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ELECTROLYTIC PROCESS FOR PREPARING MANGANESE AND MANGANESE DIOXIDE SIMULTANEOUSLY

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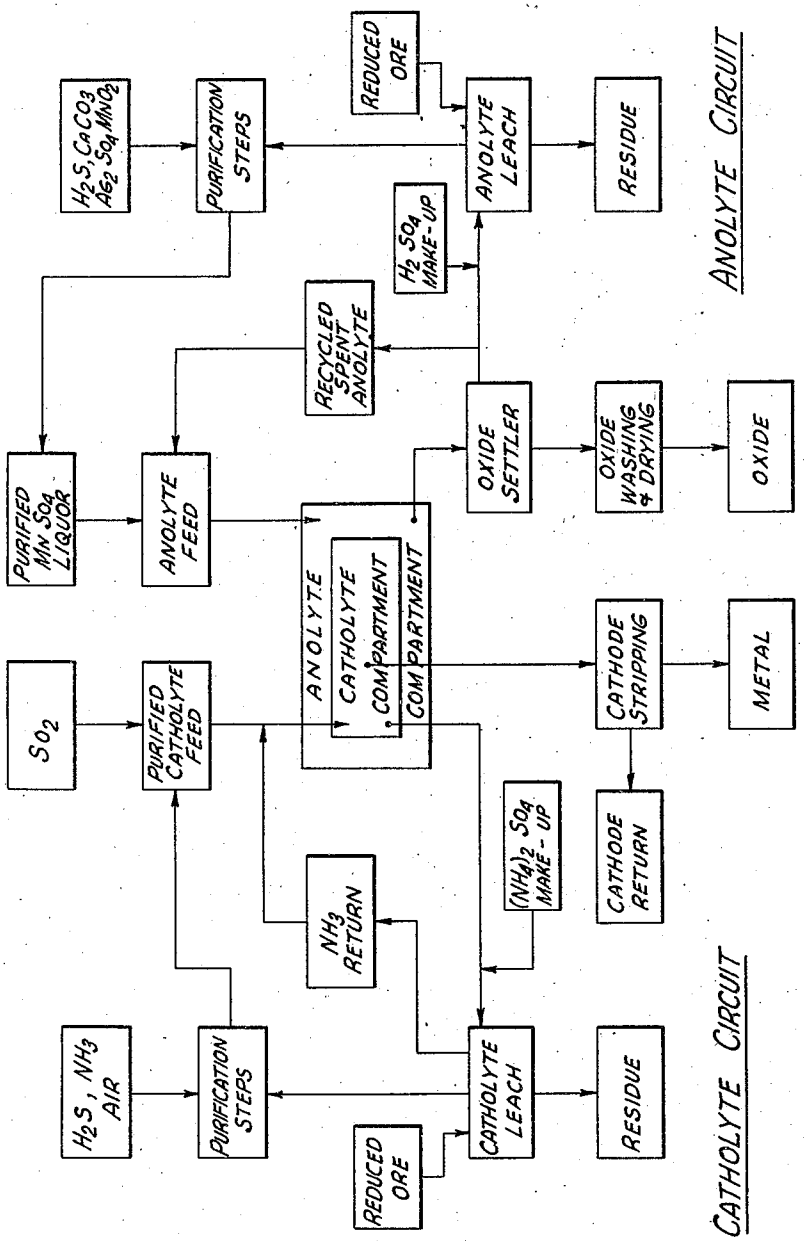

INVENTORS
THOMAS A. MITCHELL
DONALD C. MITCHELL

BY Watson, Bristol, Johnson & Leavenworth
ATTORNEYS

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ELECTROLYTIC PROCESS FOR PREPARING MANGANESE AND MANGANESE DIOXIDE SIMULTANEOUSLY

Thomas Austin Mitchell and Donald Cooper Mitchell, Torrance, Calif., assignors to American Manganese Corporation, Dover, Del., a corporation of Delaware

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8 Claims. (Cl. 204—96)

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The invention relates to a process for the winning of manganese. More particularly, it pertains to the deposition of metallic maganese and formation of manganese dioxide and includes correlated improvements and discoveries whereby their production may be enhanced.

An object of the invention is to provide a process whereby metallic manganese and manganese dioxide are simultaneously formed.

A further object of the invention is the provision of a process in accordance with which metallic manganese is deposited in a catholyte and manganese dioxide simultaneously formed in an anolyte of differing compositions.

An additional object is to provide a process for the winning of manganese and formation of manganese dioxide in which constancy of action and of concentration of catholyte and of anolyte are maintained.

Another object of the invention is to provide a process for the simultaneous deposition of manganese and formation of manganese dioxide which may be readily, effectively and economically carried out to a desired commercial extent.

A still further object of the invention is the provision of a process whereby metallic manganese is deposited and manganese dioxide formed under the influence of an electric current with continuous formation and removal of manganese dioxide.

A more particular object of the invention is to provide a procedure which entails retention of manganese values in a catholyte and in an anolyte by separate contacting thereof with a mass containing manganous oxide, as a reduced manganese ore.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others thereof, which will be exemplified in the process hereinafter disclosed, and the scope of the invention will be indicated in the claims.

In the practice of the invention a deposition of metallic manganese and simultaneous formation of manganese dioxide is effected under the influence of an electric current. The manganese is produced on a cathode from an alkaline catholyte containing manganese sulfate and ammonium sulfate, and formation of manganese dioxide is brought about at an anode in an anolyte containing manganese sulfate and sulfuric acid. The cathode and anode are immersed in

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the electrolytes in separate compartments, these compartments being set up through utilization of a diaphragm of slight porosity.

A principal feature of the procedure resides in the simultaneous and continuous electrolysis of two different electrolytes, one on each side of a porous diaphragm. As above indicated, the catholyte liquor contains manganese sulfate and ammonium sulfate and, in addition thereto, there may be a content of free ammonia and this electrolyte is continuously electrolyzed to form metallic manganese. The presence of free ammonia leads to a reaction thereof with sulfate ions to form ammonium sulfate. A factor in the procedure is the maintenance of an excess of free ammonia in the catholyte. A continuous flow of catholyte through a catholyte chamber of the electrolytic apparatus is occasioned through circulation, and there is also a separate circulation and hence continuous feed of the anolyte to, through and from an anolyte chamber. The anolyte is an acidified manganese sulfate solution of known strength containing sulfuric acid, and the electrolysis results in a continuous formation of manganese dioxide with production of sulfuric acid taking place at the same time.

As a result of the formation of manganese dioxide the manganese sulfate concentration is decreased, whereas that of the sulfuric acid increases and reaches a value at which it is desirable to circulate the electrolyte through the anolyte chamber, and by so doing formed manganese dioxide in suspension is continuously removed. The diaphragm which sets up independent anolyte and catholyte chambers in the electrolytic apparatus is of a slightly porous material, which may be ceramic, and it acts mainly as a carrier of the electric current between the anode and the cathode and does not permit any marked migration of sulfuric acid or of sulfate ions from the cathode to the anode chamber. This has been demonstrated in practice inasmuch as the amount of free ammonia required to maintain the desired concentration in the catholyte is directly proportional to the amount of manganese deposited. Moreover, the amount of manganese dioxide formed in the anolyte is directly proportional to the amount of sulfuric acid produced therein.

A carrying out of the procedure brings about the simultaneous production of pure metallic manganese and high grade manganese dioxide in amounts which occasion an appreciable reduction in power cost, especially with respect to deposition of manganese metal. Effective opera-

tion of the process requires one kind of electrolyte about the cathode and another about the anode, with separation thereof by, desirably, a ceramic diaphragm which may constitute a rectangular vessel or tank containing the catholyte with the cathode immersed therein. The electrolytic apparatus or cell can be operated with a number of diaphragms, for example, up to 10, and the space about them is occupied by the anolyte in which the anodes are immersed, then being one more anode than cathode. A separate continuous flow or circulation of catholyte and anolyte may be maintained through the cell in order to retain the proper concentration of manganese between the electrodes, and more particularly with respect to the anode in order to remove the manganese dioxide produced. The catholyte, by suitable means, may be distributed to the various cathode chambers and recollected or reassembled as it flows from them. A like arrangement may be utilized for introduction and removal of the anolyte from the anode chambers or spaces.

A suitable construction is to form the bottom of the cell as a hopper which receives the manganese dioxide dropping from the anodes. A discharge pipe may lead from the hopper and terminate at a point directly outside of the cell but slightly below the level of the anolyte. Thereby anolyte containing suspended oxide is withdrawn and the oxide may be recovered in settling tanks. A more rapid circulation of anolyte is set up than of catholyte in order to insure removal of the manganese dioxide. The catholyte initially may contain about 75 grams manganese sulfate and about 200 grams of ammonium sulfate per liter, and this may be circulated through the cell until the manganese sulfate content has decreased to from 50 to 60 grams per liter. During this period the ammonium sulfate concentration is increased to about 220 grams per liter because of the addition of ammonia to the catholyte prior to its entrance into the cell or reaction zone. A replenishment of manganese sulfate and simultaneous consumption of ammonium sulfate is effected by treating catholyte with a material containing manganous oxide, as a reduced manganese ore, i. e., the manganese dioxide initially present in the ore has, by a reducing action, been converted to manganous oxide. Reaction between the ammonium sulfate and manganous oxide takes place with formation of manganese sulfate and ammonia which is given off as gas and utilized through introduction into the catholyte as it flows back to the cell.

It is desirable that the catholyte be purified subsequent to its contact with the reduced ore and prior to its flowing into the cell inasmuch as small amounts of various elements, as iron, arsenic, nickel, cobalt, copper, etc. have been taken up and which interfere with the electrolytic action. One mode of operation entails contacting only a part of the spent catholyte with the reduced ore, with obtainment of a liquor containing 150 grams of manganese sulfate per liter. This liquor also contains unreacted ammonium sulfate and may be admixed with another or remaining fraction of spent catholyte to prepare a fresh batch of catholyte liquor for introduction into the cell and which would contain about 80 grams manganese sulfate and 200 grams ammonium sulfate per liter. The anolyte initially may contain about 150 grams manganese sulfate and about 75 grams sulfuric acid per liter, and this may be circulated through the cell until the sulfuric acid content has increased to about 90 grams. A portion of the anolyte liquor is then treated with a reduced manganese ore for reduction in sulfuric acid concentration through reaction with manganous oxide. Thereby the manganese sulfate concentration may be increased to about 300 grams or more per liter, and accomplishment of this may require addition of some concentrated sulfuric acid to the anolyte liquor. As in the case of the catholyte a purification of the anolyte liquor may be carried out in order to remove those metals, as iron, arsenic, etc., which are dissolved from the reduced ore. Removal of deposited manganese from the cathodes may be carried out about every three days, or as may be considered necessary by withdrawing the cathodes from the electrolyte and stripping the deposited metal therefrom with clean electrodes being substituted for those withdrawn.

More particularly, the practice of the invention follows the flow sheet illustrated in the drawing, in which the various steps are shown and indicated by appropriate legends. The procedure involves the simultaneous deposition of manganese dioxide with maintenance of two separate and distinct electrolyte systems, one an anolyte system in which manganese dioxide is formed, and the other a catholyte system in which manganese metal is produced. An electrolytic cell makes up the principal reaction zone and is composed of two separate sections, one of which may be situated within the other, with formation of two concentric compartments separated by inner section walls which constitute a diaphragm and may be a slightly porous ceramic-like cup or cell. The cathode or cathodes, e. g. of stainless steel, are suspended within the cup or diaphragm, and the anodes which preferably are sheets of lead outside. With a proper regulation of temperature and current density we have found that the anodes are self-cleaning through a constant dropping off of the formed manganese dioxide, whereas the cathodes are removed and replaced at suitable intervals depending upon the current density and thickness of the deposit of manganese metal. Following stripping of the metal from the cathodes they are again prepared for use and at a suitable time placed within the cells. The process may be carried out with an over-all cell temperature from about 20° to about 30° C., and at a current density which may range from about 18 to 30 amperes per square foot on both anode and cathode.

The anolyte being circulated may have a concentration from about 100 to about 200 grams of manganese sulfate and from about 50 to 100 grams of sulfuric acid per liter. A flushing out of the oxide is accomplished by circulation of the anolyte and following settling by a suitable means the clarified liquor is returned to the reaction zone. If desired, a part of the anolyte may be removed from the system, either periodically or continuously, with an addition at the same time of fresh manganese sulfate liquor, either neutral or along with some of the spent anolyte. Thereby sulfuric acid which is formed simultaneously with the manganese dioxide is removed, and the cell replenished with manganese sulfate. It is probable that manganese dioxide is formed at the anode in accordance with the following equation:

$$MnSO_4+H_2O+O=MnO_2+H_2SO_4$$

The oxygen called for arises at the anode due to electrolysis of water. In the catholyte the concentrations of manganese sulfate and ammonium sulfate are sufficiently low to obviate crystal for-

mation at the operating temperature, and the solution initially may contain about 75 grams manganese sulfate, 200 grams ammonium sulfate and from about 5 to about 10 grams free ammonia per liter. We have found that a small amount of sulfur dioxide serves to inhibit oxidation of manganous hydroxide in suspension, and this amount may be from about 0.2 to 0.5 grams per liter. The spent catholyte flowing from the cell contains about 50 grams manganese sulfate, 220 grams ammonium sulfate and 2 grams free ammonia per liter. An amount of free ammonia is reacted during the electrolysis, which corresponds substantially to the following reaction:

$$MnSO_4+2NH_3+2H=Mn+(NH_4)_2SO_4$$

Hydrogen arises from the electrolysis of water and the catholyte circuit is considered to be an ammonium sulfate-ammonia cycle, inasmuch as ammonia is recovered from ammonium sulfate during contact with a reduced manganese ore, and this ammonia reused through introduction into the catholyte prior to its entrance into the reaction zone.

Two separate and distinct reduced ore contacting and purification circuits are employed, with the catholyte system recovering ammonia. The anolyte leach or ore treatment is a neutralization of sulfuric acid by means of manganous oxide forming manganese sulfate and water. A purification of the anolyte liquor may be accomplished through oxidation with respect to iron and arsenic, chlorine removal by means of a soluble silver salt, hydrogen sulfide treatment at a pH value of 5.5 with heating to 70 to 80° C. if desired and, finally, removal of excess hydrogen sulfide. When so purified the anolyte liquor is in condition for introduction into the cell or reaction zone.

Treatment of the reduced ore with the circulating catholyte is somewhat more involved than that of the anolyte, inasmuch as it is accompanied by a simultaneous and continuous recovery of amomnia. The reaction with manganous oxide is believed to take place according to the following equation:

$$MnO+(NH_4)_2SO_4=MnSO_4+H_2O+2NH_3$$

A slightly reduced pressure on the leaching system assists in the removal of the ammonia which is formed and the ammonium sulfate is not entirely replaced by manganese sulfate inasmuch as it is desired to produce as nearly as possible a liquor of proper composition for introduction into the cell. Purification of the liquor comprises oxidation with air with respect to iron and arsenic and treatment with hydrogen sulfide or ammonium sulfide to remove small amounts of other metals, as cobalt and nickel, with removal of any excess sulfide by treatment with ammonia.

An adjustment of the final desired concentration may be effected through addition of some of the catholyte coming from the cell, and an addition of sulfur dioxide gas may be made in an amount from about 0.2 to 0.5 grams per liter. Following this the catholyte is in readiness for the addition of ammonia, which is introduced just prior to the catholyte entering the cell. We have found it advisable to recirculate a portion of the catholyte over a period, for example, several hours, in order to decrease the manganese content, and when so doing the recirculated catholyte is treated with ammonia gas prior to reentry into the cell. The ammonia gas arising from treatment of the reduced ore is a mixture of ammonia and water vapor. This water vapor may be condensed in a suitable heat exchanger and the free ammonia is conducted to ammonia addition units for introduction into the catholyte with attending pH control. The condensed water vapor contains ammonia, and this may be recovered by stripping with high pressure steam. If desired, a portion of the catholyte may constitute a medium for generation of ammonia through treatment with calcium hydroxide whereby ammonia gas is liberated and may be combined with that arising from the treatment of reduced ore.

A carrying out of the foregoing procedure results in the simultaneous production of metallic manganese and manganese dioxide. The oxide, which is in hydrated form, may be removed from the anolyte by means of a thickening settler, and the thickened oxide pulp filtered and washed to remove manganese sulfate and sulfuric acid. This may be accomplished through employment of acid-proof continuous drum filters spaced by repulping steps. The washed oxide may be suitably dried and then classified and packed. Metallic manganese is deposited in a condition of high purity upon the cathodes, which are removed, dipped in a dichromate bath, and washed with water. The cathodes are then dried and the metal stripped therefrom. This may be packed as stripped from the cathodes, or it may be melted and cast.

The foregoing procedure is characterized by the features that an anolyte is maintained separate and distinctly different from a catholyte, and furthermore that there is no admixture of catholyte and anolyte at any time. It is one of our findings that the anolyte, being essentially an aqueous solution of manganese sulfate and sulfuric acid, should not contain any ammonium sulfate if a high current efficiency with respect to oxide formation is to be obtained. Consequently, at no time is there a mixing of the anolyte with the catholyte. Additionally, a sulfuric acid cycle is maintained for the anolyte and an ammonium sulfate-ammonia cycle for the catholyte, and the cell or reaction zone is so designed that the oxide formed may be continuously and effectively removed. Moreover, a neutralization of sulfate ions set free by the deposition of metallic manganese with free ammonia is preferred, and there is thus set up an ammonia-ammonium sulfate cycle in which ammonia is suitably regenerated and returnd to the reaction zone.

A tight and slightly porous diaphragm is employed which we have found acts as a carrier for the current while effectively inhibiting passage of the solutions. This permits neutralization of sulfate ions in the catholyte circuit while keeping the two circuits separate. In practice we produce about two pounds of manganese dioxide for each pound of metallic manganese without any increase in current input, and this results in a decrease in the required kilowatt hours per pound of product. Furthermore, the metallic manganese produced has a purity of over 99% and the manganese dioxide simultaneously formed is also of a high purity.

We have obtained an apparent efficiency of about 50% in the production of metal and of about 30% in the production of manganese dioxide when all the kilowatt hours consumed are referred either to the metal or to the oxide. However, when the combined production of metal and oxide is referred to the manganese, then

there is an attending efficiency of about 80%. It will be observed that metal production and manganese dioxide formation, take place at the same time and from the same electrical current. We have obtained some results of about 50% current efficiency for the metal and about 60% current efficiency for the oxide, which would mean 110%, as the same current produces both products. Moreover, the production of two pounds of manganese dioxide for each pound of manganese metal means that three pounds of product are obtained instead of one pound, as is the case when metal alone is produced.

Since certain changes may be made in carrying out the above process without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all statements of the scope of the invention which, as a matter of language, might be said to fall therebetween.

Having described our invention what we claim as new and desire to secure by Letters Patent is:

1. A process for winning manganese and preparation of manganese dioxide which comprises electrolytically depositing metallic manganese on a cathode from an alkaline catholyte containing manganese and ammonium sulfates, and simultaneously electrolytically forming manganese dioxide at an anode in an anolyte containing manganese sulfate and sulfuric acid the weight ratio of oxide to manganese being about two to one, said catholyte containing initially about 75 grams of manganese sulfate and about 200 grams of ammonium sulfate, from about 5 to about 10 grams free ammonia and from about 0.2 to 0.5 gram sulfur dioxide per liter and said anolyte having a concentration during electrolysis from about 100 to about 200 grams of manganese sulfate and from about 50 to 100 grams of sulfuric acid per liter, said catholyte and anolyte being circulated and maintained separate throughout the action.

2. A process for winning manganese and preparation of manganese dioxide which comprises electrolytically depositing metallic manganese on a cathode from an alkaline catholyte containing initially about 75 grams manganese sulfate, about 200 grams ammonium sulfate and from about 5 to about 10 grams free ammonia per liter, and simultaneously electrolytically forming manganese dioxide at an anode in an anolyte having a concentration during electrolysis from about 100 to about 200 grams manganese sulfate and from about 50 to about 100 grams sulfuric acid per liter, the weight ratio of oxide to manganese being about two to one, said deposition and formation being effected at a temperature from about 20° to about 32° C. and a current density from about 18 to about 30 amperes per square foot of anode and cathode surface, and circulating and maintaining catholyte and anolyte separately with contact with a reduced manganese ore.

3. A process for winning manganese and preparation of manganese dioxide which comprises electrolytically depositing metallic manganese on a cathode from an alkaline ctaholyte containing initially about 75 grams manganese sulfate, about 200 grams ammonium sulfate and from about 5 to about 10 grams free ammonia per liter, and simultaneously electrolytically forming manganese dioxide at an anode in an anolyte having a concentration during electrolysis from about 100 to about 200 grams manganese sulfate and from about 50 to about 100 grams sulfuric acid per liter, the weight ratio of oxide to manganese being about two to one, said deposition and formation being effected at a temperature from about 20° to about 32° C. and a current density from about 18 to about 30 amperes per square foot of anode and cathode surface, circulating and maintaining catholyte and anolyte separately with contact with a reduced manganese ore, and introducing ammonia into circulating catholyte prior to its entrance into the reaction zone.

4. A process for winning manganese and preparation of manganese dioxide which comprises electrolytically depositing metallic manganese on a cathode from an alkaline catholyte containing manganese and ammonium sulfates, simultaneously electrolytically forming manganese dioxide at an anode in an anolyte containing manganese sulfate and sulfuric acid, the weight ratio of oxide to manganese being about 2 to 1, and circulating and maintaining catholyte and anolyte in separate circuits with leaching of separate sources of material containing manganous oxide in each circuit.

5. A process for winning manganese and preparation of manganese dioxide which comprises electrolytically depositing metallic manganese on a cathode from an alkaline catholyte containing manganese and ammonium sulfates, ammonia, and sulfite ions, and simultaneously electrolytically forming manganese dioxide at an anode in an anolyte containing manganese sulfate and sulfuric acid, and circulating and maintaining catholyte and anolyte in separate circuits with leaching of separate sources of material containing manganous oxide in each circuit, the weight ratio of oxide to manganese being about 2 to 1.

6. A process for winning manganese and preparation of manganese dioxide which comprises electrolytically depositing metallic manganese on a cathode from an alkaline catholyte containing manganese and ammonium sulfates, simultaneously electrolytically forming manganese dioxide at an anode in an anolyte containing manganese sulfate and sulfuric acid, the weight ratio of oxide to manganese being about 2 to 1, and circulating and maintaining catholyte and anolyte in separate circuits with leaching of separate sources of reduced manganese ore in each circuit.

7. A process for winning manganese and preparation of manganese dioxide which comprises electrolytically depositing metallic manganese on a cathode from an alkaline catholyte containing manganese and ammonium sulfates, simultaneously electrolytically forming manganese dioxide at an anode in an anolyte containing manganese sulfate and sulfuric acid, the weight ratio of oxide to manganese being about 2 to 1; said deposition and formation being effected at a temperature from about 20° to about 32° C. and at a current density from about 18 to about 30 amperes per square foot of anode and cathode surface, and circulating and maintaining catholyte and anolyte in separate circuits with leaching of separate sources of material containing manganous oxide in each circuit.

8. A process for winning manganese and preparation of manganese dioxide which comprises electrolytically depositing metallic manganese on a cathode from an alkaline catholyte containing

manganese and ammonium sulfate, simultaneously electrolytically forming manganese dioxide at an anode in an anolyte containing manganese sulfate and sulfuric acid, the weight ratio of oxide to manganese being about 2 to 1, circulating and maintaining catholyte and anolyte in separate circuits with leaching of separate sources of material containing manganous oxide in each circuit, and introducing ammonia and sulfur dioxide into circulating catholyte prior to its entrance into the reaction zone.

THOMAS AUSTIN MITCHELL.
DONALD COOPER MITCHELL.

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