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 PROCESS FOR THE ELECTROLYTIC PRODUCTION OF PERMANGANATE.
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Fig. I.

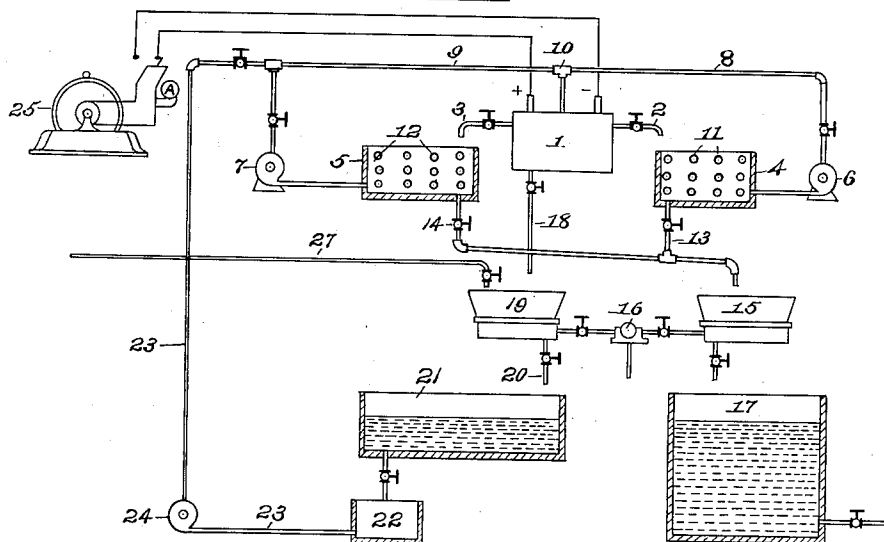
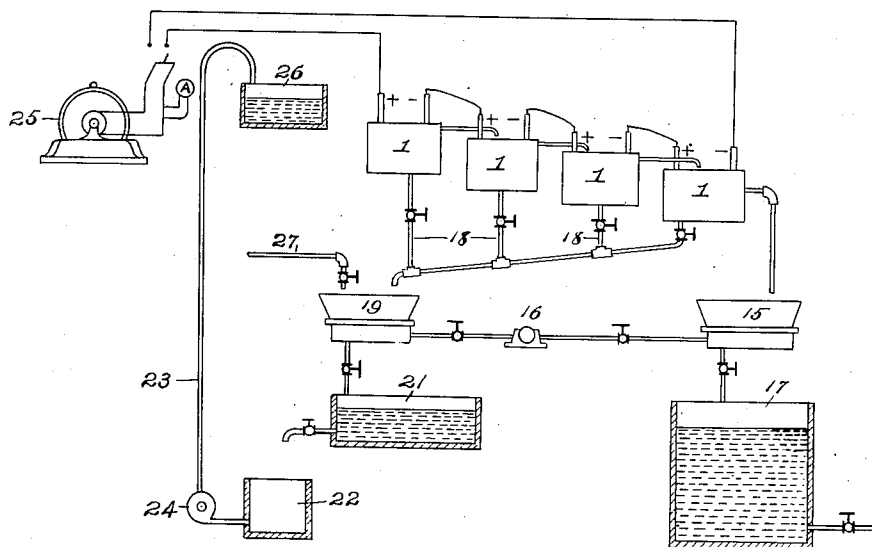


Fig. II.



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PROCESS FOR THE ELECTROLYTIC PRODUCTION OF PERMANGANATE.

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Specification of Letters Patent.

Patented Nov. 30, 1920.

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To all whom it may concern:

Be it known that we, ROBERT E. WILSON and WILLIAM G. HORSCH, citizens of the United States, and residing at Washington, in the District of Columbia, have invented Processes for the Electrolytic Production of Permanganate, of which the following is a specification.

Our invention relates to processes for the production of permanganate, more especially to processes wherein manganese is converted by oxidation into permanganate. More specifically, our improvements relate to processes wherein a manganese containing anode is electrolyzed in a suitable solution and our invention consists in improvements in the various steps and details of the process to make long continued, commercial operation feasible.

Many attempts have been made in the past to devise a method whereby permanganates, especially the alkali permanganates, could be produced electrolytically on a commercial scale. The attempts have generally not been successful and it is the object of our invention to improve the existing processes so as to eliminate the causes of failure of these processes. Our improvements consist in conducting the electrolysis with specially cast ferro-manganese anodes of special shape, removing the apparent passivity therefrom periodically, cooling the anolyte and circulating the same, regulating the composition and concentration of the electrolyte and avoiding a low alkali concentration. We have thus been enabled to utilize commercial ferro-manganese, which has hitherto not been considered feasible for permanganate production. By a system of circulation the process has been made continuous.

Much difficulty has been encountered in the electrolysis by reason of the large and rapid increase in voltage necessary to maintain the anodic oxidation of the manganese. It was observed that after 12-18 hours, the current efficiency became very low, being negative in some cases, i. e., the concentration of permanganate decreased, and the voltage rose to values not explainable by the diminution in conductivity due to migration of sodium to the cathode compartment. If the electrolysis was still carried on, the voltage rose so high as to make almost impossible any electrolysis at all. It was noted

that after long runs, the electrodes were covered with a firm, adherent coating consisting principally of manganese dioxide with some iron oxide. We considered that either this coating or the passivity exhibited by metals after electrolysis was responsible for the increase in voltage. To obviate this difficulty, we have discovered that periodically cleaning the surface of the electrodes, as by means of a sand blast approximately every 24 to 36 hours, almost entirely removes the apparent passivity of the anodes.

We have found that cooling the anolyte is important. In the earlier runs, where sufficient cooling had not been provided for, high temperatures (40°-50° C.) accompanied the high voltage which manifests itself when the anodes become passive. The low yields then obtained are attributed to the passivity rather than to the high temperature. In two experiments where the average temperature was 6.5°, the current efficiency was 1.5 to two times as great as at 25°. The voltage, though it was a little higher at the lower temperature, was nearly enough the same so that the energy consumption was decreased in about the same ratio as that in which the current efficiency was raised. The temperature to be selected, of course, is that at which the combined cost of energy and cooling is a minimum. At present, a temperature not far above room temperature seems to be most practical, since temperatures above 35° give poor results.

We have found that a high current density, 60-90 amperes per square foot, gives high efficiency. Higher current densities give equally good current efficiency but require too high a voltage.

Our process as applied to the production of sodium permanganate, consists in electrolyzing a solution of sodium hydroxid, sodium carbonate or sodium bicarbonate in a series of diaphragm cells, using specially cast anodes of commercial ferro-manganese (75-85% Mn). The diaphragms may be of asbestos paper strengthened by a perforated iron plate or of filtros or electrofiltros in the pores of which has been precipitated $\text{Fe}(\text{OH})_3$. Of the three electrolytes used, sodium hydroxid has the highest conductivity, but the carbonate and bicarbonates have the advantages of low cost and better current efficiency. The bicarbonate gives the

highest current yield of any electrolyte we have tried. A good procedure is to have a mixture of carbonate and bicarbonate as anolyte, using the hydroxid as catholyte to reduce cell resistance. We have found that when caustic alkali is used as anolyte, concentrations in the neighborhood of 2% are fatal to successful operation, and in practice an alkali concentration of 1-6% is always avoided. This applies even if the 2% free alkali be in the presence of a considerable excess of carbonate or permanganate.

We prefer to use sodium hydroxid as catholyte and sodium carbonate as anolyte, continuously circulating and cooling the same. The hydroxid has a lower resistance, but certain concentrations are detrimental; therefore we use the hydroxid as catholyte and allow it to heat up to decrease the cell resistance. Alkali carbonates have been found suitable anolytes, and since the oxidizing reaction goes on more rapidly, more efficiently, and more nearly to completion in the cold, the anolyte is cooled either by circulating it to and from cooling tanks or by coils in the anode chambers.

In the accompanying drawings, Figure 1 shows a diagrammatic arrangement of apparatus for carrying out the electrolysis while Fig. 2 shows an apparatus especially adapted for continuous operation.

A series of diaphragm cells is provided (Fig. 1), from the anode compartments of which extend valved overflow pipes 2, 3, to the cooling tanks 4, 5, whence pumps 6, 7 force liquid back through pipes 8, 9, 10 into the cells 1. Cooling coils 11, 12 are situated in the tanks 4, 5 respectively. In the bottom of the cooling tanks are valved drain pipes 13, 14 leading to the suction filter 15 operated by pump 16. Storage tank 17 receives the filtered permanganate liquor. A valved sludge pipe 18 leads from the bottom of the cells 1 to the suction filter 19 also operated by pump 16. A valved pipe 20 leads from the filter to the sludge wash tank 21. The dissolving tank 22 for carbonate is connected to the anode chambers by pipes 23 and pump 24 forces the solution into the cells. The generator 25 is the source of current. The modification shown in Fig. 2 differs from Fig. 1 mainly in that the cooling tanks, 4, 5 are omitted and cooling coils (not shown) are placed in the anode chambers of the cells arranged in cascade. A supply tank 26 is placed so as to give a continuous feed of electrolyte.

The following examples show how the process is carried out in practice when applied to the preparation of sodium permanganate.

I. Semi-continuous process.

A 12-17% solution of NaOH is placed in both chambers of cells 1 (Fig. 1) the anodes

and cathodes of which are ferro-manganese and iron respectively. The generator is started and controlled so as to maintain a potential of 7 volts and a current density of 70 amps. square foot in each cell. The anolyte is circulated through the pipe 2, cooling tank 4, pump 6, pipes 8 and 10, and cells 1. When the alkali concentration falls to 6-8%, the circulation is cut off and the anolyte is led into tank 5 where it is treated with an excess of solid NaHCO_3 or of CO_2 to quickly neutralize the alkali, since alkali contents in the neighborhood of 2% cause loss of permanganate. The liquid is again circulated through the cells as before, the electrolysis being continuous. By further successive additions of normal carbonate in the cooling tank 5 from time to time, a high concentration of NaMnO_4 can be produced. When the solution of permanganate has become of the desired or maximum strength, the valve pipe 13 is opened and the solution dumped into suction filter 15. The filtered permanganate collects in storage tank 17 for concentration or immediate use. The sludge of MnO_2 and $\text{Fe}(\text{OH})_3$ left on the filter is removed from time to time. At intervals the sludge from the bottom of the cells is tapped off and passed through the suction filter 19, washed with water from supply pipe 27 into the wash tank 21. Carbonate contained in 22 is dissolved in the weak wash liquor, from tank 21 and the solution elevated by pump 24 into the cells to be electrolyzed.

II. Continuous process.

The cathode chambers of cells 1 (Fig. 2) are filled with 20% NaOH solution. A 15% (nearly saturated) solution of Na_2CO_3 is placed in supply tank 26 and in the anode chambers of the cells and the current started. The solution is run continuously from the supply tank to the anode chambers of the cascaded cells successively until it is sufficiently concentrated with permanganate. Then it is tapped from the last cell 1 into the suction filter 15 where the sludge is removed. The permanganate solution goes to storage tank 17 for use. From time to time the sludge from the bottom of the cells is tapped off as in example one and the weak permanganate washings saturated with carbonate and returned to supply tank 26. This process is continuous.

It is to be understood that, although we have described the semi-continuous process in connection with Fig. 1 the apparatus there shown is not limited to the semi-continuous process but is well adapted to the continuous process also. In the claims below the term "carbonate" is used to denote the normal carbonate, bicarbonate and mixtures of the two. The term "acid carbonate" is intended to include both bicarbonate and carbonic acid.

Having thus described our invention we claim as new:

1. A continuous process for the electrolytic production of permanganate which consists in electrolyzing a solution of a salt of an inorganic acid giving an alkaline reaction as anolyte, with a hydroxid as catholyte and an anode containing manganese, continually adding said salt solution, and circulating the electrolyte.

2. A continuous process for the electrolytic production of permanganate which consists in electrolyzing alkali metal carbonate solution as anolyte with caustic alkali solution as catholyte and an anode containing manganese, continually adding alkali carbonate solution, and circulating the electrolyte.

3. A continuous process for the electrolytic production of permanganate which consists in electrolyzing an alkali metal carbonate solution as anolyte, with caustic alkali solution as catholyte and an anode containing manganese, continually adding alkali carbonate solution, cooling the anolyte, and circulating the electrolyte.

4. A continuous process for the electrolytic production of sodium permanganate which consists in electrolyzing a concentrated sodium carbonate solution as anolyte, with caustic soda solution as catholyte and an anode containing manganese, continually adding sodium carbonate solution, cooling the anolyte, and circulating the electrolyte.

5. A continuous process for the electrolytic production of permanganate which consists in maintaining a circulation of alkali carbonate from anode chamber to anode chamber of a cascade of cells containing ferro-manganese anodes, cooling the anode chambers, maintaining a high current density in the cells, and periodically treating the anodes to prevent apparent passivity and increase of voltage.

6. A continuous process for the electrolytic production of sodium permanganate which consists in maintaining a circulation of sodium carbonate from anode chamber to anode chamber of a cascade of cells containing ferro-manganese anodes, cooling the anode chamber to below 30° C., maintaining an anodic current density of approximately 70 amperes per square foot in the cells, sand-blasting the anodes approximately every 36 hours, maintaining a caustic soda catholyte and allowing the same to heat up.

7. A continuous process for the electrolytic production of permanganate which consists in establishing a concentrated caustic alkali solution in both anode and cathode chambers of a cell having anodes containing manganese, electrolyzing the same until the alkali concentration is relatively low, adding an excess of an acid carbonate to quickly neutralize the alkali in the anolyte,

adding normal carbonate to the anolyte while circulating and cooling the same, continuing the electrolysis meanwhile, adding carbonate periodically, and removing permanganate solution from the circulating anolyte.

8. A process for the electrolytic production of permanganate which consists in electrolyzing a concentrated hydroxid solution with anodes containing manganese, until the hydroxid concentration is relatively low and then adding an acid salt to quickly neutralize the hydroxid.

9. A process for the electrolytic production of permanganate which consists in electrolyzing a concentrated caustic alkali solution with anodes containing manganese, until the caustic alkali concentration is relatively low and then adding an excess of an acid carbonate to quickly neutralize the alkali.

10. A process for the electrolytic production of permanganate which consists in electrolyzing a concentrated caustic alkali solution with anodes containing manganese, until the caustic alkali concentration drops to approximately 6%, and then adding an excess of an acid carbonate to quickly neutralize the acid.

11. A process for the electrolytic production of permanganate which consists in electrolyzing a concentrated caustic alkali solution with anodes containing manganese, until the caustic alkali concentration drops to approximately 6%, adding an excess of an acid carbonate to quickly neutralize the alkali, and continuing the electrolysis of the solution.

12. A process for the electrolytic production of permanganate which consists in electrolyzing a concentrated caustic alkali solution until the concentration drops to approximately 6%, circulating and cooling the electrolyte meanwhile, then quickly neutralizing the caustic alkali, by adding an acid carbonate, and continuing the electrolysis of the solution.

13. A process for the electrolytic production of permanganate which consists in electrolyzing a concentrated caustic alkali solution until the concentration drops to approximately 6%, circulating and cooling the electrolyte meanwhile, then quickly neutralizing the caustic alkali by adding an acid carbonate, continuing the electrolysis of the solution, and repeatedly treating the solution with carbonate and electrolyzing continuously until the permanganate produced is of the desired concentration.

14. A process for the electrolytic production of sodium permanganate which consists in electrolyzing a concentrated caustic soda solution until the concentration drops to approximately 6%, circulating and cooling the electrolyte meanwhile, then quickly

neutralizing the caustic soda with bicarbonate of soda or carbon dioxid, continuing the electrolysis, and repeatedly treating the solution with sodium carbonate and electrolyzing continuously until the desired concentration of sodium permanganate is obtained.

15 15. In a process of producing permanganate, electrolyzing the anolyte at a temperature of approximately 5° C.

10 16. In a process for the production of permanganate, electrolyzing a cooled anolyte and a heated catholyte.

15 17. A step in the process for the electrolytic production of permanganate which consists in electrolyzing concentrated alkali

carbonate as anolyte with alkali hydroxid as catholyte.

18. A step in the process for the electrolytic production of sodium permanganate which consists in electrolyzing concentrated sodium carbonate as anolyte with sodium hydroxid as catholyte. 20

19. In the process for the electrolytic production of permanganate by electrolyzing a caustic alkali solution with a manganese containing anode, the step which consists in interrupting the electrolysis of the solution when the caustic alkali content becomes relatively low. 25

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