top of a heat exchanger **76**. The liquid enters the heat exchanger at a temperature between 25° F. and 30° F. and passes over coils or through cells **78** made either of Monel metal or of steel clad on the acid side with Monel metal. The compressed air used in the cooling chamber **58** is delivered to the heat exchanger **76** by means of a compressor **80** and passes through the coils **78** and is discharged from the top of the heat exchanger **76** through the conduit **82**. The heat exchanger is so designed that the temperature of the air leaving the heat exchanger is below 100° F. and the temperature of the liquid below 60° F. From the heat exchanger **76** the liquid is pumped by means of a pump **84** to the top of a second heat exchanger **86**. The air to be cooled and compressed is delivered to the bottom of heat exchanger **86** by means of a first stage compressor **88** and the cooled air passes from the top of the tank through the conduit **90** to the second stage compressor **80**. The heat exchanger **86** may be of various types. In small scale operation good heat transfer can be had by spraying the liquid through sprays **92** into the chamber through which the air passes. Splash boards **94** are generally used with such sprays. The liquid is preferably introduced at a pressure above 100 pounds per square inch and is withdrawn through the pipe **96** equipped with a pressure regulating valve **98**. To avoid injury to the second stage compressor **80**, the heat exchanger **86** must be designed to prevent carry-over of entrained solution. Not only is the air cooled in the heat exchanger **86**, but the solution is heated to a temperature between 70° F. and 90° F. This solution which contains from 6 to 8% of ferrous sulphate and 8 to 10% of sulphuric acid and has approximately 80% of the original volume of the waste pickle liquor in conduit **26** is conducted through the conduit **96** to the last pickling tank **16**. This tank **16** is preferably provided with a transverse rubber partition **100** about 15 feet from the end of the tank and the recovered acid is delivered to the tank at the exit end thereof as shown in Figure 1. Make-up acid and steam is introduced to the tank **16** on the side of the partition **100** opposite the conduit **96**. In this way the drag-out loss consists almost entirely of recovered acid with the fresh make-up acid and water mixing with the recovered acid, thus diluting the ferrous sulphate and increasing the efficiency of the solution. In batch pickling, it is preferred to dip the sheets or other material into a vat of recovered acid heated with steam to above 180° F. and then finish the pickling in fresh acid. However, this procedure is not always advisable since the ferrous sulphate has an inhibiting effect which can be taken advantage of by using the recovered acid as an intermediate or finishing bath.

In cooling the spent acid solutions to temperatures below −21° F., ice separates and continues to separate as the temperature is lowered to −15° F. This ice, which separates as small crystals suspended in the solution, rises to the surface as a slush. In tanks **66** and **68**, which are provided with sloping tops, it is possible to remove this ice through an outlet **102** at the highest point in the top of the tank. This slush contains only a small amount of the acid and ferrous sulphate which adheres to the ice crystals so that the removal of the slush results in concentrating the acid and salt in the remaining solution, which in turn, causes more of the ferrous sulphate to crystallize. This ice may be permitted to remain in the system as a temperature regulator, especially when operating on a minimum amount of compressed air. If desired, the ice may be removed and used in the second heat exchanger **76** to lower the temperature of the compressed air. When it is desired to reduce the quantity of the solution returned to the pickling baths, the ice is kept out of the system entirely and used as a cooling medium elsewhere.

It is also possible to recover manganese by the use of our invention. When initially starting the plant in operation, only ferrous sulphate crystallizes out of the solution, but in time, manganese sulphate accumulates in the solution until it begins to crystallize along with the ferrous sulphate. When this condition is reached, a valve **104** in line **26** is closed and a quantity of hot spent acid is removed

from the system through conduit **106**. Flow of the solution in conduit **106** is controlled by valve **108**. This solution is delivered to a manganese treating plant **110** where it is treated with air and lime to precipitate iron, thus leaving the manganese in solution. Alternatively the wet crystals may be dissolved in water, the ferrous sulphate oxidized to ferric sulphate, and the solution treated with a suitable base to precipitate the iron and leave the manganese in solution.

It will be understood that the described method may be applied in the treatment of any spent acid solution produced in any way, not only for the recovery of ferrous sulphate and sulphuric acid, but for the recovery of any salt, the solubility of which decreases with the temperature of the solution and any acid that remains in the solution at the temperature at which the salt crystallizes. In place of compressed air, any other suitable gas may be used.

In place of using tanks **32** and **38** the spent pickle liquor may be cooled to between 100° F and 110° F. by flash operation by using the apparatus shown in Figure 4. In this embodiment of our invention the conduit **26** is connected through a manifold **112** to two perforated pipes **114** and **116** from which the spent acid drops upon horizontal splash boards **118** and **120** located in a vacuum chamber **122**. From the ends of these splash boards the acid drops to a series of inclined cleated boards **124** which spread the spent acid over a large surface and retard its flow through the vacuum chamber. The vacuum in the chamber **122** may be maintained in several ways as by means of a water jet condenser **126**. Water is introduced into the water jet condenser **126** through a conduit **128** and discharged therefrom into a trap **130**.

In operation, the spent acid solution drawn into the vacuum chamber **122** at a temperature between 180° F. and 205° F. will boil, thus filling the chamber with water vapor which passes from the chamber **122** through an outlet **132** connected to the condenser **126** where it condenses, thus maintaining a low pressure in chamber **122**. As the only source of heat is the solution itself and since heat is absorbed by the water in vaporizing, the vaporized water cools the water in the liquid. Since the vapor pressure of water at 100° F. is about 55 millimeters of mercury and since each pound evaporated at this temperature absorbs approximately 1000 B. t. u., it is apparent that each pound of water evaporated will cool approximately 10 pounds of water from 200° F. to 100° F. The vapor pressure of spent acid solutions is lowered considerably by the acids and salts dissolved therein, the vapor pressure being lowered about 12 millimeters for each 5% of acid and about 11 millimeters for each 15% of ferrous sulphate in solution, or about 23 millimeters for both. Therefore, the solution gives off vapor rapidly in a vacuum at a temperature of 100° F. The operation requires some time since the vapor must be drawn off and condensed so that the actual drop of temperature obtained also depends on the rate of flow through the apparatus. To hold a vacuum in the chamber **122** the liquid must be pumped out as fast as it flows in. This removal may be accomplished by connecting a pump directly to the bottom outlet **134** of the chamber **122**. However, it is preferred to extend the outlet **134** to a trap **136** from which the liquid is withdrawn through a pipe **138** by means of pump **140**, which delivers the cooled spent acid to the tower **46**.

While several embodiments of our invention have been shown and described it will be apparent that other adaptations and modifications may be made without departing from the scope of the following claims.

We claim:

1. The method of treating spent pickling solutions for the recovery of free acid and a salt thereof, which comprises exposing the solution to air at atmospheric temperature to cool the liquid to a temperature below 110° F., expanding compressed air cooled to at least approximately —100° F. into a chamber containing the partially cooled liquid to cool the liquid to a temperature below 20° F., collecting the cold solution and permitting it to stand until salt crystals of the desired size have formed, and separating the crystals from the liquid.

2. The method of treating spent pickling solutions for the recovery of free acid and a salt thereof according to claim 1, in which the compressed air is cooled by exposing it to the liquid from which the salt has been separated.

3. The method of continuously pickling steel which comprises removing the spent acid solution from the entry end of the pickling line, exposing the solution to air at atmospheric temperature to cool the liquid to a temperature below 110° F., expanding compressed air cooled to at least approximately —100° F. into a chamber containing the partially cooled liquid to cool the liquid to a temperature below 20° F., collecting the cold solution and permitting it to stand until salt crystals of the desired size have formed, separating the crystals from the liquid, heating the liquid from which the salt has been separated by exposing it to the compressed air prior to its expansion into the chamber, returning the reheated solution into the opposite end of the pickling line and passing steel through the pickling line.

4. The method of continuously pickling steel according to claim 3 in which concentrated acid and hot water are added to the last named end of the pickling line to raise the acid concentration to the desired point and to increase the volume of added fluids to that of the solution removed from the opposite end of the line.

5. In the method of continuously pickling steel, the improvement which comprises removing the spent acid solution from the entry end of the pickling line, expanding compressed air cooled to at least approximately —100° F. into a chamber containing the liquid to cool the liquid to a temperature below 20° F., collecting the cold solution and permitting it to stand until salt crystals of the desired size have formed, separating the crystals from the liquid, heating the liquid from which the salt has been separated by exposing it to the compressed air prior to its expansion into the chamber and returning the reheated solution into the opposite end of the pickling line.

6. In the method of continuously pickling steel according to claim 5, the additional step of adding concentrated acid and hot water to the last named end of the pickling line to raise the acid concentration to the desired point and to increase the volume of added fluids to that of the solution removed from the opposite end of the line.

7. Apparatus for cooling a liquid which comprises a tank for containing the liquid, a chamber at the top of the tank extending upwardly therefrom at an angle thereto, a sloping louver in said chamber over which the liquid flows into the tank, nozzles at the lower part of the tank for introducing compressed gas into said tank, a pair of tanks at the lower end of said first tank in communication therewith, a valve for each of said pair of tanks for controlling the flow of liquid thereto, a second pair of tanks one above the other, means for introducing the liquid into the top of the first of said second pair of tanks, a gas conduit leading from the top of said louver to the bottom of said top tank, a conduit leading from the bottom of the top tank to the bottom of the lower of said second pair of tanks, and a liquid conduit leading from the top of the lower tank to the top of the louver.

8. Apparatus for cooling a liquid according to claim 7 including a heat exchanger, a conduit leading from the bottom of each of the first named pair of tanks to the top of the heat exchanger, a compressor for introducing the gas into the bottom of said heat exchanger, and a gas conduit leading from the top of said heat exchanger to the said nozzles.

9. Apparatus for cooling a liquid which comprises a tank for containing the liquid, a chamber at the top of the tank extending upwardly therefrom at an angle thereto, a plurality of solid boards arranged in said chamber

with their top surfaces arranged at a slight angle to the horizontal and sloping in the same direction, the lower end of each board extending over the upper end of the board immediately therebeneath, the lower end of each board being spaced horizontally a substantial distance from the board immediately thereabove, the liquid flowing over each board to the board immediately therebeneath and hence into the tank, nozzles at the lower part of the tank for introducing compressed gas into said tank, a pair of tanks at the lower end of said first tank in communication therewith, a valve for each of said pair of tanks for controlling the flow of liquid thereto, a vacuum chamber, a conduit for introducing the heated liquid into said vacuum chamber, and a liquid conduit leading from said vacuum chamber to the top of the boards.

10. Apparatus for cooling a liquid according to claim 9 including a heat exchanger, a conduit leading from the bottom of each of the first named pair of tanks to the top of the heat exchanger, a compressor for introducing the gas into the bottom of said heat exchanger, and a gas conduit leading from the top of said heat exchanger to the said nozzles.

11. Apparatus for cooling a liquid which comprises a tank for containing the liquid, a chamber at the top of the tank extending upwardly therefrom at an angle thereto, a plurality of solid boards arranged in said chamber with their top surfaces arranged at a slight angle to the horizontal and sloping in the same direction, the lower end of each board extending over the upper end of the board immediately therebeneath, the lower end of each board being spaced horizontally a substantial distance from the board immediately thereabove, the liquid flowing over each board to the board immediately therebeneath and hence into the tank, nozzles at the lower part of the tank for introducing compressed gas into said tank, a pair of tanks at the lower end of said first tank in communication therewith, a valve for each of said pair of tanks for controlling the flow of liquid thereto, a heat exchanger, a conduit leading from the bottom of each of the pair of tanks to the top of the heat exchanger, a compressor for introducing the gas into the bottom of said heat exchanger, and a gas conduit leading from the top of said heat exchanger to the said nozzles.

12. Continuous strip pickling apparatus comprising a series of pickling tanks through which the strip passes, a louver, a conduit leading from the pickling tank at the strip entry end to the top of the louver for introducing the waste pickle liquor thereto, a tank beneath the louver communicating therewith, nozzles at the lower part of the tank for introducing compressed gas into said tank, a pair of tanks at the lower end of said first tank in communication therewith, a valve for each of said pair of tanks for controlling the flow of liquid thereto, a heat exchanger, a conduit leading from the bottom of each of the pair of tanks to the top of the heat exchanger, a compressor for introducing gas to be compressed into the bottom of said heat exchanger, a gas conduit leading from the top of said heat exchanger to the said nozzles, and a conduit leading from the bottom of the heat exchanger to the pickling tank at the strip exit end.

13. Continuous strip pickling apparatus according to claim 12 including means in the first said conduit for cooling the liquor to a temperature below 110° F.

14. Continuous strip pickling apparatus comprising a series of pickling tanks through which the strip passes, means for cooling the waste pickle liquor to a temperature below 110° F., a conduit leading from the tank at the strip entry end to the said cooling means, a tank for the liquor, a second conduit leading from the cooling means to said last-named tank, nozzles at the lower part of the last-named tank for introducing compressed gas into said last-named tank, a heat exchanger, a third conduit leading from the bottom of said last-named tank to the heat exchanger, and a conduit leading from the bottom of the heat exchanger to the pickling tank at the strip exit end for delivering the liquor thereto.

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