

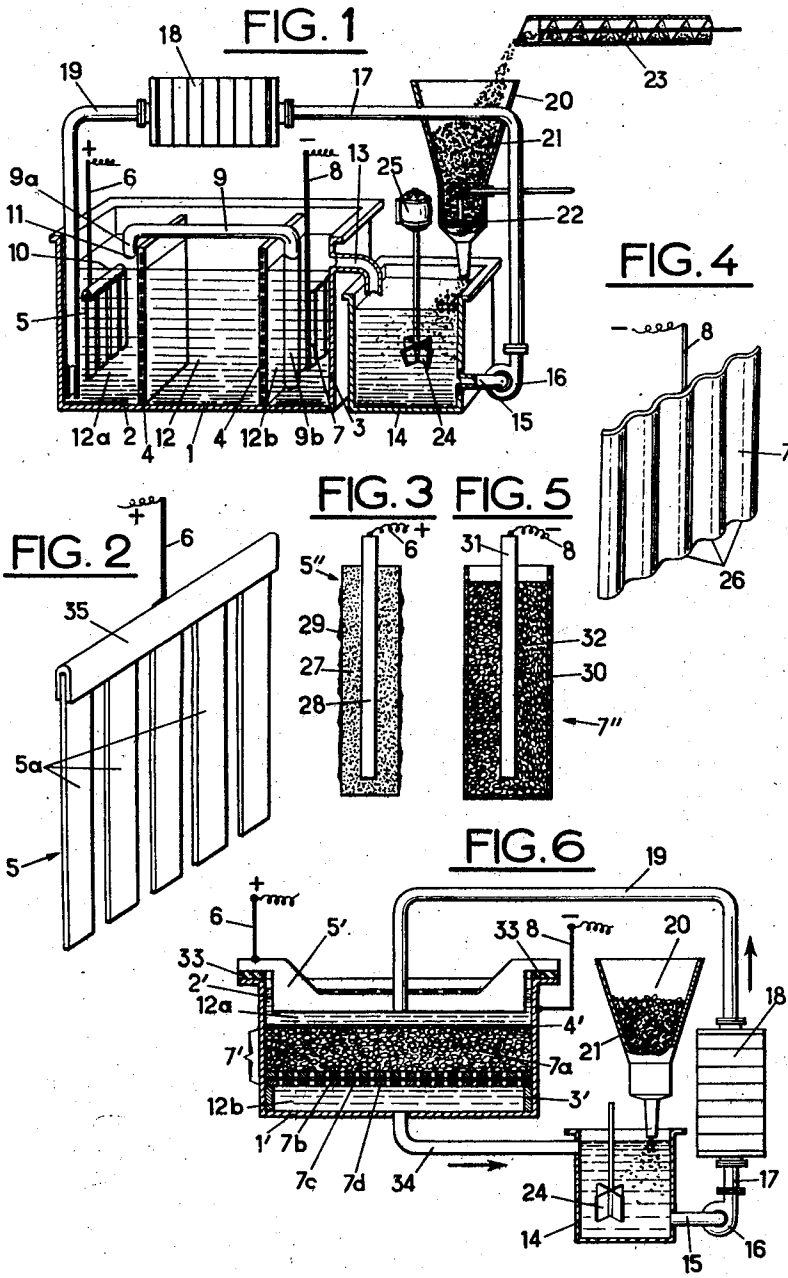
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DEVICES FOR PRODUCING MANGANESE DIOXIDE BY ELECTROLYSIS

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DEVICES FOR PRODUCING MANGANESE DIOXIDE BY ELECTROLYSIS

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The present invention has for its object an improved device by means of which manganese dioxide of higher quality may be manufactured by electrolysis at a reduced cost.

It is known that the electrolysis of a manganese salt between a cathode (made, e. g., of lead) and a lead anode in a galvanic battery results in a deposit of manganese dioxide on said anode. When the electrolysis is performed in the usual manner, in a tank having no porous diaphragm between the anode and the cathode and without stirring the bath, the anode becomes covered with a layer of manganese dioxide, and the cathode with a complex deposit comprising metallic manganese and manganous hydroxide, hydrogen being liberated at said cathode. It is established that simultaneously the bath becomes acid in the anodic region and alkaline in the cathodic region.

The gelatinous deposit on the cathode is a poor conductor of electricity and, accordingly, creates an additional resistance to the flow of the current. To overcome such resistance, it is, therefore, necessary to increase the potential difference between the electrodes to an inadmissible extent.

Accordingly, it has already been proposed to remove the gelatinous deposit formed on the cathode by continuously stirring the bath in order to mix the acid anodic solution and the alkaline cathodic solution, thus preventing the cathodic region from becoming too alkaline. However, such stirring does not create the best operating conditions for the electrolysis, inasmuch as, in the course of the electrolysis process, the average acidity of the bath regularly increases, because manganese is being continuously withdrawn from the bath.

In order to mitigate the aforesaid drawback and to avoid the formation of an insulating layer on the cathode, it has been proposed to give a relatively considerable degree of acidity to the bath, so that, in the cathodic region, the pH remains in all points below the pH corresponding to the precipitation of the manganous hydroxide. Most existing installations operate with such a relatively low pH. However, when operating in this well known manner, it is difficult to adjust the pH of the different regions, and, particularly, to give it the necessary optimum value at the anode as well as at the cathode. As a matter of fact, it is difficult to correctly control the mixing process by stirring and convection.

Now, we have found that there are optimum values for the anodic bath as well as for the cathodic bath.

When operating with a well defined current density and at a temperature which also is well defined, it is found that the aspect, and, particularly, the adherence, of the manganese dioxide deposited on the anode vary as the pH of the bath in that region. We have found that a very low acidity—in the order of 2 to 3 gr. of H₂SO₄ per liter—produces a satisfactory adherence (that is to say, sufficient to prevent the dioxide from peeling off from the anode and from spreading into the bath, while,

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at the end of the operation, enabling a suitable removal of the dioxide deposited on the anode).

Similarly, there is an optimum value of acidity for the cathodic region. This is particularly true when the cathode comprises impure manganese dioxide (as is the case in some forms of our invention) which must be reduced to the form of manganous salt, on account of the fact that the reducing power of the manganese dioxide is so great that the cathodic potential is very negative and the acidity of the bath surrounding the cathode is low. It appears, therefore, that also for the cathode it is desirable to select a pH which is as high as possible but, however, quite distant from the pH corresponding to the precipitation of the manganous hydroxide.

Accordingly, the invention provides a device by means of which manganese dioxide may be manufactured by electrolysis, wherein the pH in the anodic region and the pH in the cathodic region may be separately best adjusted, so as to provide a suitable adherence of the manganese dioxide on the anode, and a good reduction of the impure manganese dioxide contained in the cathode.

The invention provides a device wherein the stability of the composition of the bath is maintained during the electrolysis process, so that said composition is constantly equal or close to the optimum composition.

The invention also provides a galvanic tank suitable for the preparation of manganese dioxide, which is characterized by the fact that it is subdivided into an anodic compartment and a cathodic compartment by at least one diaphragm, means being provided for drawing solution from the anodic compartment, which is fed to the cathodic compartment, and for bringing a fraction of the solution, drawn from the cathodic compartment, back into the anodic compartment.

The invention further provides an electrolytic device for preparing manganese dioxide, which operates with a small quantity of solution which is continuously regenerated, said device comprising a galvanic tank divided, by at least one porous diaphragm, into one anodic compartment and one cathodic compartment; means connecting the anodic compartment with the cathodic compartment and enabling the solution to pass from one compartment into the other; a vessel for receiving the solution from the cathodic compartment; means for introducing a regenerating manganese compound into said vessel; filtration means; means for drawing regenerated solution from said vessel and for carrying the same to said filtration means; and means for carrying the resulting filtrate into the anodic compartment of said galvanic tank.

The invention also provides a galvanic tank which operates under a low electrode potential difference lower than or equal to 3.5 volts and, preferably, close to one volt.

In one embodiment of the invention, the electrodes are vertically arranged within the galvanic tank, and means, such as a siphon, are provided for carrying the solution from the upper portion of the anodic compartment to the lower portion of the cathodic compartment and other means are provided for carrying the solution contained in the upper portion of the cathodic compartment to the lower portion of the anodic compartment.

In such a galvanic tank having vertical electrodes, the anode may comprise metal bands (for instance, made of lead or stainless steel covered with a thin layer of lead deposited by electrolysis), laid side by side on a common support, while the cathode may comprise a similar metal band, but of corrugated form.

In a modified form, the active portion of the cathodes may comprise granulated native manganese dioxide which is reduced by the current into manganous protoxide, then into manganous Mn⁺⁺ ions, thus becoming the source of

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the manganese to be transformed into dioxide at the anode, while the anode comprises an agglomerate of pure manganese dioxide (for instance, electrolytic manganese dioxide) made from a thick paste formed with said pure dioxide and a syrup of manganese nitrate (said plate being strongly compressed within a mould, and, after being withdrawn from the mould and dried, heated up to a temperature in the vicinity of 180° C.).

A modified form of anode comprises a metal sheet or wire gauze which has been covered with a layer of manganese dioxide by dipping it, for instance, in a syrup of manganese nitrate, then drying and calcinating the resulting covering in order to transform it into manganese dioxide.

In a modified form of our improved device, the galvanic tank comprises substantially horizontal electrodes, the anode being disposed above the cathode; the cathode comprises a granulated mass of native manganese dioxide, at least one electrically conducting perforated sheet, and a filtering cloth; means being provided for drawing solution from the lower portion of the tank (below the cathode) and for carrying it back, after regeneration and purification, to the upper portion of said tank (above the anode).

These and other objects and advantages of the invention will more fully appear from the following description, given by way of merely illustrating various embodiments suitable to carry it into practice, and taken in connection with the somewhat diagrammatical drawings in which:

Fig. 1 shows, in perspective view, a vertical cross-section of a first embodiment of our improved device according to the invention, with vertically disposed electrodes;

Fig. 2 shows the anode of the device shown in Fig. 1, drawn at a larger scale;

Fig. 3 shows a modified form of said anode;

Fig. 4 shows the cathode of the device shown in Fig. 1, drawn at a larger scale;

Fig. 5 shows a modified form of said cathode; and

Fig. 6 is a cross-section of a second embodiment of our device, wherein the electrodes are substantially horizontal.

Our improved device as shown in Fig. 1 essentially comprises a galvanic tank 1 subdivided into an anodic compartment 2 and a cathodic compartment 3, by means of porous walls or partitions 4 constituted by a web made of superpolyamid, of asbestos or any equivalent material.

In the compartment 2 is an anode 5 (shown in Fig. 2 at a larger scale and described in a more detailed manner hereinafter) connected by a cable 6 to the positive terminal of a suitable D. C. source (not shown).

In the compartment 3 is a cathode 7 (shown in Fig. 4 at a larger scale, and described in greater detail hereinafter) made of an electrically conducting, corrosion resistant material, e. g. of lead, said cathode being connected, by a cable 8, to the negative terminal of the above mentioned D. C. source (not shown).

A siphon 9 provides for passing solution from the upper portion of the anodic compartment 2 to the lower portion of the cathodic compartment 3.

Up to a suitable level 10 (somewhat below the opening 11 of siphon 9), the tank 1 is fed with a suitable electrolyte 12, such as a solution of a manganese salt, e. g. a solution of manganese sulfate containing 25 gr. of manganese per liter and acidulated by 15 gr. of sulfuric acid H₂SO₄ per liter.

When utilizing a tank such as 1 in Fig. 1, we have found that excellent results are obtained with a current density of one ampere per square decimeter, at the anode as well as at the cathode, for an electrode potential difference of 3 volts, when the temperature becomes stationary in the vicinity of 70° C.

When utilizing such a current for performing an electrolytic decomposition, the Mn⁺⁺ ions flow towards the

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cathode where they lose their charge to give either metallic manganese or (by a secondary reaction) hydrogen and manganous hydroxide Mn(OH)₂, while, at the anode, the SO₄[—] ions lose their charge and produce nascent oxygen by secondary reaction (a fraction of this oxygen provides for the oxydation of the manganese sulfate, while the remainder is liberated as gas).

Owing to the utilization of diaphragms, such as 4, according to the invention, the pH may be separately adjusted to its optimum value, on the one hand, in the anodic compartment 2, and, on the other hand, in the cathodic compartment 3. This prevents the formation of a complex deposit on the cathode, which would present a high electrical resistance in the known producing methods, and the manufacturing operations may be performed with the reduced electrode potential difference (3 volts), as previously described.

As previously described, in the course of operation, the cathodic region has a tendency to become less and less acid, while the anodic region becomes more and more acid.

According to a feature of our invention, in order to maintain a practically constant acidity in each anodic and cathodic compartment during the electrolysis, a circulation is provided between the solutions respectively located within the anodic compartment 2 and cathodic compartment 3, for instance, in the following manner:

(1) The siphon 9 is such that its short branch 9a (ending into the opening 11) dips somewhat into the upper portion of electrolyte 12a within the compartment 2, while the long branch 9b dips into electrolyte 12b within the compartment 3 down to the vicinity of the bottom of said compartment;

(2) The tank comprises an overflow 13 so provided on the side of the cathodic compartment 3 that the electrolyte 12b within said cathodic compartment 3 may flow into a vessel 14 at the lower portion of which is connected a pipe 15 which leads into a pump 16. Said pump, constructed of a corrosion resistant metal, such as 18% Cr-8% Ni steel, drives the solution from the vessel 14 through a pipe 17 into a filter-press 18, from which the filtered solution reaches the anodic compartment 2 through a pipe 19.

Provided that, during the electrolysis, the average acidity of the bath shows a tendency to increase due to the elimination of manganese as dioxide depositing on the anode, it is necessary to constantly bring the average acidity back to a constant value, by continuously adding a suitable quantity of an alkaline component containing manganese to the electrolyte solution. To this end, through a spout 20, is added a powdered manganese compound 21 (such as manganese carbonate or protoxide), such addition being controlled by a rotary distributor 22, and said spout 20 being fed by means of a spiral conveyor or Archimedean screw 23. A stirring device 24, driven into rotation by a motor 25, provides for a thorough mixing of the powder 21, coming from the spout 20, with the solution within the vessel 14.

As above specified, said powder 21, coming from the spout 20, is utilized for neutralizing the aforesaid increase in acidity of the electrolyte and for maintaining the manganese content of the bath substantially constant.

Thus, with the aid of the siphon 9 and of the unit comprising the overflow 13, the vessel 14, the pipes 15, 17 and 19, and the pump 16, the pH of the solution in the anodic compartment 2 is maintained at a constant value, and the pH of the solution in the cathodic compartment 3 is also maintained at a constant value.

In a modified form of circulating system, the siphon 9 is deleted when the diaphragms 4 are sufficiently permeable, so that the hydrostatic balance is sufficient to cause a circulation of electrolyte from the anodic region towards the cathodic region.

Some electrode arrangements particularly suited for

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being utilized with a tank, such as 1 in Fig. 1, and shown in Figs. 2 to 5 are described hereinafter.

It is advantageous to utilize cathodes having a large surface and a small overall size, in order to be able to reduce the density of the cathodic current to a value lower than or equal to one ampere per square decimeter, and, consequently, to reduce the insulating deposit of manganous hydroxide on the cathode. With this end in view, each cathode 7 may comprise (as shown in Fig. 4) a metal sheet, of lead or other suitable electrically conducting material, forming corrugations, such as 26.

The anode 5, as shown in Fig. 2 at a larger scale, comprises several thin lead bands 5a, the thickness of which is, for instance, of about 2 mm. Such bands 5a are secured side by side (at a small distance from each other) by their upper end portion to a support 35 in the shape of a clamp, in order that they may be readily positioned and removed.

Since the electrolytic manganese dioxide deposited on the bands 5a is very brittle, the stripping of said deposit from said bands is easily performed by sufficiently bending the bands 5a, when they are covered with manganese dioxide, thereby easily breaking, peeling off or, in any other manner, separating such deposit from the anode. After having removed the manganese dioxide, each band 5a is straightened and planished without deteriorating it, in order to be able to insert it again into the support 35.

While remaining within the scope of our invention, the anode may comprise a plate or cylinder of electrolytic manganese dioxide (Fig. 3). To this end, a thick paste is prepared with electrolytic manganese dioxide, reduced in fine powder, and a syrup of manganese nitrate dissolved in water. Then said paste is strongly compressed into moulds. It is dried, and heated up to a temperature of 180° C., for causing the decomposition of the manganese nitrate into nitrous vapors and manganese dioxide, the latter providing a reinforcing element for the anodes thus produced and imparting them their mechanical strength.

For providing current input contact members for the anodes, before heating a plate or cylinder mass 27 of manganese dioxide to 180° C., as above described, a contact member, such as 28, in the form of a lead band or of a gas carbon plate, is being embedded into said mass 27.

When said input contact member 28 is made of lead, said contact member is not in direct contact with the bath, thereby largely avoiding an eventual corrosion effect leading to the formation of lead sulfate, which might pollute the collected dioxide.

When said input contact member 28 is made of gas carbon or graphite, the dioxide stripping operation is omitted and the anodes may merely be crushed with their carbon core. As a matter of fact, the depolarizing element in cells consists of a mixture of carbon and manganese dioxide, and this is the principal commercial use to which electrolytic manganese dioxide is put.

Similarly, the cathode may comprise a briquet or compressed element made of native manganese dioxide (which may be mixed with carbon powder to impart a sufficient electrical conductivity to it); said element may be advantageously stored in a sack or similar container. For instance, as shown in Fig. 5, a cathode, such as 7'', may be produced by utilizing a porous container or a bag made of filtering cloth, such as 30, inside of which are placed a lead strip 31 electrically connected to a wire 6 and surrounded with granules 32 of native manganese dioxide, passing, for instance, the screen No. 20 (corresponding to 20 meshes in a length of 27.77 mm.) in the French classification.

In the cathodic region the electrolyte acts as a strong reducing agent; therefore, the native manganese dioxide is reduced and forms manganese sulfate which is diffused into the solution. In this manner, the composition of the electrolytic solution is maintained substantially constant and, accordingly, the quantity of powder, such as

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22, to be introduced through a spout, such as 20, may be reduced.

Another advantage of utilizing a cathode made of manganese dioxide resides in that the manganese dioxide acts as a depolarizing agent, thus permitting the reduction of the electrode potential difference necessary to produce the electrolysis, thereby reducing the corresponding expense of energy.

With the specific embodiment wherein native manganese dioxide is utilized at the cathode, such impure manganese dioxide is dissolved at the cathode and a deposit of practically pure manganese dioxide is obtained at the anode.

In Fig. 6 is shown an embodiment of our invention having horizontal electrodes, which is particularly suitable when utilizing a cathode containing oxygen compounds of manganese. The same reference numbers are used for designating similar or corresponding elements in Figs. 1 and 6, such numbers being provided with a prime (') in Fig. 6.

The improved device shown in Fig. 6 comprises a tank 1' subdivided into an anodic compartment 2' and a cathodic compartment 3', by a very porous diaphragm 4'. In the anodic compartment 2' are disposed anodes, such as 5' (the sole anode visible in Fig. 6), constituted by sheets of lead, while, in the cathodic compartment 3', is embedded a complex cathode 7' comprising:

A granulated mass of native manganese dioxide calibrated, for instance, with screen No. 20, as above described;

A perforated sheet 7b made of lead;

A filtering cloth 7c; and

A perforated sheet 7d made of lead.

The lead sheet 7b is electrically connected to the tank 1', which is made of an electrically conducting material, such as lead.

The anodes 5' (electrically insulated from the tank 1', by insulating blocks 33) are electrically connected to the positive terminal of a source of current (not shown) by a conducting cable 6, while, by a cable 8, the negative terminal of said source is electrically connected to the tank 1', which, as above mentioned, is in electrical contact with the sheet 7b of the cathode.

The anodic solution 12a may easily diffuse through the diaphragm 4' of the anodic compartment 2' into the cathodic compartment 3' to mix with the cathodic solution 12b.

Besides, at the lower portion of the tank 1' is provided a discharge pipe 34 carrying the cathodic solution 12b into a vessel 14 from which said solution is taken by a pipe 15 delivering it into a pump 16 which drives the cathodic solution back through a pipe 17, a filter-press 18 and a pipe 19, in order to bring said solution into the anodic compartment 2'.

As in the case of the embodiment of Fig. 1, a powdered manganese compound 21 may be introduced into the vessel 14 through a spout 20 (the feeding device supplying powder 21 to the spout 20 is not shown in Fig. 6), a stirring device 24 mixing the powder and the acid solution which are contained within said vessel 14.

In the embodiment shown in Fig. 6, the cathode 7' comprises a granulated mass of native manganese dioxide, thus avoiding the expense of reducing the manganese dioxide MnO₂ into manganese protoxide MnO, and reducing the consumption of energy by lowering the electrode potential difference, for instance, from 3 volts to one volt.

Furthermore, due to the presence of manganese dioxide at the cathode, there is no hydrogen evolution at the cathode, on account of the fact that the hydrogen produced by electrolytic decomposition is burnt by the manganese dioxide. Moreover, the cathode is depolarized by the same manganese dioxide.

When utilizing a cathode such as 7' shown in Fig. 6, the manganese dioxide progressively disappears, and,

consequently, from time to time (for instance, every 24 hours) it is necessary to refill the cathode 7' by adding a new layer of native dioxide to it.

In order that those skilled in the art may better understand how our present invention is carried into effect, 5 two illustrated examples are given hereinafter:

Example 1

In a device of the type as shown in Fig. 1, i. e. comprising a galvanic tank with an anode constituted by several thin lead bands, such as shown in Fig. 2, and a cathode made of a corrugated sheet of lead, such as shown in Fig. 4, is introduced a solution of manganese sulfate, containing 25 gr. manganese per liter, and sulfuric acid, containing 15 gr. SO_4H_2 per liter. During the electrolysis operation, the temperature has been maintained at 70° C. and a current density of one ampere per square decimeter has been applied at the anode and at the cathode. For a gap of 5 cm. between the electrodes, a potential difference of 3.5 volts is applied between the electrodes. 20 1,300 gr. of manganese dioxide have been produced per 1,000 ampere-hours, that is to say a consumption of energy per 1,000 gr. of manufactured MnO_2 equal to:

$$\frac{3.5 \times 1,000}{1.3} = 2,690 \text{ watt-hours, i. e. } 2.69 \text{ kwh.}$$

In order to neutralize the excess of acidity of the bath, 830 gr. of manganese protoxide have been added per 1,000 gr. of manufactured manganese dioxide.

An excellent manganese dioxide has been obtained, 30 which was perfectly suited to the manufacture of dry cells.

Example 2

In a galvanic tank with horizontal arrangement of the electrodes, such as shown in Fig. 6, the cathode comprising native manganese dioxide and the anode comprising a sheet of lead, the operation has been conducted as follows.

A solution of manganese sulfate, containing 25 gr. manganese per liter and 15 gr. H_2SO_4 per liter, has been introduced into the tank. The operating temperature was 70° C. For an exposed surface of 1 square meter at the anode and at the cathode, a current intensity of 100 amperes has been applied, that is to say a current density of 1 ampere per square decimeter at the anode and at the cathode. It was possible to reduce the potential difference to one volt; the delivery of the pump was 50 liters per hour.

Under such conditions, and a 24 hour-operation (after which it has been necessary to refill the electrode, on account of the dissolution of the native manganese dioxide), 1,400 gr. of manganese dioxide (particularly suited for the manufacture of dry cells) have been produced per 1,000 ampere-hours, that is to say a consumption of energy per 1,000 gr. of manufactured manganese dioxide equal to:

$$\frac{1.0 \times 1,000}{1.4} = 710 \text{ watt-hours, i. e. } 0.71 \text{ kwh}$$

a consumption of energy which amounts but to about 25% of the consumption of energy found in the first example.

In order to neutralize the excess of acidity, it has been necessary to add 82 gr. manganese protoxide MnO per 1,000 gr. of manufactured manganese dioxide MnO_2 , that is to say a quantity equal to about one tenth of the quantity added in the case of the first example.

While we have illustrated and described what we deem to be preferred embodiments of our invention, it must be understood that various changes and substitutions including the size, shape, number, and arrangements of parts, and the nature and the composition of utilized products, may be made without departing from the spirit of our invention and it is not our intention to limit its scope other than by the terms of the appended claims. 75

In the foregoing description as well as in the appended claims, the words "anode" and "cathode" may just as well cover a single element or several ones. For instance, the anode may comprise several aligned bands, as shown in Fig. 2, or several parallel vertical strips (the whole unit constituting a "horizontal anode"), as in the embodiment shown in Fig. 6.

What we claim is:

1. A device for manufacturing manganese dioxide by electrolysis, comprising a tank unit adapted to receive an electrolyte constituted by a manganese salt and subdivided, by at least one diaphragm, into one anodic compartment with at least one anode and one cathodic compartment with at least one cathode located below said anodic compartment, each cathode comprising a granulated mass of native manganese dioxide and at least one perforated electrically conducting sheet supporting said mass of manganese dioxide; means for withdrawing electrolyte from said cathodic compartment and for adding thereto a manganese compound, and means for thereafter delivering said withdrawn electrolyte into said anodic compartment.

2. A device for manufacturing manganese dioxide by electrolysis, comprising an electrically conducting tank unit adapted to receive an electrolyte constituted by a manganese salt; at least one diaphragm, subdividing said tank unit into one anodic compartment with at least one anode and one cathodic compartment with at least one cathode and located below said anodic compartment, each cathode comprising a granulated mass of native manganese dioxide, a perforated electrically conducting sheet, a filtering cloth member and a second perforated sheet member, in superposed disposition with said perforated sheet members supporting said mass of manganese dioxide, and means for electrically connecting said perforated conducting sheet with said electrically conducting tank unit; means for withdrawing electrolyte from said cathodic compartment and for adding thereto a manganese compound, and means for thereafter delivering said withdrawn electrolyte into said anodic compartment.

3. A device for manufacturing manganese dioxide by electrolysis, comprising a tank unit adapted to receive an electrolyte of the type containing a manganese salt, said tank being subdivided into an anodic compartment provided with at least one anode and a cathodic compartment provided with at least one cathode, each cathode comprising a granulated mass of native manganese dioxide, and means for maintaining a constant acidity in said compartments, comprising means through which said electrolyte is continuously transferred from said anodic compartment to said cathodic compartment, means for withdrawing electrolyte from said cathode compartment and adding thereto a manganese compound and means for thereafter delivering said withdrawn electrolyte into said anodic compartment.

4. A device according to claim 3, wherein the anodic and cathodic compartments are disposed side by side and the electrodes are substantially vertical.

5. A device according to claim 4, wherein the anode comprises a metal sheet member covered by a layer of pure manganese dioxide.

6. A device according to claim 4, wherein the anode comprises a metal sheet member covered by a layer of pure manganese dioxide obtained by dipping the same into a syrup of manganese nitrate, drying the same, and finally calcinating it.

7. A device according to claim 4, wherein the anode is made of pure manganese dioxide.

8. A device according to claim 4, wherein the anode is made of pure manganese dioxide obtained from a thick paste, made of pure manganese dioxide and a syrup of nitrate of manganese, strongly compressed in a mould, withdrawn from said mould, and finally heated up to a temperature in the vicinity of 180° C.

9. A device according to claim 4, wherein the active portion of said cathode comprises native manganese dioxide.

10. A process for producing manganese dioxide in an electrolytic tank having separate anode and cathode compartments which process comprises the steps of introducing into said cathode compartment an electrolyte comprising a manganese salt, which electrolyte has the minimum acidity required to prevent precipitation of manganese hydroxide, and introducing into said anode compartment an electrolyte likewise comprising a manganese salt and having an acidity which results in the satisfactory adherence of the manganese dioxide formed to the anode, and maintaining a constant acidity in each compartment by continuously withdrawing electrolyte from said anode compartment and introducing it into said cathode compartment while simultaneously withdrawing electrolyte from said cathode compartment, increasing the alkalinity and manganese content thereof, and then introducing it into said anode compartment.

11. A process as claimed in claim 10 in which the acidity in said anode compartment is of the order of 2 to 3 grams of H_2SO_4 per liter.

12. A process as claimed in claim 11 in which a potential difference no greater than 3.5 volts is maintained between said anode and said cathode with a current density of one ampere per square decimeter.

13. A process as claimed in claim 10 in which said acidities are regulated in part by varying the volume of electrolyte transferred from each compartment to the other.

References Cited in the file of this patent

UNITED STATES PATENTS

1,322,000	Ellis	Nov. 18, 1919
1,878,244	Laury	Sept. 20, 1932
2,011,171	Baker	Aug. 13, 1935
2,340,254	Stewart	Jan. 25, 1944
2,341,356	Briggs	Feb. 8, 1944
2,424,958	Clemens	Aug. 5, 1947
2,741,591	Dewey	Apr. 10, 1956

FOREIGN PATENTS

14,988	Great Britain	of 1896
--------	---------------	---------