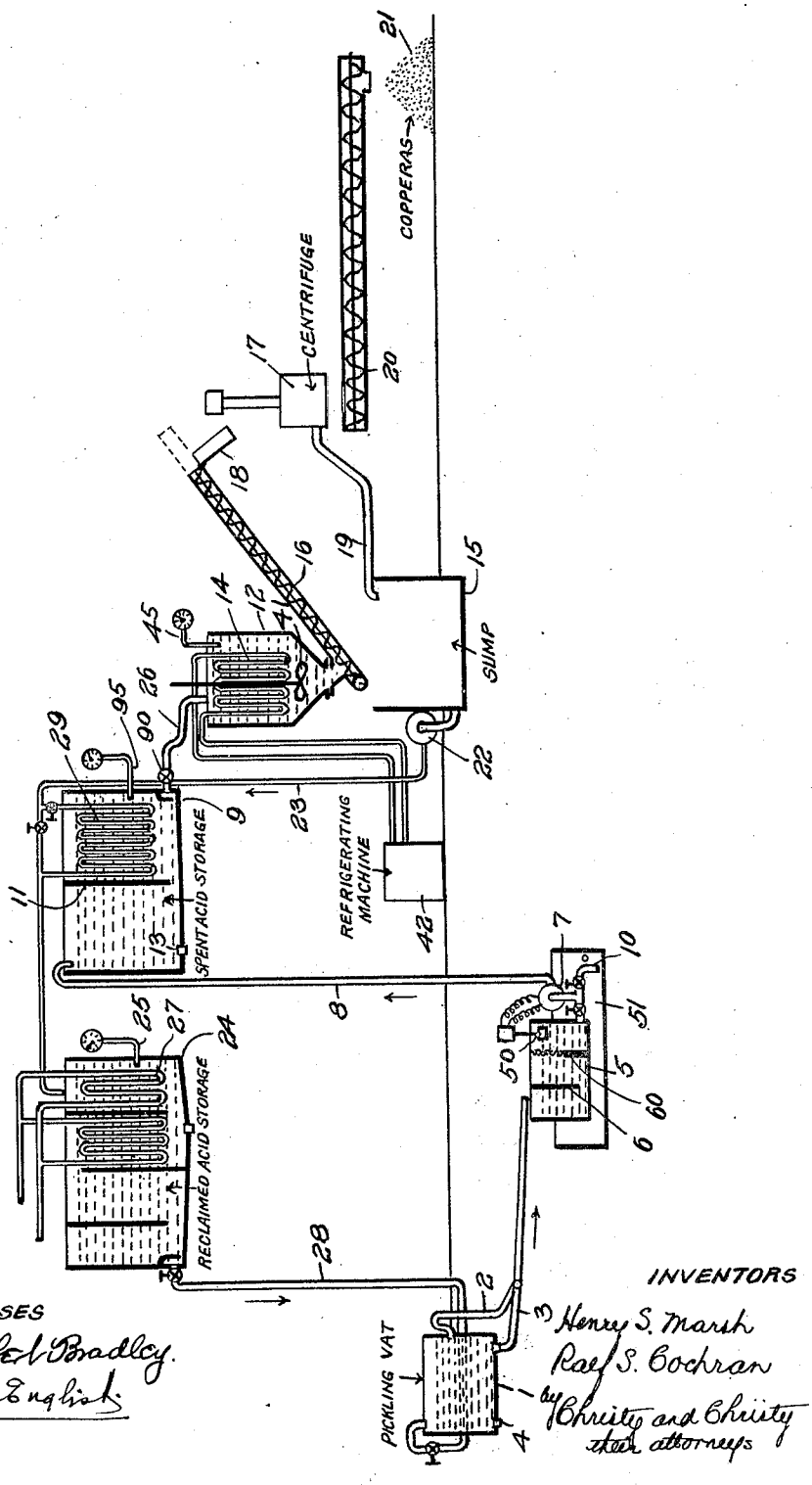
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METHOD OF RECLAIMING SPENT PICKLING SOLUTIONS

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METHOD OF RECLAIMING SPENT PICKLING SOLUTIONS.

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In Letters Patent of the United States, granted February 22, 1921, and reissued June 7, 1921, Re. 15,119, and in Letters Patent No. 1,450,216, granted April 3, 1923, we have described and claimed a method of reclaiming spent pickling solutions. The second of the said patents concerns certain improvements on the first. Our present invention has to do with further improvements.

In the accompanying drawing an installation in which our invention may be performed is diagrammatically shown.

A pickling vat is indicated at 1, and in it, as will be understood, the pickling operation takes place. The pickling solution is essentially a weak solution of acid, ordinarily sulphuric acid, and as the operation of pickling progresses the sulphuric acid reacts with the metal of the articles under treatment, forming, in the typical case of the pickling of steel articles, iron sulphates. These salts, so derived, go into solution as they are formed, and their presence in solution in the pickling bath tends to retard the continuance of the reaction. A point is reached when the solution is no longer serviceable, and yet it contains, not iron sulphates only in solution, but appreciable quantities still of unconverted acid. It is with the enfeebled and unserviceable pickling solution that we have to do. It is not only uneconomical for the steel manufacturer to throw this spent pickling solution away as waste, but, as a practical matter, this material, escaping as inevitably it must into the drainage system of the locality, will polute the water of streams, rendering it destructive to life. We deal with the spent solution, remove from it its burden of metallic salt, and return its free acid content again to the pickling vat, where, so liberated, it is again effective. We so conduct our operations that the metal salt is recovered as copperas, in the form of finely divided crystals, and in a condition of relatively great purity. So recovered, the copperas is marketable, and proportiontely the steel-making operation is rendered less costly.

From the pickling vat 1 we withdraw the spent pickling solution through either the pipe 2 or the pipe 3. The pipe 2, it will be observed, acts as an overflow pipe. The pipe 3 is adapted to drain the vat. Pipe 2, then, is adapted for the practice of our invention in continuous operation: fresh supplies of acid continuously enter the vat at one end (as presently will be explained) through pipe 28, while at the other end the depleted solution is continuously being withdrawn through pipe 2. This is our preferred procedure. Alternately, through pipe 3 the entire contents of vat 1 may from time to time when the effectiveness of the acid is spent be withdrawn, and, after the vat has so been emptied, it will be understood that a fresh supply of acid may be introduced. It will be observed that in the drawing the overflow pipe 2 is shown to emerge from vat 1 through a gooseneck. This expedient may be adopted, in order to withdraw the solution from a point below the surface, without disturbing the layer of foam which for reasons not now important the manufacturer may desire to maintain upon the surface of the pickling bath within the vat. If, as may be the case, the maintenance of a layer of foam upon the surface of the bath in the pickling vat be not desired, the goose-neck in pipe 2 need not be employed. For, if the goose-neck be present, floating impurities will accumulate in the vat, and it is preferable that these be carried to tank 5, where, as presently will be explained, provision is made for their removal. In any case, however, such large floating articles as splinters from the walls of the vat, floating to the surface, will be removed from vat 1.

The vat 1 may additionally be provided with a bottom vent 4 having a removable closure, through which (the opening to the pipe 3 being at the time closed) the vat may be cleaned when there is need.

From the vat 1 the spent solution is led, conveniently by gravity, to a receiving tank 5. In this tank adventitious solid objects may be removed, and to that end the tank is shown to be provided with a partition 6, affording passage beneath only, and with a second partition 60, ported at a point elevated from the bottom. Thus both floating and sinking matter may be removed from the liquid to be treated. The tank 5 maintains a pool, whence the spent solution may be pumped to an elevated tank 9. The flow

of solution from tank 5 to tank 9 is through a pipe 8. The solution which flows through pipe 8 is hot, and the conditions of installation (remoteness of tank 9 from tank 5, for example) may be such that the solution within pipe 8 is liable to be chilled and in consequence the pipe liable to become clogged with precipitated crystals. Against such danger we take preventive measures. The pump arranged in pipe 8 for causing the solution to flow from tank 5 to tank 9 is advantageously a pump of centrifugal type, indicated at 7. The pipe 8 and the pump 7 tend to drain, when tank 5 is empty, back into the tank. The pump 7 is so placed that, so long as the tank 5 is full, it is submerged, and therefore primed. Automatic means may be provided, as by a float 50, for setting the pump in operation when the liquid in tank 5 rises to a certain level. When the quantity of liquid in tank 5 fails and the surface recedes to the level of the opening into pipe 8, pipe 8 and pump 7 immediately drain back into the tank. A valve-controlled branch 10 from pipe 8 may be employed, through which such quantities of solution as overflowing from tank 5 may have collected in the pit 51 in which the tank is advantageously situated, may be pumped into tank 9.

The tank 9 is elevated, that the liquid may descend from it by gravity through the reclaiming apparatus. It may be provided with a partition 11, arranged to permit passage of fluid beneath it only, as additional means of removing floating foreign substances from the liquid which advances for further treatment. The bottom of tank 9 may be sloped to an orifice 13 with a removable closure, through which orifice the tank may on occasion be washed out. Within the tank 9, on the delivery side of partition 11, a coil 29 may be arranged, through which coil, the reclaimed solution may be caused to flow. And, in operation, fresh supplies of acid may at this point be introduced, all as presently will be more fully explained. It is, manifestly, unnecessary to show special apparatus for introducing fresh supplies of acid to tank 9.

From tank 9 through a conduit 26 the liquid passes to a crystallizing tank. This crystallizing tank may, within the knowledge of the art, be built either for continuous or for intermittent operation. By way of example, and not as a limitation upon our invention in its broader aspect we show a tank 12, for intermittent operation. This tank 12 is filled and emptied in continuing alternation as operation progresses. Accordingly, escape from tank 9 is under the control of a manually operated valve 90. The conduit 26 is preferably in the form of an open trough, because the liquid at this stage in its progress has become chilled to a temperature not greatly exceeding the point of crystallization, and since within the range of variation in actual working conditions there may on occasion be such a wide and unintended departure from normal that crystals will form within this conveyor, it is made accessible for the removal of such crystalline growth.

Within the crystallizing tank 12 are arranged cooling coils 14 and an agitator 41. The cooling coils carry any suitable cooling fluid, as, for instance, ammonia from a compressor 42. The agitator keeps the body of solution within the tank in motion and very greatly increases the effect of the cooling coils upon it. The result is that finely divided copper as crystals rain from the solution, descend by gravity, and are directed by the hopper-shaped bottom of tank 12 to a conveyor 16.

This conveyor, shown in preferred form as a screw conveyor, carries the crystals as they are formed to a centrifuge. When, in the course of treatment of a tank-full of solution within tank 12, the delivery of crystals fails, the operator by that fact has advice that the operation has been carried to its practicable limit. He then opens manually a closure which is provided for a bottom orifice in tank 12 and the liquid within the tank then escapes to a sump 15. This liquid is pickling solution, relieved of its adulterating burden of sulphate of iron in solution. Furthermore, the crystallization of copperas has effected the removal of a large quantity of water, so that the liquid which passes to the sump is (regardless of the acid additions, preferably made in tank 9) good usable pickling solution, of strength not far from normal.

It would be quite possible to cause sump 15 to serve immediately as a storage tank, from which in properly measured quantities the reclaimed solution might be returned to the pickling vat 1; but, preferably, a storage tank 24 is interposed, to which the solution may be pumped from sump 15, and from which it may pass to the vat. The pump 22 employed for pumping may be a centrifugal pump arranged with relation to the sump after the same manner as has been described of pump 7; that is to say, adapted to be submerged and so primed as the sump fills, and adapted to drain into the sump when the sump is empty. The bottom of tank 24 may for purposes of cleaning be particularly constructed in the manner already described with respect to tank 9.

The stream on its way to storage tank 24 may by obvious connections provided with controlling valves be carried either directly to the tank 24, or through the coil 29 within tank 9, already described. The coil within tank 9 constitutes a heat exchanger, the hot liquid which otherwise fills tank 9 gives up

to the advancing stream of reclaimed solution part of its heat, bringing it nearer to the crystallization point, and bringing the reclaimed solution within the coil nearer to service temperature.

Within the storage tank 24 the solution may by means of steam coils 27 be brought to service temperature.

And, if copper or analogous adulterant be present to an annoying extent, iron sulphide may be introduced in tank 24. The use of iron sulphide is explained in our co-pending application, Serial No. 749,981, filed November 14, 1924.

The reclaimed and properly prepared solution is returned to the pickling vat 1 through pipe 28. This pipe is valve-controlled, to the end that the rate of supply may be properly determined and varied.

Recording thermometers 95, 45, and 25 may be provided for tanks 9, 12, and 24, that, according to the readings, valves may be adjusted and speeds changed, to establish most advantageous conditions.

Within the pickling vat itself temperature may be maintained by suitable means. We find the injection of superheated steam practically adequate; the desired temperature may thus be maintained with relatively little dilution.

The separated copperas crystals are intermittently delivered to a centrifuge 17. A convenient arrangement is that particularly shown in the drawing. The conveyor trough is prolonged to an extension 18 which swings between the discharge position shown in full lines and the discharge-withholding position indicated in dotted lines. The crystals are (so far as concerns the operation of the centrifuge) continuously advanced upward along the conveyor 16, and, the extension 18 being in its full-line position, this stream of crystals as it advances is spilled through extension 18 to the centrifuge. The centrifuge at this time is rotating slowly. When the centrifuge is thus fully loaded, the extension 18 is swung to the dotted-line position, and the centrifuge is spun rapidly, separating from its load the liquid component. Following upon this the remaining crystalline content is discharged from the centrifuge to a suitable receptacle, as for example the conveyor 20. The centrifuge thus relieved of its load is immediately made ready for reloading. Thereupon the extension 18 upon the conveyor 16 is swung again to full-line position, and the charging of the centrifuge recommences. The continued delivery of crystals through the conveyor 16 has meanwhile accumulated in the elevated extension 18.

The discharge of the conveyor 16 is at a higher level than that of the liquid in tank 12, to the end that much of the liquid may drain from the crystals, before they advance through extension 18 to the centrifuge.

From the centrifuge the separated liquid is returned through a conductor 19 to sump 15, while the crystals are conveyed, as by the instrumentality indicated at 20, to the place of delivery 21.

Operation is as follows. Understanding the plant to be in operation, and the vat 1 to be receiving successive charges of material to be pickled, the vat is full of pickling solution which constantly is undergoing chemical change; the acid is combining with iron, forming sulphates which as they are formed go into solution. Fresh acid in properly measured quantities is entering vat 1 through pipe 28, while at the remote end of the vat, spent solution in corresponding quantities is passing out through pipe 2. This escaping spent solution collects initially in tank 5, where solid bodies of one sort and another, chiefly splinters of wood from the walls of the pickling vat, are for the most part removed, and whence the solution is pumped to the elevated tank 9. As it is pumped, and as it collects in tank 9 the solution is appreciably cooled, and here again it may be remarked that the parts are so arranged that, in case of failure of supply, the pipe 8 and pump 7 will empty automatically, and solution will not remain to effect precipitation of crystals upon their walls.

Within tank 9 the solution is further cooled —notably so, if the return flow is through coil 29, as ordinarily it will be. Thus the solution is brought approximately to the temperature of crystallization. Incidentally, and this is an important feature and itself a matter of invention, fresh supplies of acid, such as may be required to afford to vat 1 a solution of the desired degree of concentration, are at this point introduced. Hitherto such fresh supplies of acid have been added only after the burden of copperas has been removed from the solution. We have found no disadvantage in introducing it at this earlier point; and, on the other hand, we have gained a notable advantage. For in the presence of an increased acid content the crystallization of copperas is more rapid and quantitively greater; the iron is more completely removed. And the quality is improved, for the crystals grown in such a strongly acid solution are of pure copperas, no ferric sulphate is present. The acid, so introduced may advantageously be of a strength of 60° Baumé.

From tank 9 the solution is drawn off periodically in charges which fill the crystallizing tank 12. In this tank crystallization is effected and from it the crystals and the unburdened liquid are carried in op-

posite courses. The temperature to which in tank 9 the liquid is reduced is normally from twenty to thirty degrees higher than the point of crystallization. We have found that if such be its temperature, the liquid in entering tank 12 will prevent the accumulation of crystals upon the coil 14. It is desirable that the coil 14 within tank 12 be kept clean, because its cooling effect upon the liquid within tank 12 is then more immediate, and, other things being equal, under practical conditions a range of cooling—say from 100° to 30° is effected.

The liquid is now proper for pickling; it is indeed a solution of greater strength than the pickling operation requires; but, being eventually introduced into a larger body of solution in vat 1 whose acid strength is in process of wasting away, it serves to compensate for the waste, and to keep the strength normal. The solution in sump 15 needs only to be heated, and this is by the means described accomplished in tank 24, to which the solution is pumped, and, ordinarily the stream of liquid while on its way is heated somewhat in passing through the coil 29. In tank 24 a metallic sulphide, ordinarily iron sulphide may be introduced, and the pickling solution, reacting upon it, will generate sulphuretted hydrogen. The sulphuretted hydrogen in turn will react upon salts of undesired metals (copper, for example) which may be present, and produce insoluble salts of the undesired metals. These being precipitated will separate by gravity, and the clear solution of proper acid strength and at proper temperature may in suitable quantities be returned to vat 1.

In the centrifuge the crystals are dried to about 1.5% moisture. There is no rinsing of the crystals with water. The copperas crystals which we produce are superior, because they are precipitated from a clean and acid solution, and because they are permitted to retain a small amount of moisture. If the acid were rinsed from them, or if they were thoroughly dried, they would immediately undergo change; they would in large part go over to undesirable ferric sulphate. Copperas crystals tend always to undergo this change, but our product, obtained in the manner we have described, and chiefly because of their purity and because of the small amount of free acid present upon the crystals, is safe against easy or early deterioration, and as a marketable product is of high excellence and commands a high price.

We claim as our invention:

1. In the reclaiming of spent pickling solution consisting of iron salts dissolved in weak sulphuric acid the method of procedure herein described which consists in adding to the spent solution a fresh supply of acid and removing from the so renewed solution its burden of copperas.

2. In the operation of pickling steel articles the procedure which consists in causing liquid to flow in closed cycle from the pickling vat and back to the pickling vat again, adding to the outflowing liquid fresh supplies of acid, removing from the so strengthened liquid its burden of copperas, and controlling the rate of return of the so reclaimed and strengthened liquid to the pickling vat.

3. The method herein described of reclaiming a pickling solution of sulphuric acid spent in reaction upon articles of iron, which consists in precipitating copperas by refrigeration, separating the clear solution from the precipitated copperas, reheating, causing the reheated solution to react upon iron sulphide, and separating again the clear solution from the precipitate.

4. The method herein described of reclaiming a pickling solution of sulphuric acid spent in reaction upon articles of iron, which consists in adding to the spent solution fresh supplies of acid, precipitating copperas by refrigeration from the so strengthened solution, separating the clear solution from the precipitated copperas, reheating, causing the reheated solution to react upon a metallic sulphide, and separating again the clear solution from the precipitate.

5. The method herein described of reclaiming a pickling solution of sulphuric acid spent in reaction upon articles of iron, and of obtaining copperas as a by-product in commercial condition, which consists in adding to the spent solution fresh supplies of sulphuric acid, precipitating copperas by refrigeration from the so strengthened solution, separating the clear solution from the precipitated copperas but leaving the copperas damp with dilute acid, and returning the clear solution to the pickling vat.

6. The method herein described of conducting a continuous operation of reclamation upon the pickling solution of dilute sulphuric acid used in the manufacture of iron and steel articles, which consists in withdrawing from one end of the pickling vat a stream of spent solution, adding to the so withdrawn solution fresh supplies of acid, precipitating by refrigeration from the so strengthened solution its burden of copperas, separating the clear liquid from the precipitate, heating it, returning it to the pickling vat at the end of the vat opposite to the place of withdrawal, and heating the solution within the pickling vat.

7. The method herein described of conducting a continuous operation of reclamation upon the pickling solution of dilute sulphuric acid used in the manufacture of iron and steel articles, which consists in

withdrawing from one end of the pickling vat a stream of spent solution, adding to the so withdrawn solution fresh supplies of acid, precipitating by refrigeration from the so strengthened solution its burden of copperas, separating the clear liquid from the precipitate, heating it, causing it to react upon a metallic sulphide, again separating the clear solution from the precipitate, returning it to the pickling vat at a point remote from the place of withdrawal mentioned above, and as operation progresses heating the solution within the pickling vat.

In testimony whereof we have hereunto set our hands.

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