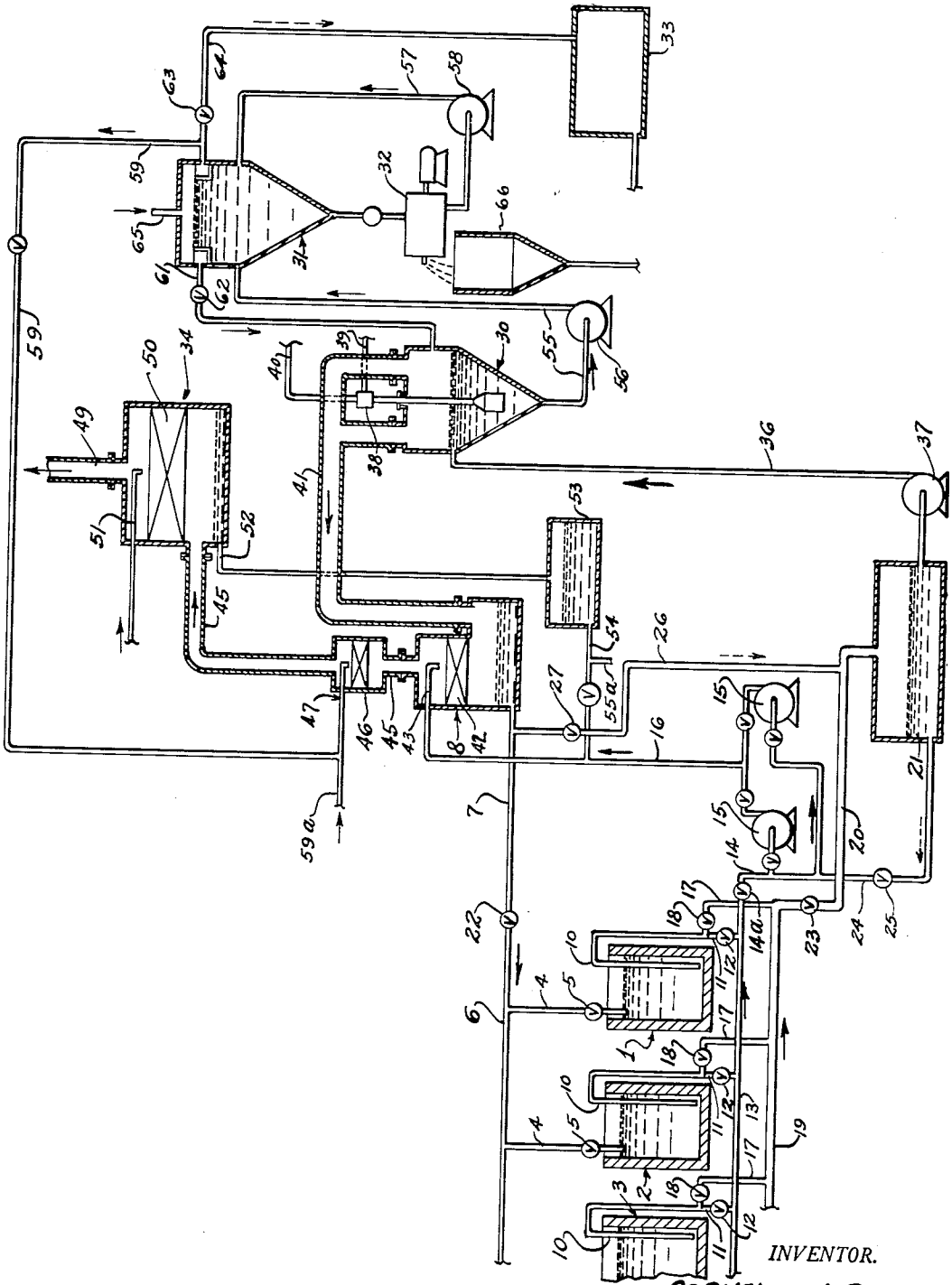
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PROCESS FOR PICKLING METAL

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PROCESS FOR PICKLING METAL

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The present invention relates to improvements in the process used for pickling metal and more particularly to a process for the pickling of steel wherein the pickling medium is continually reconditioned.

In the working of steel, for example by rolling operations whereby steel is reduced to strip, sheet or plate form, scale or rust usually are formed on the metal surface. Removal of such rust or scale is necessary to give a desired finished brightness, and at times to condition the steel for further processing steps. The scale or rust has long been removed in the generally used pickling process by subjecting the steel to the action of a sulphuric acid solution which reacts with the iron compounds constituting the rust or scale with the attendant formation of iron sulphates. In the pickling process, batches of steel in sheet, plate, or other forms are immersed in tanks of pickling solution, or in the case of continuous strip rolling, the continuous strip is passed through a vat of the pickling solution after the finish roll. Subsequent to the pickling operation the acid solution adhering on the steel must, of course, be removed by suitable rinsing.

To attain the desired pickling activity the pickling solution is commonly used at an elevated temperature, and further, agitation of either the steel or the pickling solution in the pickling tanks is maintained. The agitating devices at the tanks constitute encumbrances which often hinder the loading and removal of steel therefrom. Heat loss to the steel passed through the pickling solution or to the surroundings require or render desirable the continual heating of the solution to maintain a suitable temperature. This heating is usually and most simply effected at the tanks by injecting steam into the solution, a method tending to produce a fog or mist of acid solution above the surface of the pickling bath, which is objectionable on escape to the free atmosphere because of its corrosive or acid nature. This method of heating has the further disadvantage that condensation of the large amount of steam used in the normal course of the pickling process greatly increases the volume of the solution in the pickling tanks, thereby necessitating addition of acid to overcome dilution, and requiring oversize tanks or other means to prevent overflow. Of course, as the pickling process itself consumes acid due to the formation of iron sulphate salts, acid must be added to maintain an acid concentration which will give the desired pickling activity. During the life of the pickling solution the concentration of dissolved iron salts builds up, thereby tending to diminish the pickling rate in accordance with the ordinary laws of chemical equilibrium, so that it is necessary to increase the acid concentration to maintain a desired pickling rate. Ultimately the concentration of the iron salts becomes so high that further increase in the acid concentration is not practically effective in overcoming the iron concentration and then the solution is dumped from the tanks and replaced by fresh solution. Such pickling liquor at the time of dumping may, for example, contain by weight 5% sulphuric acid and 15% ferrous sulfate.

Clearly, this dumping procedure involves several disadvantages. The dumping of hot pickling solution and replacement by fresh solution subjects the acid resistant tank linings to the deleterious effects of thermal shock. There is a loss of unused acid, of heat energy in the hot pickling solution, and economic losses due to the cost of dumping and disposal operations. Due to the large volumes of solution involved it is uneconomic to evaporate the waste pickle liquor and the usual method of disposal has been dumping of the waste liquor into streams, lakes or sewage systems adjacent the plant; or, in some localities, hauling the large volumes of spent solution by barge for dumping in bodies of water such as the ocean or large inland lakes where the disposal of the solution is less objectionable because of the resultant high degree of dilution. Such dumping procedures, however, are objectionable in the eyes of governmental authorities because of the acid content of the solution and the high biological oxygen demand of the ferrous salts which adversely affect aquatic life. In many localities it is necessary by government regulation to neutralize the acid and remove the iron compounds, which, of course, entails the cost of labor and of an acid neutralizing and iron precipitating agent such as calcium oxide.

The present invention provides for the continuous reconditioning of pickling solution by continuous withdrawal from pickling tanks for removal of iron salts and heating to a desired temperature, with continuous return of a suitably conditioned solution to the pickling tanks. Hence there is no waste solution to be dumped. Since the pickling medium is in continuous flow through the pickling tanks the need for agitation of the tank contents can be readily obviated. Further, since heat is supplied to the pickling liquor constituents during the reconditioning operations, there is no need for heating of the tanks. Since tank agitating means are not required the design of pickling tanks can be radically changed from present designs, for no space is required for such auxiliary apparatus. Hence, the agitating devices usually encumbering pickling tanks, and the high solution dilution and corrosive fog or mist usually produced by the common tank heating systems, are eliminated.

The method of this invention is carried out by continuously withdrawing pickling solution from the tanks, a portion thereof being evaporated preferably by direct contact heating, for example by submerged combustion, to a temperature and to a concentration causing the formation of crystalline ferrous sulphate preferably the monohydrate. The evaporated solution is put through a crystallizer to effect separation of the ferrous sulphate from the residual strong acid solution, which is ultimately returned to the pickling solution. The major part of the pickling solution withdrawn from the pickling tanks is passed through a heating system wherein it absorbs latent and sensible heat energy and preferably water vapor from flue gas produced by the aforesaid evaporation. Water and acid, continually added to the system in amounts sufficient to make up the solution consumed by formation of ferrous sulfate and the drag-out losses of solution adhering to steel, may also be heated by thermal energy recovered from the evaporator flue gases. Thus the heat required to maintain the desired pickling temperature also serves for evaporation in the removal of the ferrous salts. Consequently in this invention, no dumping of pickle liquor is required and the operational and material costs usually attendant thereon are eliminated. The monohydrate salt recoverable in the process is itself of economic value, as it now appears that a

decided market is in prospect for the monohydrate preferential to the septahydrate. Even apart from this consideration, the fact that the iron salts are recovered as ferrous sulphate monohydrate rather than the heptahydrate, diminishes cost of transportation, and further diminishes heat energy loss to the process.

In consequence of the continuous recirculation and reconditioning of the pickling solution, its temperature, acid concentration and iron salt concentration, and hence the pickling rate or activity, can be readily regulated, a particular advantage where continuously rolled strip is being pickled. As there is no dumping of exhausted pickle liquor with an attendant replacement by fresh solution, which usually has a high rate of attack not only on scale and rust but also on clean steel, and as make-up acid is continually supplied to the system, sharp discontinuities in the performance of the pickling vats are eliminated. Further, the presence of residual iron salts in the reconditioned pickling liquor in this invention is controlled to a concentration permitting such salts to serve as an inhibitor of the action on clean steel without deleterious effect on the pickling rate. Thus the loss of clean steel and the consumption of acid therein is controlled. Other advantages of the invention will appear from the drawings and the following description of the invention.

In the drawing, which is a schematic representation, the battery of iron or steel pickling tanks **1**, **2**, **3** are continually supplied through inlet lines **4** having individual valves **5** from manifold line **6** with fresh, that is reconditioned, pickling acid solution flowing from liquid outlet line **7** of primary heater **8** hereinafter more fully described. At each tank used pickling solution siphoned through a tank outlet **10** is divided to pass in greatest part through line **11** with valve **12** to manifold **13** connected by line **14** to the inlet of pumps **15** for delivery by the pumps through line **16** to the solution inlet **43** of primary heater **8**; and to pass through line **17** provided with valve **18** to a manifold line **19** connected by line **20** to a pickling solution storage tank **21**, which may be buried in the ground.

As an example of the pickling solution concentrations which may be maintained, the aqueous solution leaving the primary heater **8** may be by weight 30% sulfuric acid and 10% ferrous sulfate, while the used acid leaving the pickling tanks will have a lower acid and higher ferrous sulfate content, say 29% and about 11% respectively. The change in concentrations will of course depend upon condition of the steel, rate of solution circulation through the tanks and other such variables.

Preferably the capacity of tank **21** is great enough to store the entire volume of solution in the system. By means of valves **5**, **12** and **18** flow of solution relative to each tank in the battery may be controlled and, if desired, cut off at an individual tank of the battery for repairs or other purposes. Further, to permit the solution conditioning section of the system to be operated during any time when it may be advantageous to shut down all or substantially all of the pickling battery, and also to give greater flexibility of operation, there are a valve **22** between manifold lines **6** and line **7** and a valve **23** between manifold line **19** and line **20** for isolating the pickling battery, a line **24** with valve **25** between storage tank **21** and pump inlet line **14** whereby solution may be delivered from tank **21** to heater **8**, and a by-pass **26** with valve **27** from outlet line **7** to line **20** for by passing heated solution from the heater to the storage tank.

The tanks **1**, **2** and **3** of the drawing represent generally any desired form of tank which may be adapted to the handling of the particular forms of steel or iron products of a given mill, and thus as the mill may require, may be of a form suitable for continuous countercurrent pickling of strip being rolled, or batch pickling of plates, rods, tubes and other forms. The pickling tanks **1**, **2** and **3**, the storage tank **21**, and the other apparatus components to be hereinafter described, preferably are of suitable acid resistant construction and materials, and are insulated to minimize loss of heat from solution therein.

The other major components of the pickling liquor reconditioning section of the system are an evaporator **30**, a crystallizer **31**, centrifuge **32**, strong acid storage tank **33** and secondary heater **34**. The evaporator **30** preferably is of a direct heating type, wherein the solution comes into direct contact with flame providing the heat energy, so that the flame releases energy directly to the solution, with the products of combustion and evaporated moisture being carried off together as evaporator flue gas. A submerged combustion evaporator is shown in the drawing and the process will be described primarily with reference thereto, but a tower evaporator wherein a spray of solution and flame are brought together, or an evaporator with conventional heating of the solution by heat transferred through a wall from the heating mechanism, may be used.

From storage tank **21** pickling solution drawn from the battery of pickling tanks is pumped through line **36** by pump **37** to the evaporator **30**, wherein it is heated to about 240° F. by submerged combustion burner **38** supplied with fuel through fuel line **39** and air through the compressed air line **40**. Flue gas at about 260° F., comprising the products of combustion and evaporated water pass from the evaporator through hot flue gas duct **41** to the primary heater **8**, wherein the gases pass upwardly through a section of suitable packing **42** countercurrently to the relatively cooler solution recirculated from the tanks by pumps **15** and introduced to heater **8** through liquid inlet **43** at temperatures which may be in the range, for example, of 130°–190° F. Water vapor, which may be 60% by volume or more in the flue gas, arising by evaporation of water from pickling solution and where the fuel contains combined or free hydrogen, as one of the products of combustion in evaporator **30**, is in great part condensed by the acid solution circulated through heater **8**, thereby allowing the recovery of latent heat of evaporation, while cooling of the other products of combustion results in further sensible heat recovery. Consequently heating of the recirculated solution and cooling of the flue gas is obtained. Hence the solution passing back to the tanks through lines **7** from the primary heater **8** is reheated to a temperature suitable for maintaining the desired pickling conditions, for example, at a temperature of 160° to as much as 200° F., and a great part of water evaporated at evaporator **30** is retained in the process.

The cooled gas stream from gas outlet of heater **8** say at 155°–190° F. is carried by duct **45** including a packed chamber **46** immediately above the gas outlet of heater **8** to a secondary heater **34** similar to heater **8**. Strong acid from the crystallizer **31** is, as hereinafter explained, to be combined with recirculated acid for return to the pickling battery. As this strong acid and make-up acid is delivered through a liquid inlet **47** of the packed chamber **46** to pass downwardly through the packing countercurrently to flue gas, a further absorption of water vapor from the cooled flue gas due to the relatively low water vapor pressure of the strong acid, results in a greater recovery of latent heat of evaporation. The strong acid leaving chamber **46** through duct **45** descends into the primary heater **8** to mix with the acid recirculated directly from the pickling battery by pumps **15**. Under some conditions of operation, due to the release of latent heat of vaporization, when strong acid absorbs water vapor from the flue gas, the flue gas stream may be reheated in **46**.

In secondary heater **34** partially cooled flue gas is further cooled before venting to the atmosphere through outlet **49** by passing upwardly through the packed section **50** thereof countercurrently to water introduced at inlet **51**, the resultant heated water, which may be at 135° to 170° F., being conducted from the secondary heater outlet by

line 52 to a hot water storage tank 53. A part of this hot water is fed as make-up water as required through line 54 by a pump (not shown) to line 16 for mixing with the acid circulated to heater 8, and the remainder may be directed through line 55 to hot rinse tanks (not shown) beyond the pickling battery for use in rinsing pickled steel. Make-up acid may be fed continuously at 59*a* to chamber 46 to replace acid lost as by drag-out at the pickling tanks and the formation of iron sulphates. Although not shown in the drawing, it is to be understood that provision may be made to return used acid-bearing rinse water from the hot rinse tanks to the pickling system at heater 8.

As another form of direct contact heating, a tower type evaporator may be used having a chamber into which a spray of the solution and a flame are injected for direct contact; a packed section wet by a stream of additional solution into which the hot gases produced in the spray chamber are passed to effect concentration of the additional stream and, in some degree, quenching of the hot gases; and a sump for collecting the solution concentrated in the spray chamber and packed section. A conventional evaporator, such as a Svenson evaporator, may be used but usually with a loss of the advantages of the direct heating types. In any case the flue gases from the direct heating evaporators or the water vapor stream produced in the conventional evaporator are directed to the primary heater for use therein as the heating medium.

The primary heater 8 may be of the more conventional type of heat exchanger, wherein the recirculated solution from line 16—with, if desired, strong acid from the lines 59 and 59*a*—is passed through tubes surrounded with flue gases or water vapor produced in the evaporator to effect heat transfer from the flue gases to the liquid and condensation of water vapor from the flue gases. The resulting condensate is then combined with the solution passed through the heater to restore evaporated water to the process.

In evaporator 30, operating in the ranges of solution acid concentration of about 40% to 60% and solution temperature of about 220°–250° F. with a flue gas temperature of 230°–270° F. for submerged combustion, water is evaporated from the solution to attain an acid and ferrous salt concentration and temperature causing formation of a crystalline ferrous sulfate salt, preferably the monohydrate. For example, if the solution is evaporated by submerged combustion to a sulfuric acid concentration of about 50% by weight with a temperature of about 240° F., the monohydrate salt will be formed under conditions where the solubility is approximately 10 grams per liter of solution. From the bottom of evaporator 30 concentrated pickling solution, with fine ferrous sulphate monohydrate crystals thrown down by the concentration, is continually drawn through line 55 by pump 56 for introduction at the central portion of crystallizer 31, where further crystallization and growth of ferrous sulphate monohydrate takes place. In order that the crystalline material may be removed rapidly from the environment of the burner, thereby minimizing any tendency to fuming of the acid and decomposition of the crystals in the evaporator, clear concentrated acid is returned to the evaporator from the top of the crystallizer through line 61 with control valve 62 in such volume as permits rapid circulation through the evaporator. At high operating temperature and acid concentration the anhydrous ferrous sulfate salt may be formed.

The crystallizer may be of suitable form known to the art adapted to effect crystal growth and settling of the crystals to the bottom of the apparatus for withdrawal and provided with a dam or overflow tray for discharging clarified mother liquor, that is, strong acid solution, from the top portion of the body of liquid therein. The salt settling to the bottom is drawn off continuously through the bottom of the crystallizer to centrifuge 32 where crystals and accompanying mother liquor are separated, the salt being discharged to a storage bin 66 and the mother liquor being returned through line 57 by pump 58 to the crystallizer. Make-up acid may be introduced to the crystallizer through 65, as well as at 59*a*, which may be of advantage to decrease solubility of ferrous sulfate in the crystallizer under some conditions of operation. Strong acid solution, continuously removed from the top of the crystallizer through the overflow tray, is returned at a temperature nearly that of the evaporator liquid, by pumps if necessary, through strong acid line 59, to the packed chamber 46 to effect ultimate recombination with the acid being recirculated directly through heater 8 to the pickling battery without concentration. The strong acid line 59 may, however, be joined to line 7 to mix the strong acid with acid recirculated from the tanks, after the latter has passed through the primary heater 8. Hot water from tank 53 may be used to wash the centrifuged crystals and any further operations, as drying, may be used to put the monohydrate salt in desired condition. Thus, iron salts are continuously removed from the pickling solution, so that the solution passing to the battery is reconditioned both by diminishing the iron salt content and by continuously supplying heat and makeup acid. Strong acid solution may also be drawn from the crystallizer through line 64 to the strong acid storage tank 33 for storage and for delivery therefrom as required, either to all the tanks equally or in diverse amounts to individual tanks, should it be desired that different acid concentrations be used among them.

During normal pickling operations the usual flow of liquid is that indicated in the drawings by the solid arrows. The greater portion of the solution leaving the pickling battery is diverted to heater 8, the remainder to evaporator 30. Since it is desirable to avoid extensive fuming of the acid solution in the evaporator, the acid concentration is preferably kept from exceeding 50%. Therefore, control of the temperature of the solution returned to the pickling battery in a particular system involves the ratio of solution diverted to heater 8 and evaporator 30, the amount to the evaporator being increased to permit greater heat input and evaporation without exceeding the preferable 50% maximum acid concentration. The evaporator can, of course, be operated at lower acid concentration, say 45% acid with no untoward change in general operating conditions since the solubility of the monohydrate is quite low at such acid concentration. With a given heat demand, which determines the heat input at the evaporator, if it should be necessary to remove more iron salt, the solution feed to the evaporator may be decreased to drop out or precipitate more iron salts by increasing the acid concentration at which the evaporator operates. Feeding 60°–66° Baumé makeup acid into the crystallizer at 65 will increase the acid concentration therein and so decrease iron salt solubility. With provision of means for removing from the flue gas the fumes evolved by sulfuric acid when heated and concentrated above the aforementioned preferable 50% concentration, the evaporator may be operated at such temperature and acid concentration that anhydrous ferrous sulfate is produced.

The continuous flow of pickling solution through the tanks is of further advantage where tubes, rods and other such shapes are pickled, since the tanks are readily designed so that the solution flow is directed lengthwise through the batches of such form in a tank to insure uniform, complete pickling of all surfaces.

If it is desirable to shut down the pickling line for any time, the valve 22 between lines 6 and 7 may be closed and valves 25 and 27 in by-pass lines 24 and 26 opened and set as needed, to circulate solution between heater 8 and tank 21 as indicated by dashed arrows, so that the reconditioning section of the pickling system may continue to operate, with valves 14*a* and 23 being closed after the tanks are drained. The pickling tanks thus may be emptied completely while the entire body

of solution may be circulated in the reconditioning section. Thus the operating conditions of the system and the pickling solution may be maintained substantially normal, for immediate resumption of pickling operation when the battery is put back in operation. With the storage tank 21 of sufficient capacity, the entire battery of pickling tanks may be immediately emptied, and stored under insulated conditions, even when for some reason, the solution heating components are not kept in operation.

The specific operating conditions of the apparatus and process of course are variable as required for the pickling solution concentrations, temperature and flow required by the condition of the metal being pickled, the ranges hereinbefore given being illustrative of those useful in normal hot pickling operations.

I claim:

1. In a continuous process of pickling steel and the like with a heated aqueous sulfuric acid pickling solution, the cyclic steps of passing a stream of reconditioned pickling solution produced in a subsequent step at desired temperature and acid content continuously in contact with the metal being pickled, thereby forming a used pickling solution; continuously concentrating a first portion of said used solution by direct contact flame heating to effect crystallization of a ferrous sulfate salt therein; separating the resultant concentrated solution and ferrous sulfate crystals; combining a second portion of said used solution and said concentrated solution with makeup acid and water being introduced to the process; and continuously bringing the combined solution into intimate contact with the water vapor and combustion products arising from the concentration step to condense and absorb water vapor therefrom thereby producing and heating said stream of reconditioned pickling solution.

2. In a continuous process of pickling steel and the like with a heated aqueous sulfuric acid pickling solution, the steps of passing a stream of reconditioned pickling solution, produced in a subsequent step at desired temperature and acid content, continuously in contact with the metal being pickled, thereby forming a used pickling solution; continuously concentrating a first portion of said used solution by direct contact flame heating to effect crystallization of ferrous sulfate monohydrate therein; separating the resultant concentrated solution and ferrous sulfate monohydrate crystals; combining a second portion of said used solution and said concentrated solution with makeup acid and water being introduced to the process; and continuously bringing the combined solution into intimate contact with the water vapor and combustion products arising from the concentration step to condense and absorb water vapor therefrom thereby producing and heating said stream of reconditioned pickling solution.

3. In a continuous process of pickling steel and the like with a heated aqueous sulfuric acid pickling solution, the steps of passing a stream of reconditioned pickling solution of desired temperature and acid content continuously in contact with the metal being pickled, thereby forming a used pickling solution; continuously concentrating a first portion of said used solution by submerged combustion heating to effect crystallization of ferrous sulfate monohydrate therein; continuously separating the resultant concentrated solution and ferrous sulfate monohydrate crystals; combining a second portion of said used solution and said concentrated solution with makeup acid and water being introduced to the process; continuously bringing the combined solution into intimate contact with a stream of hot water vapor and combustion products arising from the concentration step to condense and absorb water vapor therefrom thereby producing and heating said stream of reconditioned pickling solution and producing a residual stream of partially cooled combustion products and water vapor; and continuously bringing said residual stream into direct intimate heat exchange contact with a relatively cool water stream to heat said water stream as a source of said makeup water.

4. A process for regenerating a used aqueous sulfuric acid pickling solution for re-use in pickling steel and the like at desired temperature and acid concentration, comprising the steps of continuously concentrating a first portion of said used solution by submerged combustion heating to effect crystallization of a ferrous sulfate salt therein; separating the resultant concentrated solution and ferrous sulfate salt crystals; continuously combining a second portion of said used solution and said concentrated solution with makeup acid and water being introduced to the process to reestablish the desired solution concentration; and continuously bringing the combined solution into intimate contact with the water vapor and combustion products arising from the concentration step to condense and absorb water vapor therefrom and thereby produce a regenerated pickling solution of the temperature and acid concentration desired for re-use.

5. In the process of pickling steel and the like continuously with a heated sulfuric acid pickling solution, the steps of passing a stream of pickling solution, continuously regenerated by subsequent steps at desired temperature and acid content, in contact with metal being pickled thereby forming a used pickling solution; dividing the used solution into a first and second stream and continuously heating the first stream of the used solution for evaporating water therefrom to effect crystallization of a ferrous sulfate salt and to produce an evaporator gaseous effluent containing water vapor; separating ferrous sulfate salt crystals from the evaporated solution to produce continuously a strong acid solution stream; continuously mingling the strong acid solution with said second stream to form a combined stream of solution; continuously transferring heat energy from said evaporator gaseous effluent to one of the said second and combined streams; and returning the combined stream to the first step.

6. In the process of pickling steel and the like with a heated sulfuric acid pickling solution, the steps of passing a stream of pickling solution, continuously regenerated by subsequent steps at desired temperature and acid content, in contact with metal being pickled thereby forming a used pickling solution; dividing the used solution into a first and second stream and continuously heating the first stream of the used solution for evaporating water therefrom to effect crystallization of a ferrous sulfate salt and to produce an evaporator gaseous effluent containing water vapor; separating ferrous sulfate salt crystals from the evaporated solution to produce a strong acid solution stream; continuously mingling the strong acid solution with said second stream to form a combined stream of solution; continuously transferring heat energy and water vapor from said evaporator gaseous effluent to one of the said second and combined streams; and continuously returning the combined stream to the first step.

7. In the process of pickling steel and the like with a heated sulfuric acid pickling solution, the steps of passing a stream of pickling solution, continuously regenerated by subsequent steps at desired temperature and acid content, in contact with metal being pickled thereby forming a used pickling solution; dividing the used solution into a first and second stream and continuously heating the first stream of the used solution for evaporating water therefrom to effect crystallization of ferrous sulfate monohydrate and to produce an evaporator gaseous effluent containing water vapor; separating ferrous sulfate monohydrate crystals from the evaporated solution to produce continuously a strong acid solution stream; continuously mingling the strong acid solution with said second stream to form a combined stream of solution; adding make-up acid to one of said streams; continuously transferring heat energy from said evaporator gaseous effluent to one

of the said second and combined streams; and returning the combined stream to the first step.

8. In the process of pickling steel and the like with a heated sulfuric acid pickling solution, the steps of passing a stream of pickling solution, continuously regenerated by subsequent steps at desired temperature and acid content, in contact with metal being pickled thereby forming a used pickling solution; dividing the used solution into a first and second stream and continuously heating the first stream of the used solution to a temperature of from about 220° F. to about 250° F. for evaporating water therefrom to effect crystallization of a ferrous sulfate salt and to produce an evaporator gaseous effluent containing water vapor; continuously separating ferrous sulfate salt crystals from the evaporated solution to produce a strong acid solution stream; mingling the strong acid solution with said second stream to form a combined stream of solution; continuously transferring heat energy and water vapor from said evaporator gaseous effluent to one of the said second and combined streams; and continuously returning the combined stream as regenerated solution to the first step.

9. In the process of pickling steel and the like with a heated sulfuric acid pickling solution, the steps of passing a stream of pickling solution, continuously regenerated by subsequent steps at desired temperature and acid content, in contact with metal being pickled thereby forming a used pickling solution; dividing the used solution into a first and second stream and continuously heating the first stream of the used solution for evaporating water therefrom to effect crystallization of a ferrous sulfate salt from an evaporated solution of from about 40% to 60% by weight sulfuric acid concentration and to produce an evaporator gaseous effluent containing water vapor; continuously separating ferrous sulfate salt crystals from the evaporated solution to produce a strong acid solution stream; mingling the strong acid solution with said second

stream to form a combined stream of solution; continuously transferring heat energy and water vapor from said evaporator gaseous effluent to one of the said second and combined streams; and continuously returning the combined stream as regenerated solution to the first step.

10. In the process of pickling steel and the like with a heated sulfuric acid pickling solution, the steps of passing a stream of pickling solution, continuously regenerated by subsequent steps at desired temperature and acid content, in contact with metal being pickled thereby forming a used pickling solution; dividing the used solution into a first and second stream and continuously heating the first stream of the used solution to a temperature of from about 220° F. to about 250° F. for evaporating water therefrom to effect crystallization of a ferrous sulfate salt from an evaporated solution of from about 40% to 60% by weight sulfuric acid concentration and to produce an evaporator gaseous effluent containing water vapor; continuously separating ferrous sulfate salt crystals from the evaporated solution to produce a strong acid solution stream; mingling the strong acid solution with said second stream to form a combined stream of solution; continuously transferring heat energy and water vapor from said evaporator gaseous effluent to one of the said second and combined streams; and continuously returning the combined stream as regenerated solution to the first step.

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