Nov. 20, 1962 J. Y. WELSH 3,065,155

ELECTROLYTIC MANGANESE DIOXIDE PROCESS

Filed Sept. 2, 1960

5 Sheets-Sheet 1

Fig. 1.

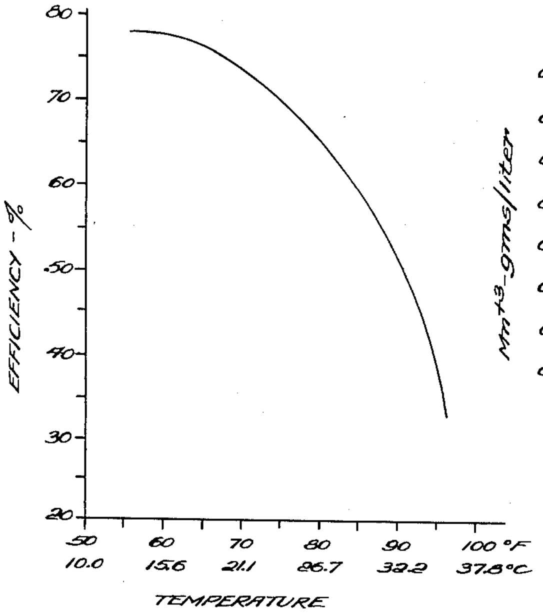


Fig. 3.

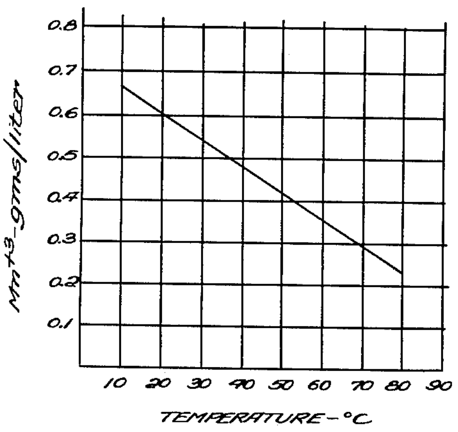
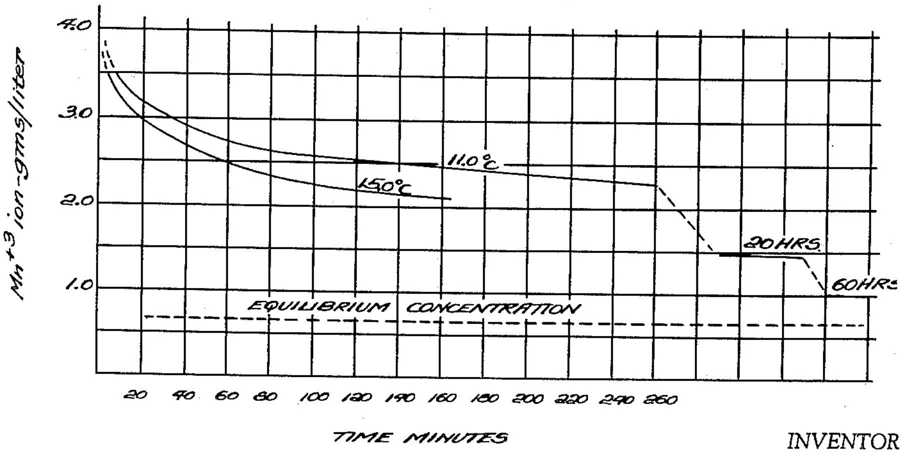


Fig. 2.



INVENTOR

Jay Y. Welsh,

BY Pierce, Scheffler & Parker

his ATTORNEYS

Nov. 20, 1962 J. Y. WELSH 3,065,155

ELECTROLYTIC MANGANESE DIOXIDE PROCESS

Filed Sept. 2, 1960

5 Sheets-Sheet 2

Fig. 4.

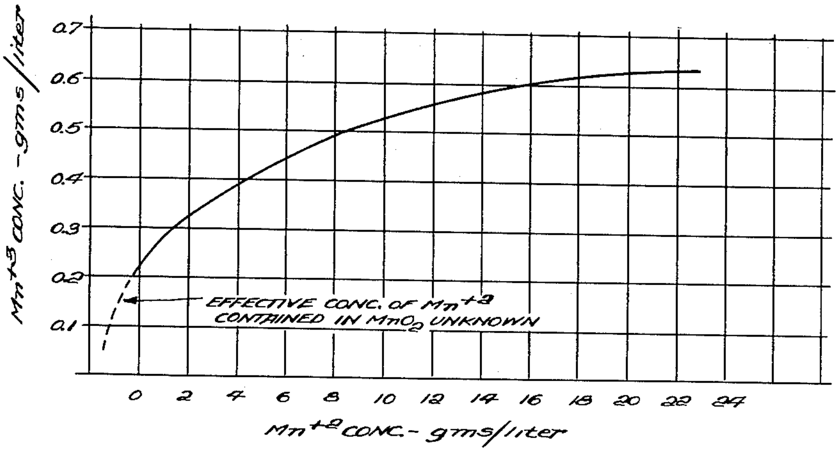
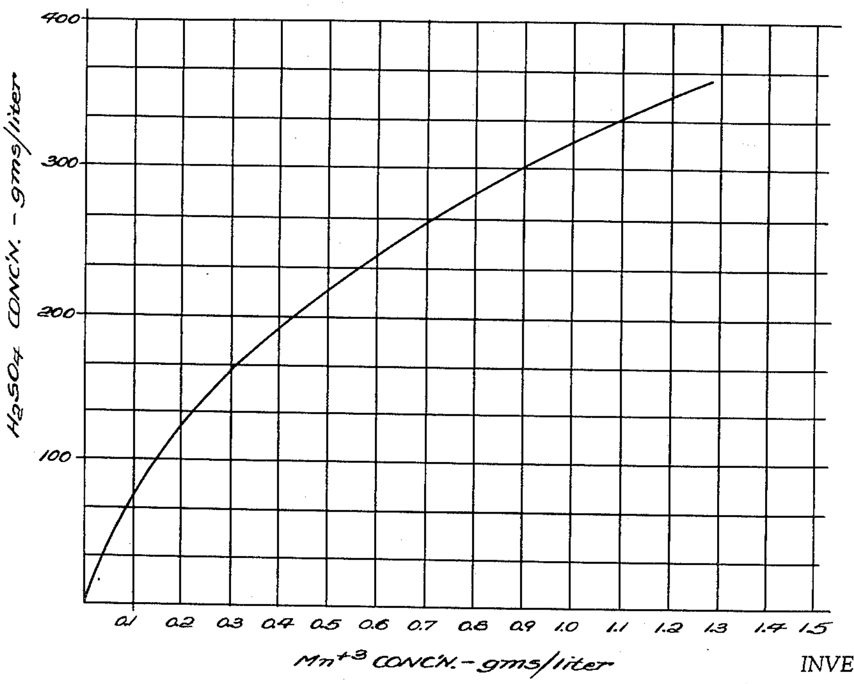


Fig. 5.



INVENTOR

Jay Y. Welsh,

BY Pierce, Scheffler & Parker

his ATTORNEYS

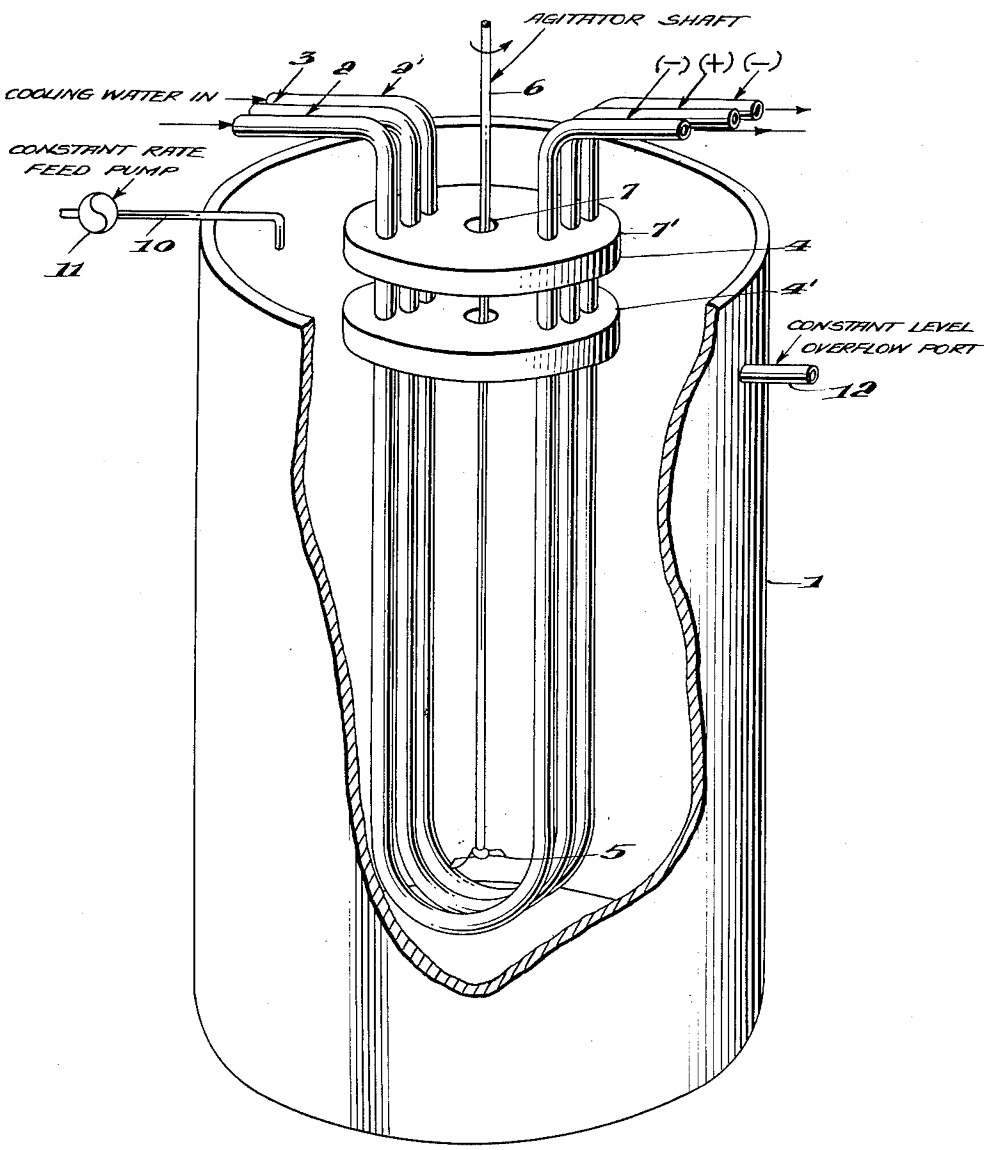
Nov. 20, 1962 J. Y. WELSH 3,065,155

ELECTROLYTIC MANGANESE DIOXIDE PROCESS

Filed Sept. 2, 1960

5 Sheets-Sheet 3

Fig. 6.



INVENTOR

Jay Y. Welsh,

BY Pierce, Scheffler & Parker

his ATTORNEYS

Nov. 20, 1962 J. Y. WELSH 3,065,155

ELECTROLYTIC MANGANESE DIOXIDE PROCESS

Filed Sept. 2, 1960

5 Sheets-Sheet 4

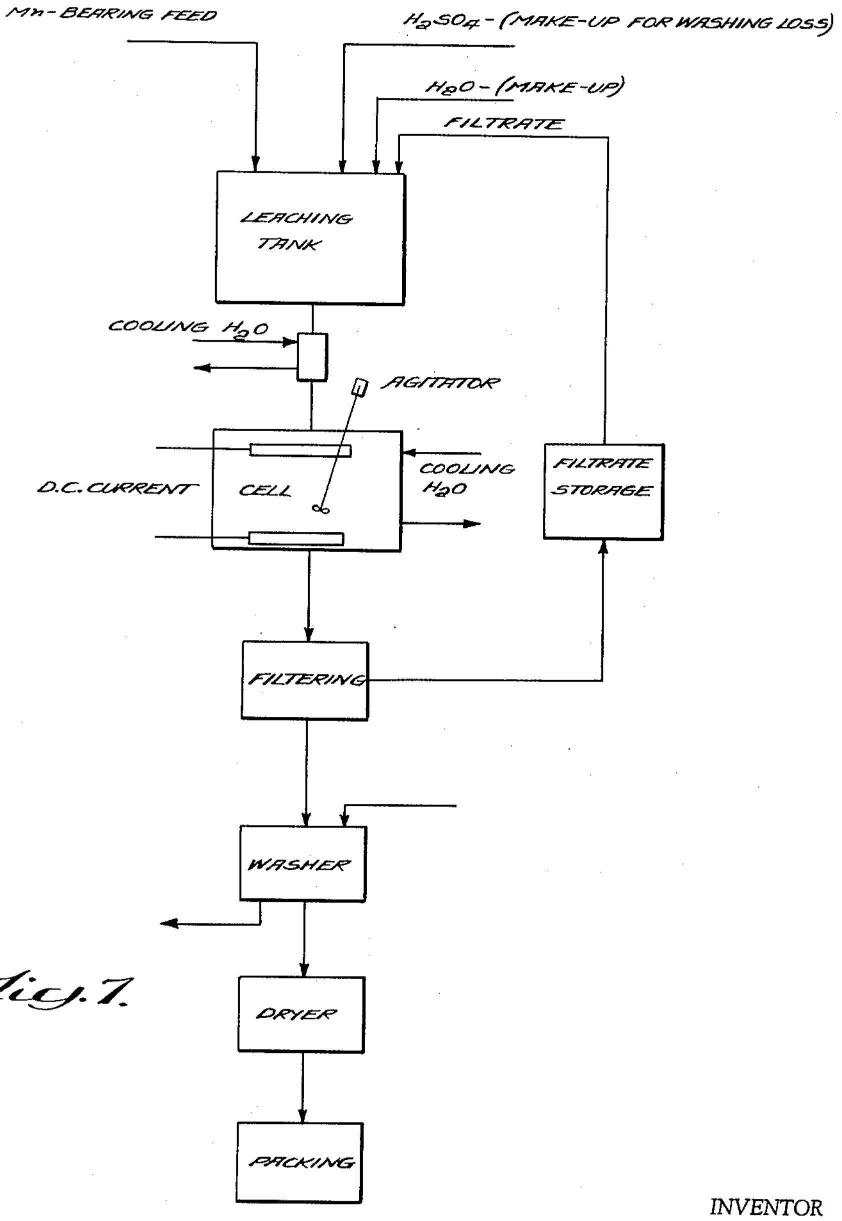


Fig. 7.

INVENTOR

Jay Y. Welsh,

BY Pierce, Scheffler & Parker

his ATTORNEYS

Nov. 20, 1962 J. Y. WELSH 3,065,155

ELECTROLYTIC MANGANESE DIOXIDE PROCESS

Filed Sept. 2, 1960 5 Sheets-Sheet 5

Fig. 8.

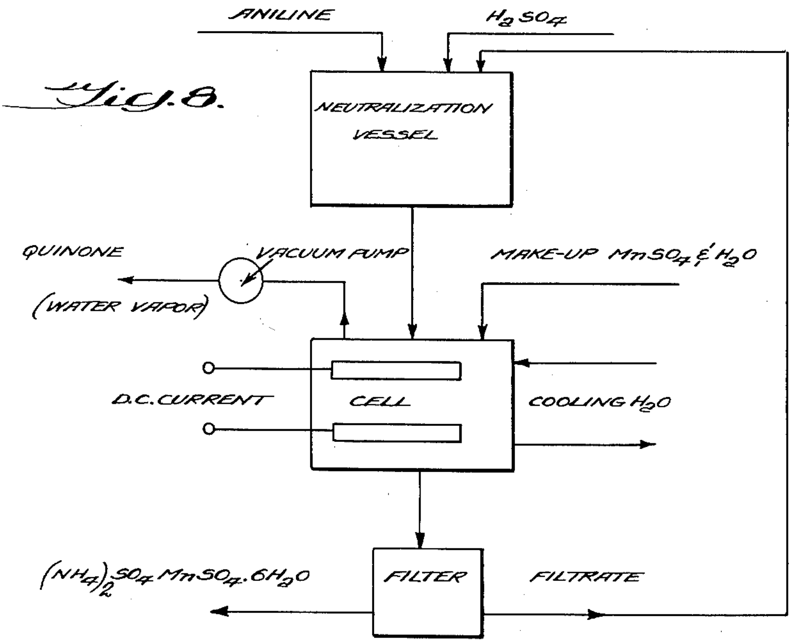
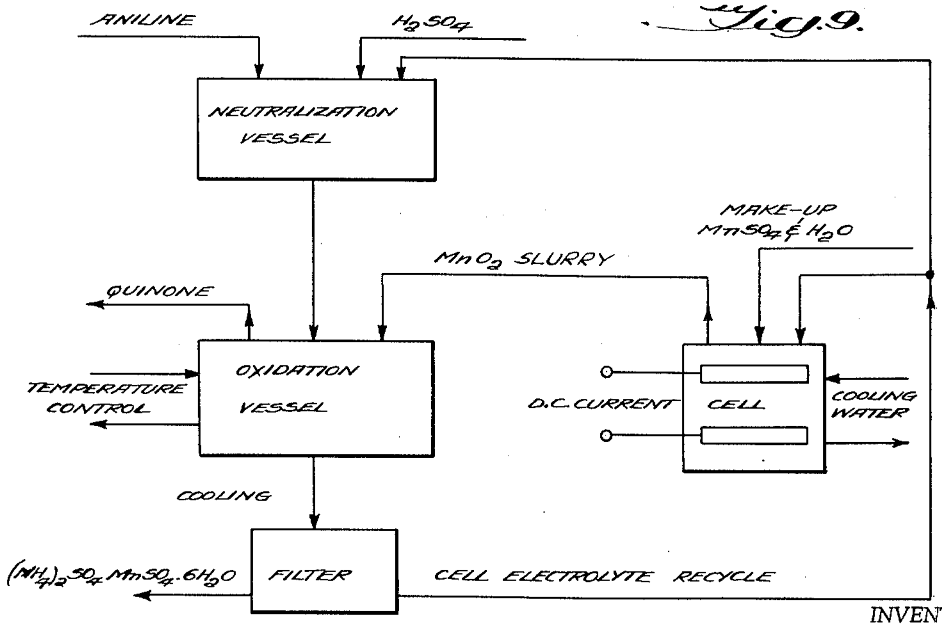


Fig. 9.



INVENTOR

Jay Y. Welsh,

BY Pierce, Schaeffler & Parker

his ATTORNEYS

United States Patent Office

3,065,155

Patented Nov. 20, 1962

3,065,155
ELECTROLYTIC MANGANESE DIOXIDE PROCESS

Jay Y. Welsh, Brainerd, Minn., assignor, by mesne assignments, to Manganese Chemicals Corporation, a corporation of Maryland

Filed Sept. 2, 1960, Ser. No. 53,812
4 Claims. (Cl. 204—83)

This invention relates to the production of high-quality particulate manganese dioxide especially suitable for use as depolarizer material in Leclanche cells, and is concerned with an improved electrolytic process of making the same.

It heretofore was known to produce manganese dioxide by the electrolysis of an aqueous solution of manganese sulphate, and it was known that—in at least some instances—the resulting products were, after the necessary grinding and other after-treatments, useful as depolarizer material. In the heretofore conventional electrolytic "batch" process manganese dioxide was deposited in relatively "massive" form on the anode (usually graphite or lead), from which latter it had to be stripped; thereafter, the stripped-off deposit had to be ground to suitable particle size and otherwise processed before becoming useful as "battery oxide." In a typical procedure of this sort the electrolyte contained 20–150 g./l. $MnSO_4$ and 2–80 g./l. H_2SO_4; the temperature of the bath was above normal room temperature (e.g., normally above 80° C. and even up to 100° C.); and the current density was in the neighborhood of 10 to 20 amp./sq. ft.

This combination of conditions precludes the formation of Mn^{+3}ion.

In lieu of the above-described commercial batch process, it has been proposed to effect the electrolysis of an aqueous (acidic, or neutral) solution of $MnSO_4$, in a continuous procedure, in a compartmented cell wherein the feed to the anode compartment contained about 150 g./l. of $MnSO_4$ and about 75 g./l. of H_2SO_4 and wherein the temperature was about 25° C. and the current density was 18–30 amps./sq. ft. The anode product was a scaley and slimy hydrated MnO_2, which formed on the anode and sluffed off of the latter from time to time: it was brown in color, light in density and (because of its slimy nature) difficult to wash and process. The process had an efficiency of 30%.

This combination of operating conditions (relatively very low current density; relatively high concentration of $MnSO_4$; relatively low acid concentration; relatively high temperature) excluded the formation of Mn^{+3}ion in other than trace amounts.

It has been proposed, also, in respect of an electrolytic procedure practiced in a compartmented cell, to neutralize some or all of the acid liberated by the oxidation of $MnSO_4$ in the anode compartment by adding manganous or manganic hydroxide to the content of the anode compartment and maintaining the same in slurry form therein. In this procedure the anode product was hydrated "higher oxides" of manganese.

It has been determined that such a hydrated "higher oxides" product not only is difficult to process but more importantly does not constitute a satisfactory battery oxide.

I have discovered that in order to effect a precipitation of MnO_2 in the electrolyte (as opposed to deposition of the same on the anode) and to insure that the precipitate occurs in the form of particles of sufficient size to settle and filter easily, the electrolyte must contain a significant concentration of Mn^{+3}ion—say, 3 or preferably about 4 grams per liter—and the reaction

$$2Mn^{+3}+2H_2O \leftrightarrows Mn^{+2}+MnO_2+4H^{+} \quad \text{(Reaction 1)}$$

must be caused—by appropriate selection of conditions of temperature, acid concentration and current density—to proceed slowly in the body of agitated electrolyte solution or slurry, the stability of the Mn^{+3}ion being sufficiently great and the decomposition occurring at a slow enough rate to "build" large particles of MnO_2. I have found that the stability of Mn^{+3}ion (in the electrolyte) decreases with increase in temperature and also with decrease in acid concentration; and that rapid decomposition produces a finely subdivided MnO_2 product not desirable for use as battery depolarizer.

In broadest aspect, the process of the present invention is a continuous electrolytic procedure wherein an aqueous acidic solution of $MnSO_4$ is passed, in agitated state, through an uncompartmented electrolytic cell provided with a lead anode and lead cathode, the conditions of operation being so selected and controlled that Mn^{+3}ion is the substantially sole anode product and that the decomposition of the Mn^{+3}ion is made slow enough to induce the formation of relatively coarse particles of MnO_2.

The invention will be described in greater particularity and with reference to the accompanying drawing, in which

FIG. 1 is a graph showing the effect of temperature on the efficiency of the process under selected conditions;

FIG. 2 is a graph showing the rate of decomposition of Mn^{+3}ion at selected temperatures;

FIG. 3 is a graph showing the equilibrium concentration of Mn^{+3}ion versus temperature;

FIG. 4 is a graph showing the effect of Mn^{+2} concentration on the equilibrium concentration of Mn^{+3};

FIG. 5 is a graph showing Mn^{+3} concentration versus H_2SO_4 concentration under equilibrium conditions;

FIG. 6 is a representation of a cell for use in carrying out the present process;

FIG. 7 is a flow diagram of the process;

FIG. 8 is a flow diagram of a quinone-producing process integrated into the present process; and

FIG. 9 is a modification of the flow diagram of FIG. 8.

In FIG. 1, which shows the effect of temperature on efficiency, the selected operating conditions were:

(1) 400 amps. per ft.^{2}
(2) 25–30 gms./liter Mn^{+2} in slurry.
(3) 200 gms./liter H_2SO_4.

In FIG. 2 showing decomposition of Mn^{+3}ion, the constants were:

	Gms./l.
(1) H_2SO_4	200
(2) Mn^{+2}	20
(3) MnO_2	200

In FIG. 3, plotting equilibrium concentration of Mn^{+3} versus temperature, the constants were:

	Gms./l.
(1) H_2SO_4	250
(2) Mn^{+2}	20
(3) MnO_2	200

In FIG. 4, which shows the effect of Mn^{+2} concentration on the equilibrium concentration of Mn^{+3}, the constants were:

(1) H_2SO_4 concentration	gms./l.	250
(2) MnO_2 concentration	gms./l.	250
(3) Temperature	° C.	15

In FIG. 5, which plots Mn^{+3} concentration versus

H_2SO_4 concentration, the selected equilibrium conditions were:

Mn^{+2} constant at ---------------------- gms./l. -- 20
MnO_2 ---------------------------------- gms./l. -- 200
Temperature ----------------------------- °C. -- 15

As has been indicated in FIG. 2, the equilibrium concentration of Mn^{+3}ion, in an aqueous slurry of MnO_2 (Mn^{+3} produced) containing 200 g/l. of H_2SO_4 and 20 g./l. Mn^{+2}ion and 200 g./l. of MnO_2, held at a temperature of about 15° C., is within the range of 0.6–0.7 g./l. This means that if given enough time a solution initially containing more than the equilibrium value of Mn^{+3}ion will undergo decomposition until it reaches this equilibrium value, the interesting aspect of this fact being that it requires a very long time (perhaps a hundred hours or more) for the concentration of Mn^{+3}ion to even approach equilibrium value.

It is to be noticed in FIG. 2, with regard to the decomposition curves for Mn^{+3}ion, that initially the decomposition rate is quite rapid but the curves then flatten out to a very slow decline. This decomposition reaction appears to conform rather closely to a fourth order reaction (i.e., the decomposition rate appears to be roughly proportional to the concentration taken to the 4th power).

The build-up on Mn^{+3}ion, on the other hand, produced when Mn^{+2}ion reacts with active MnO_2 (such as is produced by reaction 1) in acid solution, proceeds rapidly to the equilibrium value and then (of course) remains constant, the mechanism of this reaction obviously being quite different from that of the decomposition.

The relationship between Mn^{+3}ion concentration and Mn^{+2}ion concentration in an acidic slurry of MnO_2 (250 g./l. H_2SO_4 and 200 g./l. MnO_2), is shown in FIG. 4. From this latter it is to be observed that the ratio of Mn^{+2} concentration to the square of the $(Mn^{+3})^2$ concentration is roughly constant, as predicted by the equilibrium constant of reaction 1, which is

$$K=\frac{(Mn^{+2})(H^+)^4}{(Mn^{+3})^2}$$

(H^+) Constant

FIGURE 5 shows the variation of Mn^{+3}ion with acid level, other factors remaining constant. These data also obey the equilibrium constant prediction, in that the acid concentration raised to the 2nd power divided by the Mn^{+3} concentration is roughly constant. The form of this curve gives clear indication of the necessity for a high acid level in the process of the present invention. A few figures taken from the curve may serve to show the high acid criticality:

Acid Concentration, g./l.	Mn^{+3} Concentration (or, Stability)
50–100	0.05–0.14
150	0.25
175–225	0.35–0.53

The influence of temperature is demonstrated in two ways. In FIG. 2 it is evident that the decomposition rate is markedly effected by temperature because the two curves shown are only 4° C. apart. This indicates other things being equal, that the Mn^{+3} level in an operating cell will be lower at higher temperatures.

FIG. 3 shows the effect of temperature on the equilibrium concentration of the Mn^{+3}ion in the acid slurry previously described. It shows that the Mn^{+3} concentration (or stability) is roughly reduced by ½ in going from 10° to 60° C.

According to the flow diagram shown in FIG. 7, an illustrative procedure adapted to the production of a battery-grade manganese dioxide product involves feeding to an agitated electrolytic cell a cooled slurry resulting from leaching a manganese-bearing feed with an acidic leaching liquor consisting essentially of a filtrate obtained in the process plus make-up H_2SO_4 or/and make-up water, the slurry being cooled during the electrolysis. The effluent from the agitated electrolytic cell is passed through a filter to separate solids from an acidic filtrate (which latter is recycled to the leaching step), after which the resulting filtercake is washed with water, dried and packed.

The nubbin of the process of the present invention is the discovery that under the proper conditions of temperature, acid concentration and current density manganous ion can be efficiently converted to soluble manganic ion which latter undergoes slow decomposition in the body of the agitated solution (or, slurry) to form particulate MnO_2 having excellent battery depolarized characteristics. The combination of conditions which enable such a process to take place are critical. Optimum cell conditions are as follows:

Temperature—not over 21° C. and preferably definitely lower than this;
Anode material—lead (or lead alloy);
Anode current density—400–550 amps./sq. ft. (there is a very marked drop in process efficiency below 200 amps./sq. ft.);
Cathode current density—400–800 amps./sq. ft. and desirably never lower than the anode C.D.;
Acid—H_2SO_4, 150–250 g./l.—optimum acid level 175–225 g./l. H_2SO_4;
Manganous ion concentration—10–25 g./l.
Cell mechanics—strongly agitated, with a cell geometry (ideal) that minimizes solution movement around the cathode and promotes high solution velocity around the anodes.

The process is cyclic, in that the product reaction regenerates H_2SO_4 from the $MnSO_4$ feed, which H_2SO_4 can then be cycled to leach more manganese (as $MnSO_4$) from a suitable feed material such as MnO, Mn^3O_4 or $MnCO_3$.

Because of the low temperature criterion above described, in rebuilding the Mn in solution for feeding back to the cell it is desirable if not necessary to carry out the acid leaching step in a separate reaction vessel so as to minimize heat effects. If the feed is MnO, it is not necessary to add heat to effect solution; nevertheless, the solution reaction produces excessive heat. If on the other hand, the feed is Mn_3O_4 or $MnCO_3$, added heat is necessary for effecting satisfactory solution reaction rates. In either event, the resulting solution or slurry is cooled before being fed to the electrolytic cell.

Moreover, for attaining the desirable low temperature conditions in operating the electrolytic cell the electrolyte is cooled by indirect heat-exchange with a coolant, that is to say, cooled by means of cooling coils. This cooling step may be accomplished by placing electrically isolated cooling coils in the agitated electrolyte cell or advantageously may be effected by (1) using lead pipes as the electrodes (or, lead pipe for at least the anode) and (2) passing a current of fluid coolant—desirably, cool water—therethrough.

In respect of the criticality of high anode current density, it should be mentioned that scaling of the anode surface with MnO_2 begins at 200 amps./sq. ft. and becomes increasingly worse at lower current densities. The decided drop in efficiency at anode current density of 200 a. (and lower) is believed to be due to the relative increase in the cathodic discharge process.

The following specific examples are illustrative but non-limitative of the present invention:

Example I

Agitated 10 liter electrolytic cell, electrode spacing ¼".
Ratio of anode-cathode area 1/1.
Electrodes: 1" O.D. lead pipes, water cooled.
D.C. current 180 a.

Electrode current density 400 a./ft.^{2}
Av. cell voltage 4.2 v.
Acid level in operating cell 200 g./l. H_2SO_4
Av.Mn^{+2} level in operating cell 26 g./l.
Feed—$MnSO_4$ solution containing 100 g./l. Mn^{+2} as $MnSO_4$
Feed rate 1800 ml./hr. continuous
Operating cell temperature 15.6° C.
Average electrolytic efficiency for 28 hr. run—75.4%

Product:	Percent
Mn	48.2
MnO_2	72.3
H_2O	20.0
Pb	.007

Crystal structure—delta and small gamma component.

Example II

Same cell and current conditions as Example I. Also same acid level.
Average Mn^{+2} level in operating cell—17.0 g./l.
Average cell temperature 17° C.
Feed—slurry resulting from leaching Mn_3O_4. Slurry adjusted to 100 g./l. soluble Mn^{+2} as $MnSO_4$ and containing about 95 gms./l. and MnO_2 produced by the disproportionation of Mn_3O_4
Average electrolytic efficiency through run (80 hrs.) 70.1%

Product:	Percent
Mn	51.1
MnO_2	76.9
H_2O	16.4

Crystal structure—gamma.

In the final product the weight ratio of MnO_2 from the electrolysis to MnO_2 from the disproportionation of Mn_3O_4 was about 2:1.

Example III

Same cell and current conditions as Examples I and II also same acid level.
Average Mn^{+2} level in operating cell 27 g./l.
Average temperature of operating cell 19° C.
Feed—$MnSO_4$ made from $MnCO_3$ containing .7% NH_3.
Feed adjusted to 100 g./l. Mn^{+2} as $MnSO_4$
Average electrolytic efficiency through run of 48 hrs. 67.0%

Product:	Percent
Mn	49.2
MnO_2	72.5
H_2O	21.1

Crystal structure—delta.

Examples I, II and III were carried out in the cell shown in FIG. 6.

In this apparatus (FIG. 6) the cell container **1** was an open topped, generally cylindrical, vessel in which cathodes **2**, **2'** and an intervening anode **3** were supported, in substantially parallel relation, by conventional supporting means (not shown). The electrodes were one-inch lead pipes, deeply bent into a U-shape (as shown in the drawing) to extend substantially the whole distance from top to bottom of the cell container **1**. The two cathodes were spaced about one-fourth inch on either side of the anode, being held in this spaced relationship by spacing members **4**, **4'**. An agitator **5**, fixed to an agitator shaft **6**, was disposed in the lower part of container **1**, the agitator shaft extending through apertures **7**, **7'** in spacing members **4**, **4'** to a conventional means (not shown) for rotating the agitator. Cathodes **2**, **2'** were connected to the negative pole and anode **3** to the positive pole of a source of direct current (not illustrated). The cathodes were connected to a source of relatively cold water, which cooling water was passed through the cathodes in such volume and at such temperature to maintain the cell contents at a desirably low temperature below 21° C., e.g., at 15°–17° C. Cell feed was supplied to the cell through a conduit **10** provided with a constant rate feed pump **11**, while a constant level overflow port **12** provided in the wall of container **1** maintained the electrolyte volume substantially constant.

Example IV

Agitated 9-liter electrolytic cell, electrode spacing ½". Ratio of anode to cathode area 1/1.
Electrodes—anode 1" O.D. lead rod. Cathode—four ¼" lead rods. (Separate cooling coils.)
D.C. current 45 a.
Electrode current density 440 a./ft.^{2}
Av. cell voltage 4.3 v.
Average acid level in operating cell 200 g. H_2SO_4 per liter.
Average Mn^{+2} level in operating cell 20 g./l.
Feed same as Example II.
Average feed rate—420 ml./hr. continuous.
Operating cell temperature 15° C.

Electrolytic efficiency:	Percent
1st 8 hrs. period	83.7
2nd 8 hrs. period	75.8
3rd 8 hrs. period	74.6
4th 8 hrs. period	75.0
5th 8 hrs. period	73.5
6th 8 hrs. period	73.6
7th 8 hrs. period	68.9
8th 8 hrs. period	69.3
9th 8 hrs. period	86.2
10th 8 hrs. period	76.0

Product: Same as Example II.

Dry cell battery data establishing that the product of the process is an exceptional depolarizer material are shown as follows:

Depolarizer Composition	Capacities in minutes on the Heavy Industrial Flash Light Test.	
	to 1.10 v. End Point	to 0.90 v. End Point
100% Natural African Battery Grade Ore	319	536
100% Commercial Electrolytic MnO_2	625	865
50% Commercial Hydrated MnO_2* and 50% African Ore	523	750
50% MnO_2 from present process and 50% African Ore	652	853

*Made by permanganate decomposition process. Material represents the best commercial battery grade hydrated MnO_2 available.

Experimental cell runs with acid level as the variable showed that:

At 50 g./l., the MnO_2 is formed almost completely on the anode;

Between 50 and 100 g./l., the anode is substantially free from deposited MnO_2, but the MnO_2 is formed in very close proximity to the anode and therefore at such a rapid rate that particle growth cannot take place and hence the product is a brown collodial mass wholly undesirable for battery use;

Between 100 g./l. and 150 g./l. the cell approaches what I call "normal operation"" in that the Mn^{+3}ion becomes sufficiently stable to be swept into the body of solution (or, slurry) before undergoing decomposition. In the lower part of this range the decomposition rate is still too high to facilitate desirable particle growth, but at 150 g./l. H_2SO_4 the product formation and growth begin to follow a "normal" pattern.

As noted above, the optimum acid level is 175–225 g./l. H_2SO_4.

A comparison run of the cell with 150 g./l. H_2SO_4 but at a temperature of 20° C. (instead of 15°) showed a brownish product having an undesirably fine particle size, indicating that at higher temperatures and with a minimum acid level the decomposition rate is too fast.

I have found, further, that the precipitated MnO_2—produced as described hereinbefore—may be caused to deposit, as it precipitates, on other MnO_2. Thus, I have found that particulate African ore may be suspended in the electrolyte feed and carried by the latter through the electrolytic cell, and that in its passage through the cell MnO_2 precipitated (from the electrolyte) onto each particle of the ore. Any desired ratio of natural ore to synthetic MnO_2 can be easily prepared.

This same observation holds true also in the case of a feed produced by acid leaching a Mn_3O_4 material without filtering out the resulting disproportionated MnO_2 particles. I take advantage of this phenomenon by feeding the unfiltered slurry of MnO_2 particles suspended in aqueous acidic $MnSO_4$ solution to the cell, and, in the electrolytic step, effect the deposition of the precipitated MnO_2 on these suspended particles. The resulting product, when washed and dried, is a battery-grade dioxide.

Laboratory tests have demonstrated that if the H_2SO_4 level is raised to, say, 350 g./l. or higher the apparent Mn^{+3}ion concentration can be in excess of 10 g./l. without a solid phase being present. This is equivalent in oxidizing capacity to 2 g./l. $KMnO_4$ solution. According to one aspect of the present invention I may employ the present process in an oxidizing cycle wherein the cell product—either Mn^{+3} solution or Mn^{+3} solution plus some of the very active precipitated MnO_2—is cycled through a system in which an oxidation is carried out, the reduced Mn^{+3}ion—that is to say, Mn^{+2}ion—being brought back through the cell to complete the cycle. This oxdizing material could replace acid permanganate solution, with significant cost advantage.

In processes where an acidic MnO_2 slurry is used as the oxodizing agent (e.g., in the manufacture of hydroquinone and of certain dyestuffs) I can substitute the mixture discharged from the cell, as such, as the oxidizing agent. The $MnSO_4$ resulting from the oxidation-reduction step thus is not wasted but rather is recycled through the electrolytic cell to produce more acidic MnO_2 slurry. One particular advantage of this substitution is to be seen in the maintainable high purity of oxidizing agent possible in the present process.

An example of the use of the cell as a primary oxidation source in a commercial process follows:

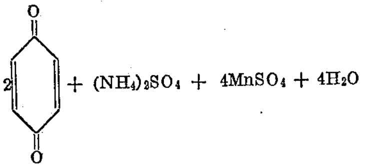
The commercial production of quinone is summarized by the following sequential chemical reactions:

(1) The neutralization reaction

$$2C_6H_5\cdot NH_2+H_2SO_4\rightarrow (C_6H_5\cdot NH_3)_2SO_4$$

(2) The oxidation reaction

$$(C_6H_5\cdot NH_3)_2SO_4 + 4MnO_2 + 4H_2SO_4 \longrightarrow$$



Step (2) may be carried out by reacting previously prepared aniline sulphate in a cold slurry of MnO_2 in sulphuric acid solution, the cold (i.e., unheated) reaction mixture being passed though the cell and the resulting quinone taken off continuously under reduced pressure. The cell temperature is maintained within the 20°–70° C. range and as near the lower limit of this range as is economically feasible. This process is illustrated in the FIG. 8 flow sheet, and the course of the reaction, in the cell is:

$$(C_6H_5\cdot NH_3)_2SO_4 + (MnSO_4\text{—}H_2SO_4\text{ solution}) \xrightarrow[\text{(oxidation)}]{\text{D.C. current}}$$
$$2C_6H_4O_2 + (NH_4)_2SO_4 + (MnSO_4\text{—}H_2SO_4\text{ solution})$$

In the process just described, the theoretical material balance is:

$$140\text{ gms. aniline} + 100\text{ gms. } H_2SO_4 + 155\text{ gms. } MnSO_4 +$$
$$110\text{ gms. } H_2O \xrightarrow[\text{D.C. current}]{\text{350 amp. hrs.}}$$
$$220\text{ gms. quinone} + 400\text{ gms. } (NH_4)_2SO_4MnSO_4\cdot 6H_2O\text{ (crystals)}$$

Under the condition that the NH_4^+ion produced by the oxidation is removed from the operating cell as a 20% slurry of $(NH_4)_2SO_4MnSO_4\cdot 6H_2O$ crystals, in cell electrolyte, there ideally are about 2000 gms. (or, 1650 ml.) of cell liquor cycled back into the aniline sulphuric acid reaction vessel, to which 190 gms. aniline and 100 gms. H_2SO_4 are added, plus heat to produce the aniline sulphate cell feed. However, in actual practice mechanical losses both of $MnSO_4$ and of H_2SO_4 and water are incurred when the $(NH_4)_2SO_4\cdot MnSO_4\cdot 6H_2O$ crystals are separated out, thus requiring make-up additions of each, desirably, by direct additions to the cell. Also, some make-up water is necessary for replacing the water removed with the quinone. As is indicated directly in the above material balance, the addition (to the cell) of 155 gms. $MnSO_4$ for each 220 gms. quinone produced is necessary for maintaining the continuity of the reaction, the ammonium sulphate crystallizing out as the double salt, $(NH_4)_2SO_4MnSO_4\cdot 6H_2O$, taking $MnSO_4$ with it.

Because of the greater opportunity of selecting optimum temperature conditions, it is advantageous to conduct the above quinone-producing process as illustrated in the flow diagram of FIG. 9, the material balance remaining essentially unchanged. Thus, by carrying out, for the most part, the aniline sulphate oxidation in a separate vessel the temperature of this vessel and its contents can be suitably adjusted to the removal of the quinone product. In both instances the cell electrolyte contains $MnSO_4$ and H_2SO_4 in the previously mentioned ranges; also, in both procedures the H_2SO_4 associated with the cell is cyclic except for handling losses associated with separation of the double salt crystals.

The H_2SO_4 added with the aniline to the neutralization vessel is entirely consumed and removed as ammonium sulphate. The manganese as $MnSO_4$ is cycled, except for (*a*) the manganese sulphate "lost" as the double salt and (*b*) handling loss connected with the crystals. Since there are 4 moles of $MnSO_4$ formed in the oxidation reduction reaction to only 1 mole of $(NH_4)_2SO_4$, it will be apparent that only one-fourth of the $MnSO_4$ is lost as the double salt with each reaction cycle: in terms of the material balance, 155 gms. $MnSO_4$ is lost for every 220 gms. quinone produced. This may be compared with procedures, practiced until now, in which a loss of 620 gms. $MnSO_4$, or more, is suffered for every 220 gms. quinone produced. Since the MnO_2 produced from $MnSO_4$ by the presently described process is less expensive than MnO_2 from medium grade ores, and since three-fourths of the MnO_2 employed in the quinone production is made by re-cycle oxidation in the cell, the favorable economics are apparent. Moreover, the one-quarter make-up in manganese per reaction cycle can be added as an MnO_2 ore, as opposed to adding $MnSO_4$ as shown in the flow sheets.

A further application of the invention is in the field of supported MnO_2 catalysts, wherein my process offers unique impregnating advantages. Thus, the particulate catalyst support (e.g., silica or alumina or any other conventional particulate inert material), in the form of a bed or slurry, may be flooded with incipiently decomposing Mn^{+3} solution and the precipitating MnO_2 be deposited over the surfaces of the support pieces. Or, a cold Mn^{+3} solution can be decomposed by heat whilst in contact with the support material. This allows a very active MnO_2 to be placed in and on the catalyst support in practically any amount desired.

I claim:

1. In an electrolytic process of producing battery-grade manganese dioxide involving the step of continuously feeding an electrolyte slurry the liquid phase of which consists essentially of an aqueous acidic solution of manganese sulphate through an electrolytic cell and simultaneously effecting electrolysis in said cell by passing unidirectional current through the electrolyte from a lead anode to a cathode immersed in said electrolyte, the improvement which consists in effecting the precipitation of manganese dioxide solely in the body of electrolyte and in the form of relatively coarse discrete particles by agitating the body of electrolyte and insuring that the body of electrolyte contains a concentration of Mn^{+3}ion of between 0.7 and 4 grams per liter, that Mn^{+3}ion is the substantially sole anode product, and that the MnO_2-producing reaction

$$2Mn^{+3}+2H_2O \rightarrow Mn^{+2}+MnO_2+4H^+$$

is caused to proceed slowly, the improved process being further characterized in that the temperature is maintained at from about 10° to about 30° C., in that the electrolyte contains from about 100 to about 350 g./l. of free H_2SO_4 and in that the average Mn^{+2}ion level in the cell is from about 10 to about 30 grams per liter.

2. The improved process defined in claim 1, in which the following conditions are observed:

Temperature of electrolysis—less than 21° C.;
Initial acidity of electrolyte—150–250 grams per liter H_2SO_4;
Mn^{+3}ion concentration—0.7–4.0 grams per liter;
Average Mn^{+2} level in operating cell—10–30 grams per liter;
Anode current density—300–550 amperes per square foot.

3. The improved process defined in claim 1, in which the electrolyte as fed to the cell is a slurry containing suspended particles of manganese dioxide.

4. The improved process defined in claim 1, in which the precipitation step is carried out in the interstices of a body of catalyst support material in and on the particles of which active manganese dioxide is deposited.

References Cited in the file of this patent

UNITED STATES PATENTS

1,352,208	Lovelace	Sept. 7, 1920
1,491,498	Tainton	Apr. 22, 1924
1,874,827	Storey	Aug. 30, 1932
2,299,428	Rossetti	Oct. 20, 1942
2,500,039	Magoffin et al.	Mar. 7, 1950