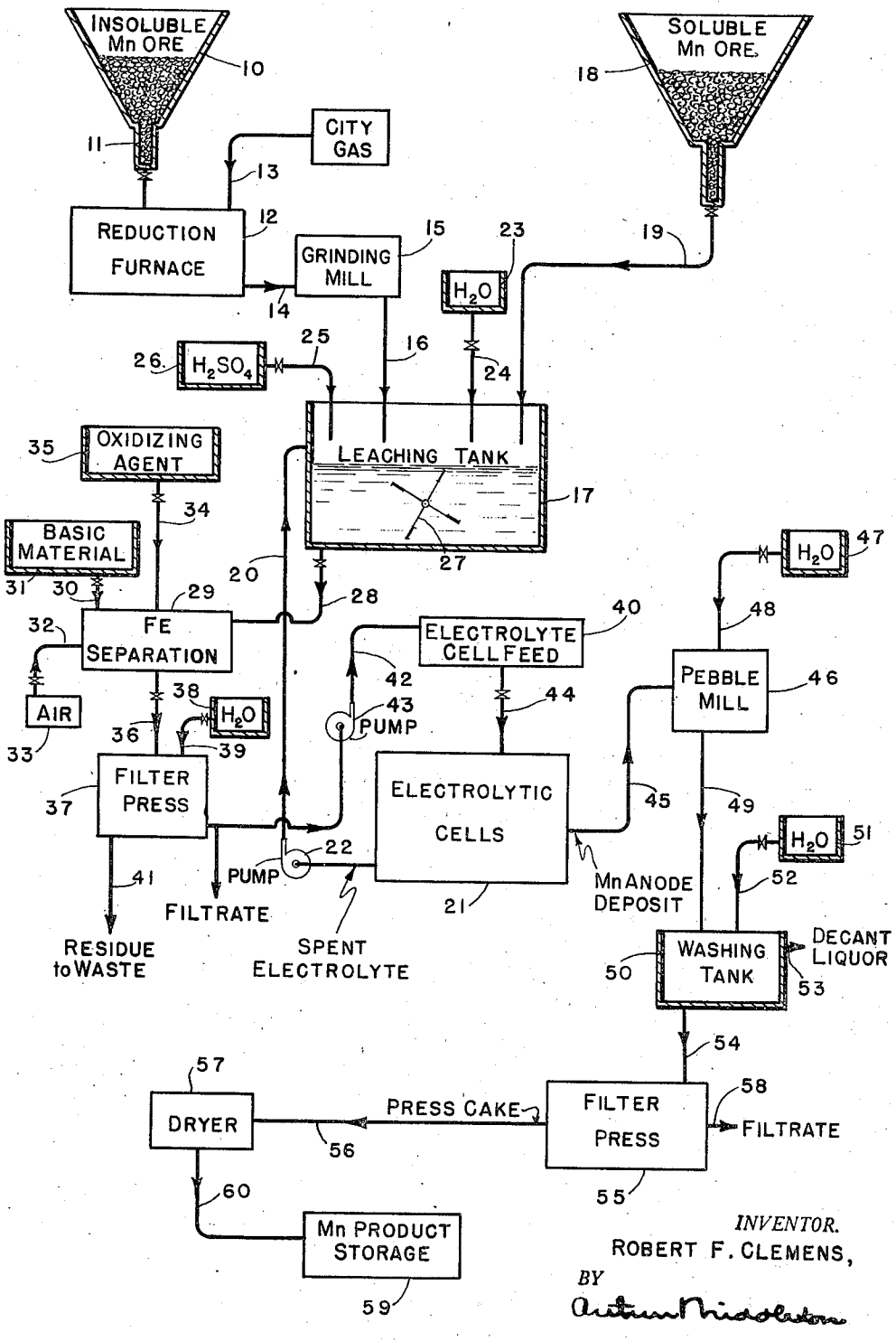
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PROCESS OF ELECTRODEPOSITING A MANGANESE DIOXIDE COMPOUND

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PROCESS OF ELECTRODEPOSITING A MANGANESE DIOXIDE COMPOUND

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1 Claim. (Cl. 204—83)

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This invention relates to a process of electrodepositing a manganese oxygen containing compound. More particularly, it has to do with the depositing anodically of such compound and in a substantially pure state.

The manganese oxygen containing compound, commonly known as manganese dioxide, MnO_2, is in great demand as a depolarizer material for use in dry cell batteries. Such compound has heretofore been obtained by suitable treatment of a manganese bearing ore.

Of the available manganese bearing ores, there is the ore known as pyrolusite, in which the manganese is primarily present in the form of an acid insoluble oxide admixed or associated with such objectionable constituents as iron oxides and silica. Another of these ores, is rhodochrosite, in which the manganese is present in the form of the acid soluble manganese carbonate but having associated therewith the objectionable constituents as iron and silica. While these ores carry a manganese content sufficiently high for commercial exploitation, it has not been possible by the treatments heretofore proposed to obtain a manganese product of sufficient purity to maintain an overall degree of efficiency as high as when employing this electrolytic manganese product as a depolarizer material.

Accordingly, an object of the present invention is to provide a process whereby a manganese product is produced which exhibits the overall high efficiency required for a satisfactory depolarizer material.

Another object of the present invention is to provide a process of electrodepositing whereby an anodically manganese oxygen containing compound is produced which is substantially devoid of iron contamination.

Still another object of the present invention is to provide a process of electrodepositing a manganese containing compound anodically in which the initial source of the manganese is a manganese bearing ore having the contained manganese present in either acid insoluble or soluble form.

A further object of the present invention is to provide a process of electrodepositing a manganese oxygen containing compound anodically in which a manganese bearing ore is employed as the initial source of the manganese.

A further object of the present invention is to provide a process of electrodepositing which will produce an anodic manganese oxygen containing compound of a high degree of purity in a commercially practical and efficient manner, and at a minimum cost.

Other features of novelty and objects will be apparent from the following description taken in connection with the accompanying drawing, wherein the single figure is a diagrammatic illustration of a system for carrying out the treatment according to the present invention.

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Referring to the drawing, manganese bearing ore containing iron as an impurity and having the manganese present as an acid insoluble compound, like pyrolusite ore, ground or otherwise reduced to particles of suitable size, for example 8 mesh size, in the hopper 10, is introduced through the pipe 11 into a roasting furnace 12, wherein it is treated to convert such manganese compound into an acid soluble form. Pyrolusite ore has the manganese present as manganese dioxide, MnO_2, which is insoluble in acid. To convert the insoluble manganese dioxide, MnO_2, in the ore into the acid soluble manganous oxide, MnO, the ore in the furnace 12 is subjected to a reducing roast. To do this city gas consisting chiefly of hydrogen, methane, and carbon monoxide, is introduced into the furnace through the line 13 in an amount sufficient to create a reducing atmosphere therein, and such furnace is then heated to a temperature of between 650° C. and 815° C., preferably 704° C., for about an hour or less. If desired, in place of roasting the ore in the presence of city gas, coal or other carbonaceous material in quantity sufficient to produce reducing conditions may be incorporated with the charge of ore and the resulting mass subjected to the same roasting operation previously described. At the completion of the roasting operation, the furnace is cooled to room temperature while maintaining the roasted charge in the reducing atmosphere. When cooled to room temperature it is stable and may be stored in contact with air without danger of re-oxidation of the manganous oxide to the acid insoluble manganese dioxide.

The thus reduced ore is conveyed through the line 14 to a grinding mill 15 wherein it is ground to particles of a size corresponding to approximately 65 or 100 mesh size. The thus ground roasted ore may then be introduced through the line 16 into a leaching tank 17 wherein it is subjected to an acid leaching operation to be subsequently described.

In place of the reduced pyrolusite ore, an ore likewise containing iron as an impurity but having the manganese present as an acid soluble manganese compound, as for example rhodochrosite ore, may be employed. Rhodochrosite ore consists essentially of manganese carbonate, and the manganese component of such carbonate is manganous oxide, MnO, which is acid soluble. Thus, the reducing roast treatment described in connection with pyrolusite ore is not at all necessary with rhodochrosite ore. This last named ore, after being ground to a suitable particle size of, for example 8 mesh size, is introduced into the hopper 10, and may be discharged therefrom

directly into the leaching tank 17 through the line 19.

To the leaching tank 17 is introduced an acid leaching liquid in the form of spent electrolyte solution resulting from a cycle of cell operation, it being supplied through the line 20 from the electrolytic cells designated by the numeral 21 by means of the pump 22. Such electrolyte solution contains manganous sulfate and free sulfuric acid. Water from the tank 23 is supplied to the spent electrolyte solution in the leaching tank through the line 24 in quantity such as to dilute it with almost enough water to make up for evaporation losses incurred during its period in the operation cycle of the electrolytic cells. The remainder of the water to bring up the water dilution of the electrolyte solution to fully compensate for evaporation losses suffered in the cell cycle is added as wash water at a later stage of the process hereinafter described. The spent electrolyte solution, after dilution, is analyzed for both manganous sulfate and free sulfuric acid content, and upon the basis of such analysis the required amount of either reduced pyrolusite ore or rhodochrosite ore to be added and acid, if any, is calculated. Should the calculations show that a quantity of dilute sulfuric acid should be added, such quantity of acid is supplied to the electrolyte solution in the tank 17 through the line 25 from the tank 26.

The leaching tank is preferably made of wood, and is provided with a simple wooden paddle type agitator as indicated by the numeral 27, said agitator being so disposed that its peripheral ends are spaced only a slight distance from the bottom of the tank. The agitator is preferably driven at a speed of about 25 revolutions per minute. With the agitator thus arranged and operated at said speed, the solids, even of a particle size of 8 mesh, will be agitated just sufficient to keep them in motion.

The spent electrolyte or leaching solution in the tank 17 is heated to a temperature of 60° C. by direct injection of steam, whereupon the agitator 27 is caused to revolve. Either reduced pyrolusite ore from the grinding mill 15 or rhodochrosite ore from the hopper 18 is then supplied to the solution in quantity corresponding to the previously calculated amount. If pyrolusite ore is selected, it is supplied to the solution through the line 16. Should rhodochrosite ore be selected, it is supplied through the line 19. The agitation causes the ore particles to be brought into intimate contact with the leaching solution, and as a result of such contact the manganous oxide contained in the ore particles reacts with the free sulfuric acid to form more manganous sulfate. This reaction, exemplified by the following equation, is exothermic and causes a temperature rise of from 5° to 10° C.

$$MnO+H_2SO_4 \rightarrow MnSO_4+H_2O+heat$$

The reaction between the manganous oxide in the ore particles and the free sulfuric acid present in the solution continues until the acidity of the resulting ore pulp mass corresponds to a pH value of between 3 and 4, whereupon it stops or is extremely slow, and for all practical purposes is complete. After agitation for about an hour, it is desirable to test the mass for its acidity. Should the test show that its acidity corresponds to a pH value of around 3, the leaching has proceeded satisfactorily. In the event that the test shows its acidity to be greater than that corresponding to a pH value of 3, a further addition of the ore in quantity sufficient to lower the acidity to a pH value of around 3, preferably between 3 and 4, is introduced into the ore pulp mass. To insure the reaction of the maximum amount of the free sulfuric acid in the leaching solution with the manganous oxide of the ore particles, the ore is preferably added in quantity in slight excess over the calculated amount. Usually, an hour is sufficient for completion of the reaction. While the reaction rate and leaching yield of manganese will increase as the fineness of the ore particles is increased, it has been found that coarse ore particles, for example 8 mesh size, give a reasonable reaction time of about 1 hour and manganese extraction yield close to 85%. Any other soluble constituents contained in the ore particles will also go into solution. One of such constituents present in the ore which readily goes into solution is iron, and since it has been found to be extremely detrimental, it is necessary that it be eliminated from the solution before the ore pulp mass is subjected to the filtering operation to be subsequently described.

In the leaching of the manganese ore thus described, the manganous sulfate removed from the electrolyte solution along with the generation of free sulfuric acid during its cycle in the electrolytic cells, is replenished by the reaction of the manganous oxide contained in the ore particles with such free acid. In a balanced system there is just sufficient free sulfuric acid in the spent electrolyte solution to bring the manganese concentration back to that desired for electrolytic cell feed. Practically, some fresh acid must be added to make up for mechanical losses and other acid consuming constituents in the ore.

Upon completion of the leaching operation, the ore pulp mass is withdrawn from the leaching tank 17 through the line 28 and is conveyed through such line to the tank designated by the numeral 29, wherein it is subjected to a treatment for the separation or precipitation of the iron out of the manganous sulfate solution. To carry out such treatment, a basic substance capable of forming a precipitate upon reaction with the free sulfuric acid contained in the ore pulp mass, preferably in slurry form, is introduced into the tank 29 through the line 30 from the supply tank 31, and such introduction continues until the acidity of the mass has been reduced to that corresponding to a pH value of between 5 and 6. The basic substance employed may be selected from the group consisting of calcium oxide, calcium hydroxide, calcium carbonate, sodium carbonate, barium oxide, barium hydroxide, barium carbonate, strontium oxide, strontium hydroxide, strontium carbonate, magnesium oxide, magnesium hydroxide, magnesium carbonate. Of the substances mentioned, it is preferred to use those of calcium. With the acidity reduced to the pH range of between 5 and 6, the mass is caused to undergo an oxidation by either subjecting it to an aeration employing compressed air for a sufficient time or to the action of an oxidizing agent, for example manganese dioxide in the form of unroasted pyrolusite ore, in sufficient amount and time to convert all of the ferrous iron to the ferric state. For aeration, the necessary compressed air is supplied to the tank 29 through the line 32 from the receptacle 33. For the oxidation employing an oxidizing agent, the agent in the required amount is introduced into the tank 29 through the line 34 from the tank 35.

The treating of the leached ore pulp mass with the lime in slurry form in an amount such as to reduce its acidity corresponding to a pH value

between 5 and 6, and subjecting it to an oxidation employing either air or manganese dioxide as the oxidizing medium, results in all of the ferrous iron compound, namely ferrous sulfate, to be thrown out of the manganese solution as ferric hydroxide precipitate along with the precipitation of calcium sulfate. It is to be noted that ferric iron is readily thrown out of solution at the pH range of between 5 and 6, while ferrous iron is precipitated out of solution at a pH range of between 7 and 8 which is too close to the pH range at which manganese is thrown out of solution to employ it for the separation of the iron in the ferrous state from the manganese solution. The reactions of this treatment may be expressed by the following equations:

With calcium hydroxide and aeration

$$4FeSO_4 + O_2 + 4Ca(OH)_2 + 2H_2O \longrightarrow 4Fe(OH)_3 \downarrow + 4CaSO_4 \downarrow$$

With calcium hydroxide and MnO_2

$$2FeSO_4 + MnO_2 + Ca(OH)_2 + 2H_2O \longrightarrow 2Fe(OH)_3 \downarrow + MnSO_4 + CaSO_4 \downarrow$$

With the completion of the addition of the lime in slurry form to reduce the acidity of the leached ore pulp mass to a pH range of between 5 and 6, it is desirable, before proceeding with the oxidation described above, to test a sample of the mass for iron content. Such test comprises the steps of filtering, acidifying the filtrate, oxidizing the acidified filtrate with permanganate, and then adding ammonium thiocyanate to the oxidized filtrate. Should the thiocyanate addition result in the formation of the characteristic red color of ferric iron, there is ferrous iron in solution in the ore pulp mass. Frequently there is enough unreduced MnO_2 in the reduced pyrolusite ore particles to oxidize any iron present in the leached ore pulp mass.

From the tank **29**, the ore pulp mass is discharged through the line **36** into a batch suction box or filter press **37**, in which it is subjected to vacuum filtration. By such filtration the manganous sulfate solution in substantially pure state and devoid of iron passes through the suction box as the filtrate while the filter cake comprising the gangue, calcium sulfate and ferric hydroxide precipitates, and silica, is retained upon the box. Upon completion of filtration, wash water from receptacle **38** is introduced through the line **39** upon the suction box in quantity sufficient to extract most of the manganous sulfate solution that may be dispersed throughout the filter cake. By this washing of the cake the remainder of the water to bring up the water dilution of the purified manganous sulfate solution filtrate to that required for an electrolyte solution cell feed, is introduced. The filter cake is withdrawn from the box **37** through the line **41** and is discharged to waste.

In place of discharging the ore pulp mass, upon completion of the iron separation treatment, into the filter press **37**, as previously described, the ore pulp mass may be permitted to settle over night in the tank **29**, and then decanted and the sludge filtered through the suction box or filter press and washed. The decant liquor is passed through the box to polish it prior to pumping to the electrolyte cell feed tank **40**.

The filtrate or manganous sulfate solution in a substantially pure state and devoid of iron is discharged from the suction box or filter press **37** through the line **42** and is conveyed through such line to the electrolyte cell feed tank **40** by means of pump **43**. The tank **40** is preferably made of wood and of a size sufficient to hold enough electrolyte solution for one 24 hour electrolytic cell cycle. From this tank **40**, the electrolyte or manganous sulfate solution substantially devoid of iron is withdrawn through line **44** and is conveyed through such line continuously to the electrolytic cells designated by the numeral **21**.

The electrolytic cells comprise rectangular shaped wooden tanks lined with lead, and having cathodes of lead and anodes of either lead or graphite suitably suspended therein. At a point adjacent the feed end of the cells is disposed a vertical U-shaped lead coil through which steam is passed to heat and maintain the cell at a temperature between 60° C. and 70° C., preferably 70° C. The cell is of size such as to accommodate 20 anodes and 21 cathodes. Each anode has an effective area of 14 square feet, and with dimensions of 3 feet by 2⅓ feet when submerged. The voltage required per cell is between 2.5 and 3.0 volts, and the optimum current density is between 6 and 9 amperes per square foot of anode surface.

A desirable hook-up of the electrolytic cells is to arrange them in banks or units of four with the electrolyte feed being introduced into the first cell and overflowing into the second cell, then into the third cell and so on, with the spent electrolyte solution overflowing from the fourth cell being withdrawn and utilized for leaching the manganese bearing ore. Electrically the cells are hooked up in a series-parallel arrangement to give amperage and voltage requirements that can be met with standard D. C. generating equipment and which will not result in excessive bus bar sizes which is a function of the amperage alone.

In the electrolysis of the electrolyte solution of manganous sulfate, manganese dioxide, MnO_2, is deposited on the anode and sulfuric acid equivalent to the managanese deposited is generated, while hydrogen is evolved at the cathode. The overall electrolysis reaction may be expressed by the following equation:

$$MnSO_4 + 2H_2O \longrightarrow MnO_2 \downarrow + H_2SO_4 + H_2 \uparrow$$

As the exact electrochemical mechanism of this anodic manganese dioxide deposit is not definitely known, it is to be understood that it is entirely different to that of the usual electrodeposition of metals which are deposited on the cathode. Investigation of such deposit as regards acidity, specific gravity, and X-ray diffraction pattern, tends to indicate that it is H_2MnO_3 rather than $MnO_2.H_2O$, but as this has not yet been actually and definitely determined it can not be stated as an established fact.

The electrochemical equivalent of manganese going through the above valence change of 2 is 1.024 grams manganese per ampere hour, which means that if 100% of the current imposed on a cell containing a manganous sulfate electrolyte is utilized to effect the above reaction, then every ampere hour of current used will result in the deposition of 1.024 grams of manganese. Actually it is not possible to utilize 100% of the electrical input to produce manganese dioxide and some of the input is wasted in merely generating oxygen at the anode. The ratio of the actual amount of manganese deposited as manganese dioxide to that which should be deposited, as computed from the above electrochemical equivalent is known as the current efficiency.

The current efficiency is affected by various factors. It tends to decrease as the acidity in-

creases, although this effect is not appreciable in the acid range of this process. Increasing the temperature tends to increase the current efficiency and this is utilized by operating at 70° C., which is about as high as practical, due to evaporation. The presence of iron and reducing agents are known to reduce the current efficiency. The greatest single variable that can be controlled is the marked effect of anode current density on current efficiency. For example, as the current density is dropped from 18 amperes per square foot of anode surface to 3 amperes per square foot of anode surface, the current efficiency rises from 20% to 75%.

From the foregoing, it is apparent that the output of each cell will depend on the electrical input and the current efficiency. Since the current efficiency decreases as the input increases, it has been found that the actual cell output increases at a relatively low rate as the current input is increased. This is especially true in going from 6 amperes per square foot of anode surface to 12 amperes per square foot of anode surface, where it is found that the output is almost constant, due to the current efficiency falling off at a rate sufficient to offset the increased current input. A current density of between 6 and 9 amperes per square foot of anode surface is, therefore, the optimum. Another factor to be considered in determining the optimum current density is the power requirements per unit of the product. As the current density goes up, the power requirements likewise go up, due to the current efficiency decreasing and to the higher voltage requirements at the higher current densities.

The deposit of manganese on the anodes is removed periodically therefrom by lifting the anodes from the cells and taking off the deposit. With graphite anodes this is best done by means of a thin stainless steel spatula which can be inserted under the sheet deposit. Occasionally sections of deposit are difficult to remove and it is best usually to let this deposit remain on the anode rather than damage same to get it off. The deposit on lead anodes can be cleaned off best by tapping the deposit with a wooden mallet which causes it to break off rather easily. It appears that an operating period of six days between cleanings is about the correct interval.

The manganese anode deposit, after removal from the anodes, comprises pieces of a size having an overall width of from ½ inch to 4 or 5 inches and a thickness of about ⅛ inch. Such deposit is introduced through the line **45** into a porcelain lined pebble mill **46**. Water from the tank **47** is supplied to the mill through the line **48**. While in the mill, the deposit is subjected to wet grinding until it has been reduced to about 95% minus 325 mesh size.

From the mill **46**, the ground manganese deposit is discharged through the line **49** into the washing tank **50**. Wash water from the tank **51** is supplied to the tank through the line **52**. In the washing tank, the ground deposit is washed by successive batch re-pulpings, settling periods, and decantations, until the sulfate content of the decant liquor is the same as the wash water. On a large enough scale, continuous washing would be advantageous. The decant liquor is discharged from the tank through the line **53**.

Upon completion of the washing, the manganese deposit is introduced through the line **54** into the filter press **55**, wherein it is subjected to vacuum filtration. The press cake resulting from such filtration is discharged through the line **56** into the drier **57**, and the filtrate is withdrawn through the line **58**. In the drier, the press cake is subjected to a temperature of about 78° C. The dried cake is discharged through the line **60** into the storage tank **59** for subsequent disintegration and packaging as a finished product.

Various specific details of procedure and conditions of operation have been set forth for the purpose of giving a clear understanding of the present invention, but it is to be understood that the invention is not limited to the exact details given, as it includes modifications and changes coming within the scope of the appended claim.

Having thus described the invention, what is claimed as new and desired to be secured by Letters Patent is:

The process of electrodepositing a manganese dioxide compound which comprises treating a leaching solution containing manganous sulfate and free sulfuric acid with a manganese bearing ore containing iron and having the manganese present as an acid soluble compound in such amount as to neutralize said acid to a degree such that the acidity of said solution corresponds to a pH value of not lower than 3 and not more than 4 to thereby cause the acid soluble manganese compound in the ore to go into the leaching solution as manganous sulfate, treating the thus leached ore pulp mass with a basic substance capable of forming a precipitate upon reaction with said acid in amount such as to reduce its acidity to a pH value of between 5 and 6, subjecting said mass to an oxidation to convert the ferrous sulfate to the ferric state thereby causing the ferric iron to be precipitated out of said solution, separating the leaching solution from said mass to obtain a purified leaching solution substantially devoid of iron, passing a direct current through electrodes immersed in an electrolyte bath of said leaching solution while maintaining said bath at a temperature of not less than 60° C. and not greater than substantially 70° C. and at a current density not less than 6 and not more than 9 amperes per square foot of anode surface to deposit on the anode the manganese in the form of manganese dioxide, and forming said leaching solution by diluting spent electrolyte withdrawn from said bath with water and adding sulphuric acid as required to obtain the said acidity of said solution.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,167,700	Laist et al.	Jan. 11, 1916
1,278,308	Cullen	Sept. 10, 1918
1,322,000	Ellis	Nov. 18, 1919
1,874,827	Storey	Aug. 30, 1932
2,299,428	Rossetti	Oct. 20, 1942
2,340,188	Jukkola	Jan. 25, 1944
2,348,742	Mantell	May 16, 1944

OTHER REFERENCES

Transactions of the American Electrochemical Society, volume 33 (1918), pages 109–124.

Transactions of the American Electrochemical Society, volume 62 (1932), pages 392–402.