May 25, 1937. J. W. BOSS 2,081,787

ELECTROLYTIC PROCESS AND APPARATUS FOR THE PRODUCTION OF CHROMIC ACID AND CAUSTIC ALKALI

Filed June 15, 1936

Fig. 1.

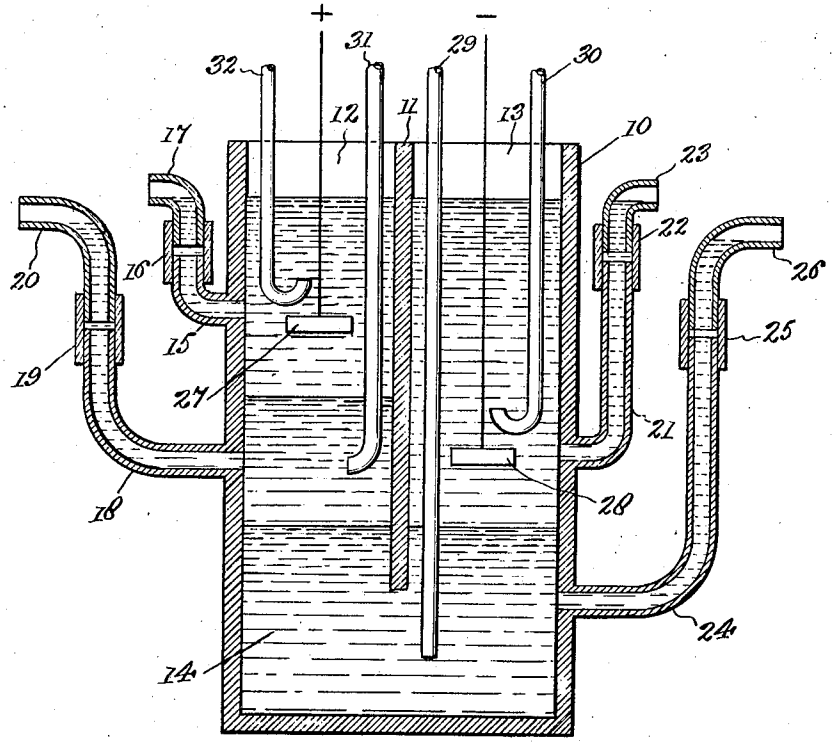
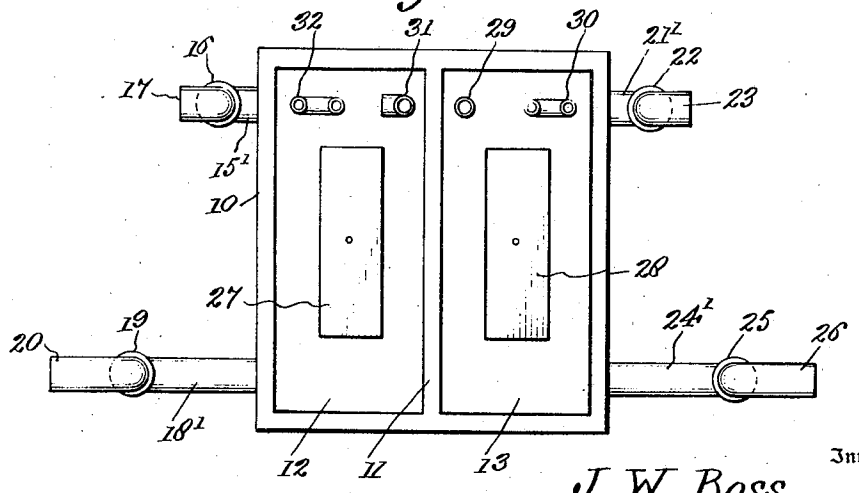


Fig. 2.



Inventor

J. W. Boss

By

Wilkinson & Mawhinney

Attorneys.

Patented May 25, 1937 2,081,787

UNITED STATES PATENT OFFICE

2,081,787

ELECTROLYTIC PROCESS AND APPARATUS FOR THE PRODUCTION OF CHROMIC ACID AND CAUSTIC ALKALI

John W. Boss, Livingston, Mont., assignor to Chromium Products Corporation, Livingston, Mont., a corporation of Montana

Application June 15, 1936, Serial No. 85,405

7 Claims. (Cl. 204—9)

The present invention relates to an improved electrolytic process and apparatus for the production of chromic acid and caustic alkali. This invention relates to an improvement in the process described in my co-pending application Serial No. 6904 and an improvement in the apparatus described in my co-pending application Serial No. 25,625.

An object of the present invention is to produce in a single cell pure chromic acid from a soluble chromate salt.

A further object is to overcome the defect caused by accumulation of sludge between the feed solution and the caustic alkali solution in cells of this type as heretofore known.

A further object is to revivify used chromium plating solutions.

Another object is to produce in a single cell both crude and finished chromic acid.

Still another object is to provide means for effecting more complete removal of basic sludge from the cell than has been possible by other means.

With the foregoing and other objects in view, the invention will be more fully described hereinafter, and will be more particularly pointed out in the claims appended hereto.

In the drawing, wherein like symbols refer to like or corresponding parts throughout the several views—

Figure 1 is a central vertical section of a cell in operating condition, and

Figure 2 is a top plan view of a modification of the cell in which the feed pipes do not lie in the same vertical plane.

This invention relates to a process and apparatus for the electrolytic production of chromic acid and of caustic alkali. In the prior art it is customary to produce chromic acid (CrO_3) by the action of an acid such as sulphuric on an alkali chromate or dichromate such as sodium chromate or dichromate. Separation of the chromic acid is accomplished by crystallization and draining off the mother liquor containing in solution other products of the reaction.

Some of the disadvantages of such a process are: That difficulty is encountered in removing other acid radicals from the chromic acid; and that the alkali originally combined as chromate or dichromate appears as a salt such as sodium sulphate. This salt is not of much value and is not suitable for use in preparing new quantities of sodium chromate.

When a used plating solution is revivified according to the procedure taught in the applications above mentioned some difficulty arises because of the precipitation of bases at the plane separating the caustic soda solution from the impure acid solution. As the acid solution underlies the caustic solution these bases or sludges tend to settle in the acid, redissolve and reprecipitate at the plane of separation. This cyclic behavior lowers the efficiency of the cell and requires an excessive flow of caustic soda solution to carry out the precipitates; it also requires closer supervision of the cell to regulate the removal of these precipitates. In the present invention as applied to revivifying used plating acid there is no contact between it and the caustic solution. Instead the caustic alkali solution floats on one part of an alkali chromate feed solution while an impure chromic acid solution floats on another part of the feed solution. The used plating acid is then mixed with pure chromic acid solution and floated on top of the impure chromic acid solution. The alkali chromate feed solution can be maintained neutral or nearly so and bases precipitated at its contact surface with the crude acid solution do not tend to redissolve but settle out towards the bottom of the feed solution.

In the drawing **10** designates the body of a cell which may be formed of glass, stoneware or other suitable material resistant to the corrosive action of the solutions employed. The cell **10** is divided longitudinally into two equal compartments by a partition **11** which extends down into the cell a substantial distance but stops short of the bottom of the cell. As shown the partition **11** extends about three-quarters of the way down into the cell. There are, therefore, formed two side compartments **12** and **13** communicating at their lower ends to form a common chamber or compartment **14**. The cell **10** is provided near the upper part of the compartment **12** with an overflow pipe **15**. A movable sleeve **16** connects the pipe **15** to the take off **17**. The distance between the take off **17** and the overflow pipe **15** may be regulated by means of the sleeve **16** to alter the rate of overflow from the compartment **12**. Also lower down in the compartment **12** but yet a substantial distance above the bottom of the partition **11** the cell **10** has a second overflow pipe **18** similarly provided with a sleeve **19** and take off **20**. In the compartment **13** approximately opposite to the overflow pipe **18** in the other compartment, is placed an overflow pipe **21** with sleeve **22** and take off **23**. At one side of the common compartment **14** and below the lower edge of the partition **11** is

placed another overflow tube 24 with sleeve 25 and take off 26. An anode 27 is suspended in the compartment 12 and a cathode 28 is suspended in the compartment 13. The anode 27 may be made of lead and the cathode 28 of iron, steel or copper. It will be noted that the anode 27 is positioned in the upper part of the compartment 12 at a region approximately opposite the overflow pipe 15 while the cathode 28 is placed lower in the compartment 13 approximately opposite the overflow pipe 21.

In the following description sodium chromate will be used as an example but it is to be understood that any alkali salt of chromic acid may be used. In filling the cell the compartment 14 is filled with a solution of sodium chromate of specific gravity, for example, 1.450. This solution is introduced through the feed pipe 29 and the solution is added until it fills the lower ends of the side compartments 12 and 13. In the compartment 13 on top of the sodium chromate solution is floated a caustic soda solution of, for example, specific gravity 1.200. This solution is added through the supply pipe 30 to substantially fill the compartment 13. In the other side compartment 12 is floated first a crude chromic acid solution of specific gravity, for example, 1.325. This solution is added through the feed pipe 31. The amount of this solution must be such as to extend from the top of the sodium chromate solution to some point below the anode 27. Finally, on top of this crude chromic acid solution is floated a pure chromic acid solution of specific gravity, for example, 1.200. This last solution is added through its feed pipe 32. It will be necessary, of course, in adding these various solutions to balance the heads of solutions in the opposite chambers so as to prevent mixing beneath the partition 11. It is also necessary, as soon as the solutions are added, that current be passed between the electrodes so as to prevent diffusion of the various solutions.

When the electrodes are connected to a suitable source of direct current the pure chromic acid solution loses basic ions to the impure solution on which it floats while the crude solution loses chromate ions to the solutions above it. The pure solution thus tends to increase in specific gravity while the impure solution loses in specific gravity. In view of this fact, it is necessary to regulate the specific gravity of the crude solution in order to prevent mixing with the pure solution as they tend to attain the same specific gravities due to the operation of the cell.

The crude solution receives from the sodium chromate solution underlying it, chromate ions and loses to the underlying solution alkali or basic ions. However, the crude solution loses chromate ions to the pure solution above it at a rate greater than the sodium chromate solution supplies these ions to it. It is, therefore, necessary to replenish the crude chromic acid solution from outside sources to maintain the supply of chromate ions. Such a source of the crude acid may be a simple cell such as described in my above identified applications. The caustic soda solution takes from the sodium chromate in the lower compartment basic ions and the solution in the compartment 13 increases both in volume and in density requiring drawing off and regulating of the density in order to maintain the plane of separation between it and the sodium chromate solution underlying it.

The sodium chromate feed solution decreases in volume due to loss of its ions as described and the plane of separation between it and the solutions floating above it moves downward toward the partition 11. It is, therefore, necessary to replenish this solution to prevent mixing of the solutions in the other compartments. The sodium chromate solution also tends to accumulate some caustic soda. Some basic substances such as aluminum, forming soluble compounds with the caustic soda, may also accumulate in this feed solution. In addition to this there is a sludge of insoluble basic materials which may appear at the separation plane between the sodium chromate and the crude chromic acid. This sludge is insoluble in the sodium chromate and eventually settles to the bottom of the cell where it lies until such time as the cell may be cleaned.

In operation of this cell it is of the utmost importance to maintain the planes of separation between the various solutions. Thus, if the sodium chromate feed solution be permitted to drop below the lower edge of the partition 11 the solutions in the side compartments will mingle and the contents of the cell destroyed. If, on the other hand, the sodium chromate solution be allowed to rise as high as the anode 28 evolution of gas will cause breaking of the plane of separation between it and the caustic soda solution. In the chamber 12 the sodium chromate solution must not rise higher than the feed pipe 31 and the overflow opening 18, which are both situated at the mid point between the lower edge of the partition 11 and the anode 27. A rise above that point would cause mixing of both feed and overflow with the sodium chromate solution. Similarly the plane of separation between the plain and crude chromic acid solutions must not drop as low as the opening of the feed pipe 31 or the opening of the overflow pipe 18 as this would cause mixing of the two chromic acid solutions. Also the plane between these acid solutions must not rise as high as the anode 27 for here gas evolution would destroy the plane of separation between the solutions.

In view of the requirement for regulating these planes of separation it will be seen to be necessary that some means of observing the planes be provided. Thus the cells themselves may be made of transparent material, for the various chromate solutions are readily distinguishable by color while the caustic soda is similarly distinguishable by its lack of color. An alternative means of observing the planes is to lower a glass tube into the cell, close the top and carefully withdraw it from the cell. The solutions carried in the glass tube will indicate by their color and planes of separation the relation existing in the cell between these solutions.

The most convenient way to operate this cell and the way for which the cell illustrated is intended is a continuous operation. It will be noted that the lower ends of the tubes 30, 31, and 32 are turned so as to direct the streams of incoming liquid away from the nearest plane of separation, the object being to avoid disturbing this plane. The feed pipes and overflow pipes are adjusted and connected with sources of solution to promote flow of these solutions through the cell to prevent a rise in specific gravity which would tend to destroy the planes of separation. The rate of overflow is adjusted by sliding the take off pipes in the sleeves so that more or less pressure will be required to force solution out of the cell.

The feed pipe 29 for the common chamber 14

communicates with a source of sodium chromate solution of the desired specific gravity and the supply is regulated to compensate for the rate of consumption of this solution in the cell. Also if the operation of the cell is being impaired by accumulation of insoluble impurities and by accumulating caustic soda in this chamber the volume of solution fed may be increased and the excess carried off through the overflow pipe **24**, this having the effect of flushing the chamber **14** of these impurities.

In operating this cell to revivify fouled plated solutions the cell is filled as described and the fouled solution introduced through the pipe **32** into the purified chromic acid layer. As pointed out above the chromic acid content of this purified layer will be increased by operation of the cell and the basic content will be decreased. These actions then purify fouled plating acid when it is introduced into the finished chromic acid layer. Since the cell is most conveniently operated by maintaining continuous flow of solution, a portion of the overflow from the pipe **15** is adjusted in specific gravity and returned to the cell through the feed pipe **32** along with a portion of the fouled acid to be purified. The portion of overflow which is not adjusted and returned is taken as product solution to be used in a chromium plating bath or for the recovery of chromic acid. In a similar manner a portion of the caustic soda solution removed through the overflow pipe **21** may be adjusted and returned through the feed pipe **30** while the remaining portion of the overflow may be withdrawn as caustic soda product solution.

Basic substances removed from the floating purified chromic acid layer in chamber **12** will be found as an insoluble mud in the feed solution in chamber **14** of the cell.

By a selection of the proper sizes of cells and current values, an acid making cell as herein described can be operated to treat solution from chromium plating cells so that the efficiency of the plating operation is maintained and the chromium content of the plating bath held constant.

In operating the cell it has been found that a current density of about 30 amperes per square foot of area of anode and of cathode chamber section works well.

Referring to Figure 2 a modification in the location of overflow pipes is seen. In this form the upper overflow pipes **15'** and **21'** are located near one end of the cell while the lower overflow pipes **18'** and **24'** are located near the opposite end of the cell. In other respects the construction is the same. The location of these overflow pipes, as well as the location of the feed pipes is subject to variation in a horizontal plane, the only requirement being that the vertical position of their outlets conform with the requirements of solution position.

It will also be apparent that the cell is not limited to the structure shown with regard to the number of anode and cathode chambers but that any desired number of these upper chambers may be provided communicating with a lower feed chamber. In such a case each anode and cathode chamber is provided with anode or cathode and with the various feed and overflow pipes.

It is obvious that various changes and modifications may be made in the details of construction and design of the above specifically described embodiment of this invention without departing from the spirit thereof, such changes and modifications being restricted only by the scope of the following claims.

What is claimed is:

1. An electrolytic process for the production of chromic acid and caustic alkali which comprises providing a feed solution of an alkali chromate, floating on said feed solution a less dense product solution of caustic alkali, floating on said feed solution independently of said caustic alkali product solution a solution of impure chromic acid less dense than the feed solution, floating on said impure chromic acid solution a less dense chromic acid product solution, and passing current consecutively through the solutions.

2. An electrolytic process for revivifying fouled chromic acid plating solutions which consists in continuously providing a feed solution of an alkali chromate, continuously providing a less dense cathode solution of caustic alkali floating on said feed solution, continuously providing a crude chromic acid solution less dense than the feed solution and floating on the feed solution out of contact with the cathode solution, continuously providing a chromic acid and fouled plating acid anode solution less dense than and floating on said crude chromic acid solution, passing current between the anode and cathode solutions, and continuously drawing off the anode solution purified by operation of the current.

3. In an electrolytic process for the production of chromic acid and caustic alkali from alkali chromates, the steps of, floating a cathode product solution of caustic alkali on an alkali chromate feed solution of greater density, floating out of contact with the cathode solution and also on said dense feed solution a less dense impure chromic acid solution, floating on said impure solution a still less dense anode product solution of pure chromic acid, and maintaining the various solutions at their proper volume and density values to retain the various floating relations among them.

4. In an electrolytic process for producing chromic acid and caustic soda, maintaining a feed solution of sodium chromate of specific gravity approximately 1.450, floating thereon a cathode product solution of caustic soda of specific gravity of approximately 1.200, floating also on said feed solution but out of contact with the cathode solution an impure chromic acid solution of specific gravity approximately 1.325, floating on said impure solution an anode product solution of pure chromic acid of specific gravity approximately 1.200, and passing electric current between the cathode and anode product solutions through the underlying solutions.

5. In an electrolytic process for the production of chromic acid from alkali chromate solutions in which the chromic acid product solution is less dense than and is floated on the alkali chromate solution and current passed between them, the step of maintaining a solution of chromic acid of intermediate density floating between the chromic acid product and the alkali chromate solutions.

6. In an electrolytic process for the production of chromic acid from alkali chromate solutions wherein independent product solutions of chromic acid and caustic alkali are floated on an alkali chromate feed solution of greater density and current passed between the product solutions through the feed solution; the step which

consists in maintaining a solution of chromic acid of intermediate density between the chromic acid product solution and the feed solution.

7. In an electrolytic process for the production of chromic acid and caustic alkali from alkali chromates, the steps of maintaining an alkali chromate feed solution, floating on said feed solution a caustic alkali cathode product solution of less density, floating also on said feed solution but out of contact with said cathode solution an intermediate solution of chromic acid of less density, floating on said intermediate solution a chromic acid anode product solution of still less density, continuously removing and adjusting each of said solutions to maintain the proper densities and returning the adjusted solutions, and passing electric current between the anode and cathode solutions through the underlying solutions.

JOHN W. BOSS.