

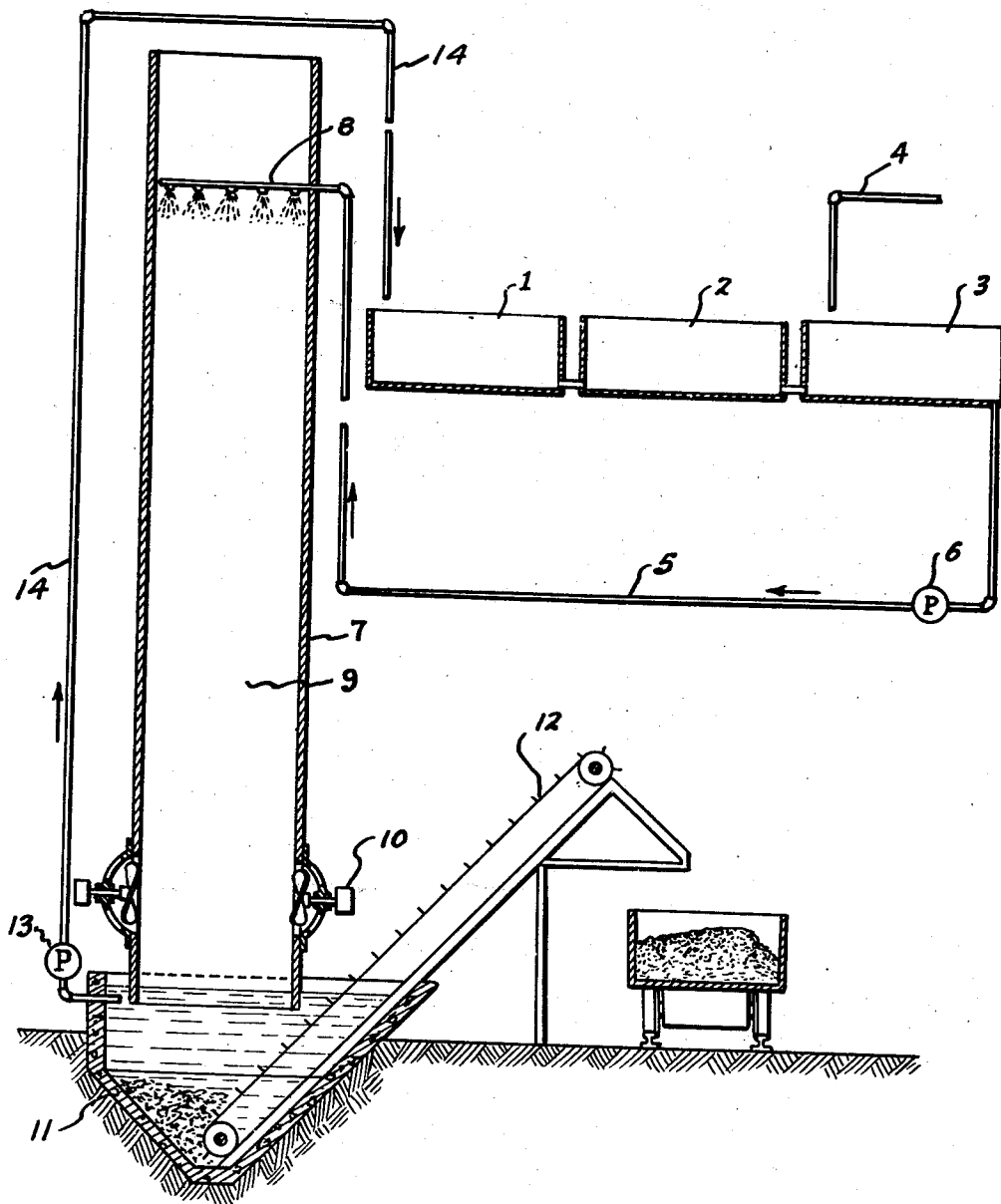
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PICKLING PROCESS

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PICKLING PROCESS

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Our invention relates to the pickling of metal sheets, and in particular to the pickling of iron, steel and ferrous alloys with a pickling agent the primary constituent of which is sulphuric acid.

5 The general pickling practice, as is well known, is to dip, or wash iron or steel sheet material or other articles in, or to pass such articles through, a solution of sulphuric acid. The operation of pickling results in the gradual depletion of the acid and the gradual building up in the solution of a relatively high concentration of ferrous sulphate. The ferrous sulphate slows down the pickling speed even if the acid concentration is artificially maintained; it has a tendency to produce deposits upon the sheets, and has other disadvantages. Consequently, the practice has been to use a pickling bath, with increasing times of treatment for the sheets, until it becomes commercially uneconomical to use it longer, and then dispose of it.

Whether the so-called spent pickle liquor is merely dumped, or whether an attempt is made to neutralize the acid remaining in it, it will be clear that large quantities of useful acid are lost. For example, starting with an acid concentration of around 6 to 10%, in a normal pickling operation at 180° to 200° F., when the ferrous sulphate content has risen as high as 14% and the acid has fallen as low as 5%, the practice is to dump the spent pickle liquor as being of no further commercial value. The loss of the 5% of acid is not compensated by any value in by-products which can be recovered from the spent pickle liquor.

35 The practice of dumping spent pickle liquor makes for stream pollution, and has been the subject of legislative notice. No very feasible plan for its disposal has hitherto been suggested. Neutralization is of value, so far as rendering the pickle liquor innocuous is concerned, but it is expensive, and still leaves a waste disposal problem. Various schemes for the removal of ferrous sulphate from the spent pickle liquor while leaving the acid have been suggested. Thus it has been proposed to concentrate the spent solution by evaporation so as to precipitate a considerable quantity of the ferrous sulphate, afterward diluting the solution, making up its acid concentration to full strength, and reusing it. Also it has been proposed to cause ferrous sulphate to precipitate by refrigerating the spent pickle liquor. Cyclical or continuous processes utilizing one or both of these schemes have been worked out. However, it will be apparent that the apparatus

and energy costs of these processes make them uneconomical; they are cumbersome; and, when it is remembered that the relative quantities of ferrous sulphate which can be precipitated in these ways is small, leaving in the regenerated solution a relatively high ferrous sulphate content, it will be seen that the pickle liquor provided by them is slow and inefficient. No such processes have, so far as we are aware, come into general use.

The fundamental objects of our invention comprise a solution of the problems presented by this state of facts. Another fundamental object of our invention is the provision of a cyclical or continuous process for the renewal of spent pickle liquor in which the energy and apparatus costs are negligible, and in which the salvaging alone of the acid lost in the usual practice represents a great saving in the cost of pickling (nearly one-third of the acid lost) and in which the value of any by-products recovered is an incidental advantage. These and other objects of our invention which will be apparent to one skilled in the art upon reading these specifications we accomplish by that certain process and by apparatus of which we shall now describe an exemplary embodiment. The drawing, to which reference will later be made, is a diagrammatic showing of an apparatus with which our process may be carried on.

Our process is premised upon the discovery that rapid and efficient pickling may be carried on in a new range. Specifically we have found that with ferrous sulphate contents ranging between 13 and 16% or thereabout, a pickling solution may be obtained which in its action is as fast as or faster than a normal pickling solution, providing the acid concentration is increased to a range of between 18 to 20%. The values given are the precise values of the ranges at which we prefer to operate. Some variation either or both ways is possible, as will presently be apparent. By the use of the words "thereabout" or "substantially" in these specifications and in the claims which follow, we contemplate variations of 1 to 2 additional percentums in either direction; but otherwise the values given are quite critical and our results will not be obtained if they are departed from radically.

Based on the discovery as set forth, an entirely new process possibility arises. For example starting with an acid content in a pickling solution of substantially 20% and a ferrous sulphate content of substantially 13%, and operating at a tem-

perature of 180° to 200° F. pickling may be done at normal or faster than normal rates at least until the ferrous sulphate content has reached substantially 16% and the acid concentration has fallen substantially to 18%. But, with such high concentrations of ferrous sulphate, the ferrous sulphate content may be reduced from substantially 16% to substantially 13% by merely cooling the liquor to room temperature, the excess ferrous sulphate precipitating out. The acid content will be made up to substantially 20% by addition of fresh acid.

This gives a cyclical or continuous process,—or even a batch process if desired,—requiring very little apparatus and no energy for evaporation or refrigeration. In fact no energy at all is required except for circulation and reheating the cooled solution. No acid is lost, and the saving in acid alone amounts to about one-third the acid cost. Crystalline ferrous sulphate or copperas is a by-product, and has a market value.

In the drawing, as an exemplary showing of apparatus and process, we have shown at 1, 2, and 3 a series of pickling tanks, interconnected for circulation, forming a continuous pickler through which strip material of sheet width and in the form of an endless band, for example, may be passed in the order of the numerals. Pickling solution is introduced into tank 1 with an acid concentration of substantially 20% and a ferrous sulphate content of substantially 13% and flows through the tanks in order. The solution is introduced hot, and/or suitable means are provided to maintain its temperature in the tanks. The rate of flow of the solution through the tanks is such, taken in connection with the rate of passage of the strip therethrough, as to build up the concentration of ferrous sulphate in the third tank to substantially 16%, and normally to reduce the acid concentration to 18%. We prefer to add acid to the third tank (when three are used) or at some point during actual pickling so as to bring the acid concentration back to substantially 20%. The addition of acid before precipitation of copperas not only assists somewhat in the precipitation, but makes pickling conditions nearly uniform throughout the pickling part of the cycle. The acid may be added through a pipe 4. The addition of acid prior to precipitation is not, however, a necessary limitation upon our invention.

At the end of the pickling part of the cycle, the liquor is delivered by means of a conduit 5 and, if necessary, a pump 6, to cooling means. Any suitable means for cooling the liquor to or nearly to atmospheric temperature may be employed. We have shown a tower 7, in the form of an open stand pipe. The liquor may advantageously be sprayed into the tower as at 8. For cooling purposes it is well to pass air through the tower in counter current to the liquor. For this purpose we have indicated a fan at 10.

At the bottom of the tower there is a tank 11 in which precipitation takes place. A scraper conveyor 12, or other suitable means may be provided to remove the precipitated copperas for such disposal as may be desired.

The liquor, which by these means has had its ferrous sulphate content reduced is returned to the first of the pickling tanks by means of a pump 13 and conduit 14. The process is thus a continuous one in the exemplary embodiment, in which the pickle liquor in the pickling part of the cycle is maintained at full strength, in

which there are no added power costs excepting the cost of circulating the liquor and blowing air through the tower, and in which atmospheric cooling only is employed.

As to the cooling, with the conditions substantially as set forth above, it is sufficient to effect the desired precipitation of copperas if the liquor is cooled from the working range of substantially 180° to 200° F. to a temperature of about 83° F. or lower. It will be seen that this is readily possible the year round in most climates by mere atmospheric cooling. If climatic conditions are unfavorable at any particular time of the year, especially when the atmospheric temperature is well above 83° F. and the humidity is very high, it will be possible to resort to various means to effect the desired cooling. Thus the air, before its passage into the tower may be dried by well known means, so that a heightened degree of evaporation in the tower will cool the liquor below atmospheric temperature. Also a slight degree of artificial cooling or refrigeration may be employed, including not only mechanical refrigeration but also the use of natural sources of cool water and the like. It will be seen, however, that the cost of such expedients is greatly reduced because it is only necessary to cool the pickle liquor to a temperature of 83° or thereabout.

The recovered copperas has a market value. It may be washed or centrifuged and sold as such; or may be converted into fresh sulphuric acid by substantially that well known process which employs pyrites as a starting material. Even if there were no value in the copperas as such, however, our process not only solves the acid disposal problem but effects a substantial saving in operating costs over the usual process in which no regeneration is attempted, and over the regenerative processes which have been suggested in the past.

Having thus described our invention in an exemplary embodiment, what we claim as new and desire to secure by Letters Patent is:

1. A pickling process for iron and steel using sulphuric acid and involving continuous regeneration of the pickle liquor, said process including the steps of carrying on the pickling operation within a temperature range of substantially 180° to 200° F., within an acid range of substantially 18% to substantially 20% of sulphuric acid, and within a ferrous sulphate range of substantially 13% to substantially 16%, continuously withdrawing the pickle liquor at a ferrous sulphate concentration not higher than substantially 16%, and cooling said pickle liquor to a temperature not substantially higher than 83° F. whereby to reduce its ferrous sulphate concentration to substantially 13%, and continuously returning the pickle liquor so treated for re-use.

2. A pickling process for iron and steel using sulphuric acid and involving continuous regeneration of the pickle liquor, said process including the steps of carrying on the pickling operation within a temperature range of substantially 180° to 200° F., within an acid range of substantially 18% to substantially 20% of sulphuric acid, and within a ferrous sulphate range of substantially 13% to substantially 16%, continuously withdrawing the pickle liquor at a ferrous sulphate concentration not higher than substantially 16%, cooling said pickle liquor to a temperature not substantially higher than 83° F. whereby to reduce its ferrous sulphate concentration to sub-

stantially 13%, and continuously returning the pickle liquor so treated for re-use, the said cooling being accomplished by spraying said pickle liquor in a column of air.

3. A pickling process for iron and steel using sulphuric acid and involving continuous regeneration of the pickle liquor, said process including the steps of carrying on the pickling operation within a temperature range of substantially 180° to 200° F., within an acid range of substantially 18% to substantially 20% of sulphuric acid, and within a ferrous sulphate range of substantially 13% to substantially 16%, continuously withdrawing the pickle liquor at a ferrous sulphate concentration not higher than substantially 16%, and cooling said pickle liquor to a temperature not substantially higher than 83° F. whereby to reduce its ferrous sulphate concentration to substantially 13%, continuously returning the pickle liquor so treated for re-use, and prior to the cooling as aforesaid, adding to said pickle liquor the quantity of acid necessary to raise its content to substantially 20% sulphuric acid.

4. A process of pickling iron and steel using sulphuric acid, which comprises circulating a pickle liquor continuously through at least one tank, said pickle liquor containing sulphuric acid in percentages continuously ranging between substantially 18% and substantially 20%, and containing ferrous sulphate in percentages continuously ranging between substantially 13% and substantially 16%, while maintaining the pickle liquor in said tank at a temperature range between substantially 180° to substantially 200° F., continuously withdrawing said pickle liquor from said tank and cooling it to a temperature at least as low as substantially 83° F., whereby to precipitate therefrom any ferrous sulphate in excess of substantially 13%, returning the pickle liquor thus treated continuously to said tank, maintaining the acid content thereof within the range stated by adding acid thereto, and pickling iron or steel by immersing it in said tank.

5. A process for the continuous pickling of iron and steel using sulphuric acid, which involves

circulating a pickle liquor through a series of pickling tanks, and between said series of pickling tanks and a regeneration apparatus, said pickle liquor containing sulphuric acid in percentages between substantially 18% and substantially 20%, and ferrous sulphate in percentages between substantially 13% and substantially 16%, maintaining said pickle liquor at a temperature ranging between substantially 180° and substantially 200° F., and in said regeneration apparatus treating said pickle liquor by spraying it in a column of air so as to reduce its temperature to at least as low as 83° F., whereby to precipitate therefrom any excess of ferrous sulphate over substantially 13%, returning the pickle liquor thus treated to said pickling tanks and reheating it to said first mentioned temperature range, and continuously passing through said tanks iron or steel material to be pickled.

6. A process for the continuous pickling of iron and steel using sulphuric acid, which involves circulating a pickle liquor through a series of pickling tanks, and between said series of pickling tanks and a regeneration apparatus, said pickle liquor containing sulphuric acid in percentages between substantially 18% and substantially 20%, and ferrous sulphate in percentages between substantially 13% and substantially 16%, maintaining said pickle liquor at a temperature ranging between substantially 180° and substantially 200° F., and in said regeneration apparatus treating said pickle liquor by spraying it in a column of air so as to reduce its temperature to at least as low as 83° F., whereby to precipitate therefrom any excess of ferrous sulphate over substantially 13%, returning the pickle liquor thus treated to said pickling tanks and reheating it to said first mentioned temperature range, and continuously passing through said tanks iron or steel material to be pickled, the acid concentration of said liquor being maintained by additions of sulphuric acid prior to said spraying step.

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