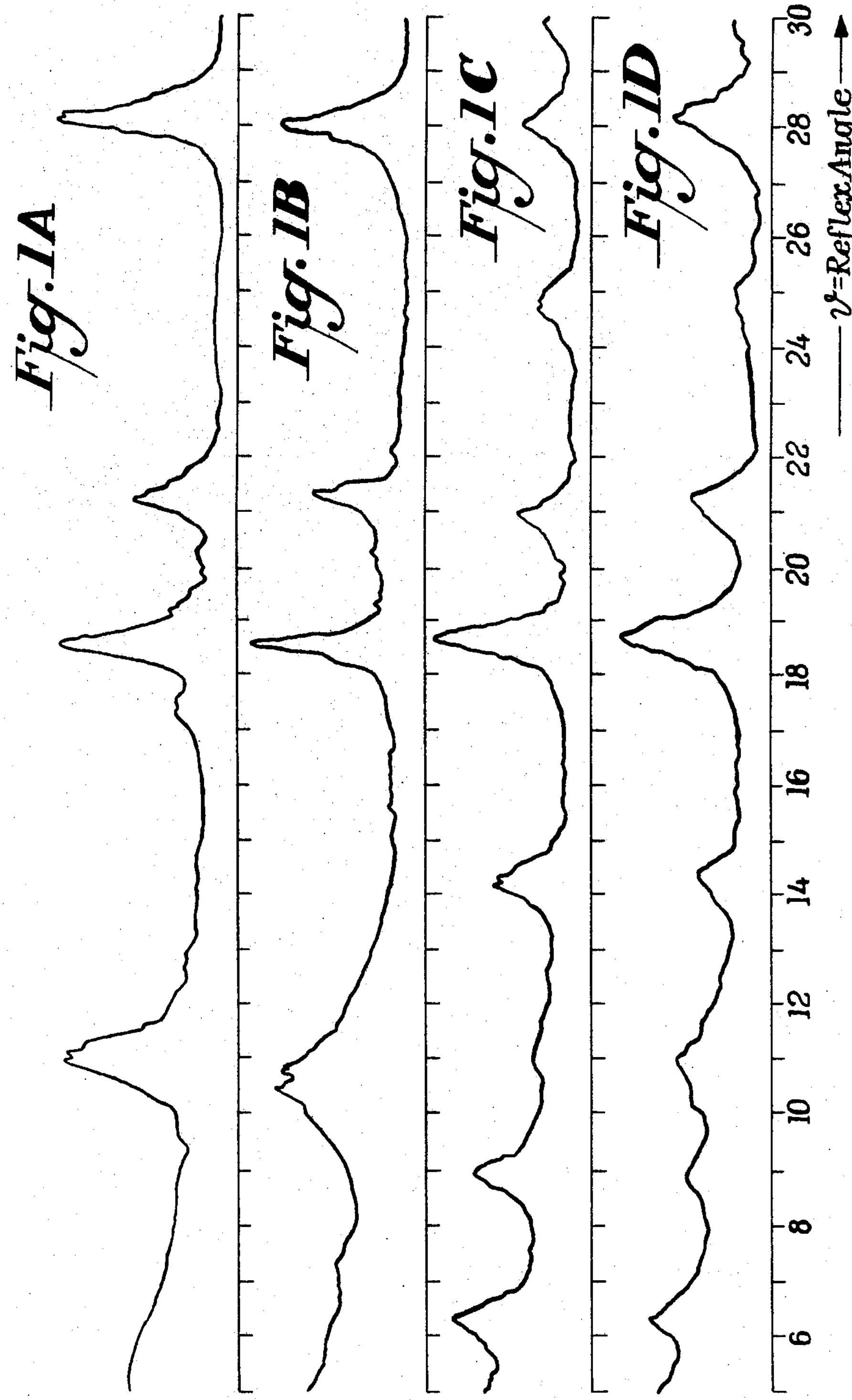
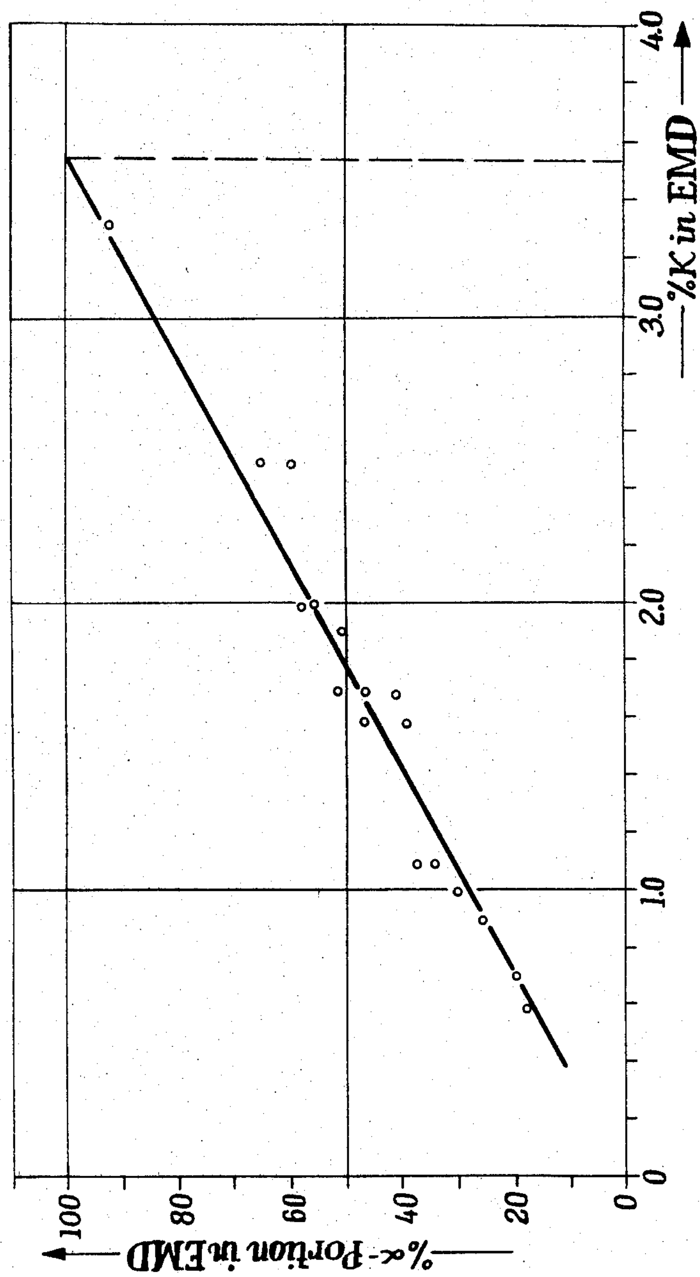
ELECTROLYTIC PRODUCTION OF MANGANESE DIOXIDE

Filed May 20, 1971 4 Sheets-Sheet 1

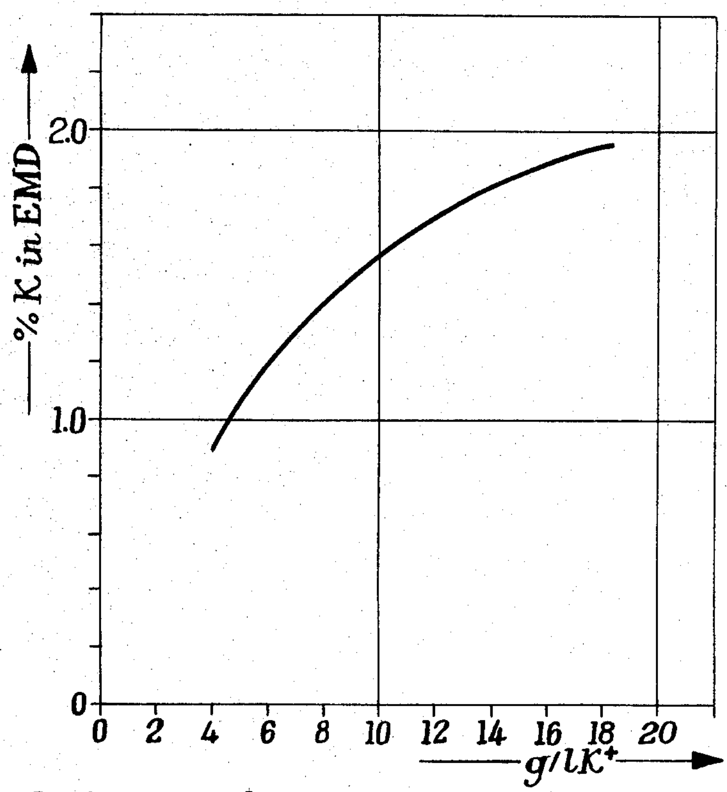


X-Ray Diagram (Goniometer Record) of Manganese Dioxide (MD)
a) γ-MD, chemically manufactured.
b) γ- Electrolytic-MD (EMD).
c) αγ -EMD with 90% α-Portion.
d) α,γ-EMD with ~60% α-Portion.



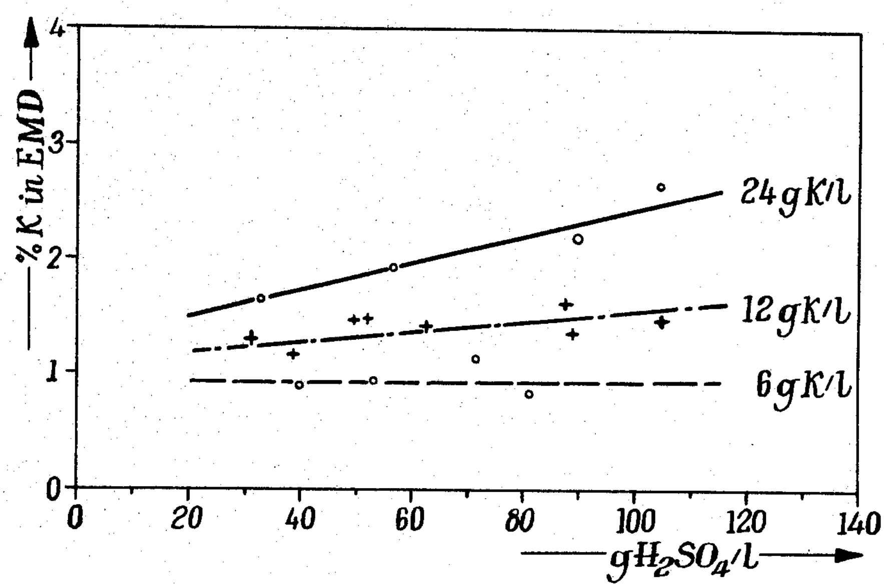
Dependence of the Portion of ∝-Modification in Electrolytic Manganese Dioxide on its Content of Potassium as Determined by X-Ray

Fig. 2.



Influence of Potassium Ion Concentration in the Electrolyte on the Potassium Content in Deposited Electrolytic Manganese Dioxide (EMD)

Fig. 3.



Influence of the Sulfuric Acid Concentration on the Incorporation of Potassium in the Lattice of Electrolytic Manganese Dioxide (EMD) at Different Potassium Ion Concentration in the Electrolyte

Fig. 4.

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ELECTROLYTIC PRODUCTION OF MANGANESE DIOXIDE

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ABSTRACT OF THE DISCLOSURE

Electrolytic production of manganese dioxide from an electrolyte consisting substantially of manganese-II-sulfate solutions in sulfuric acid. Manganese dioxide of which between 5 and 100 percent is α-modification of MnO_2, the balance being γ-modification of MnO_2, is produced with the use of an electrolyte containing potassium ions in a concentration of 1 gram/liter up to the saturation concentration, and free sulfuric acid in a concentration of between 20 and 150 grams/liter. These concentrations are maintained during electrolysis.

The present invention relates to the electrolytic production of manganese dioxide from an electrolyte consisting substantially of a manganese sulfate solution in sulfuric acid.

FIGS. 1 through 4 of the drawing show diagrammatically the influence of the various components on the characteristics of the manganese dioxide.

In the electrolytic production of manganese dioxide from a manganese sulfate solution in sulfuric acid, it is customary to use an electrolyte containing between about 20 and 60 grams/liter of manganese++ and between 5 and 100 grams/liter of sulfuric acid, at a temperature of between 70 and 98° C. Further bath constituents are contaminants which are unintentionally introduced thereinto on subjecting the manganese ore feed material to processing treatment. These contaminants include, for example calcium sulfate, magnesium sulfate, sodium and potassium sulfates.

Manganese dioxide is precipitated from all these solutions in the form of its γ-modification which has a more or less distinct X-ray crystalline structure. If use is made of a temperature higher than about 80° C. in combination with a current density of less than 1–2 amperes per square decimeter and in further combination with an acid concentration of less than about 100 grams/liter, then γ-manganese dioxide is precipitated in compact hard form on the anodes.

The ground, neutralized and washed products so made are well adapted for use as depolarization masses in Lechlanché cells and further primary cells. Electrolytically precipitated γ-manganese dioxide has more particularly been found to have a high density and to enable the construction of monocells of high ampere-hour capacity. Critical evaluation factors for this are inter alia the modification which the terminal potential undergoes as time goes on under high or low, mostly intermittent power load, and the maximum number of effective ampere hours. Depolarization masses are normally produced from a plurality of various grades of manganese dioxide as merely one manganese dioxide representative is scarcely able to satisfy the wide variety of requirements. Naturally-occurring material or chemically prepared α-manganese dioxide may also be used to this effect.

The naturally occuring α-modifications of manganese dioxide have repeatedly been tested and found to contain

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foreign ions of the group consisting of Ba^{++}, Ca^{++}, K^+ or NH_4^+. Their composition substantially corresponds to the formulae $Me_2Mn_8O_{16}$ or Mn_8O_{16}, in which Me stands for a monovalent or ½ bivalent cation. The pure Mn_8O_{16} compound could not be obtained in the α-crystal lattice.

The present invention now provides a process for making electrolytic manganese dioxide (briefly termed EMD hereinafter), which consists wholly or partially of α-modification, the eventual balance being γ-modification, and is precipitated in compact form on a suitable anode, in a manner similar to customary γ-electrolytic manganese dioxide.

The anodic oxidation of manganese sulfate solutions in sulfuric acid has unexpectedly been found to result in the formation of manganese dioxide consisting of α-modification, or presenting the α- and γ-modifications in a predetermined ratio, provided that use is made of an electrolyte having a certain concentration of potassium ions and sulfuric acid therein.

The present invention relates more particularly to the production of manganese dioxide of which between 5 and 100 percent is α-modification of MnO_2, the balance being γ-modification of MnO_2, which comprises making the said manganese dioxide by using an electrolyte containing potassium ions in a concentration of 1 gram/liter up to the saturation concentration, preferably between 4 and 40 grams/liter, and free sulfuric acid in a concentration of between 20 and 150 grams/liter, preferably between 60 and 90 grams/liter, the said concentrations being maintained during electrolysis.

Needless to say the saturation concentration of the electrolyte for potassium ions is a function of the temperature. It is about 120 grams/liter at 95° C.

By the process of the present invention it is also possible to vary the concentration of α-modification in precipitated electrolytic manganese dioxide at will and according to requirements by varying the concentration of potassium and sulfuric acid.

For the production of manganese dioxide with a low concentration of α-modification therein, it is necessary to use an electrolyte containing between 4 and 10 grams/liter of potassium ions and between 60 and 70 grams per liter of free sulfuric acid, and for the production of manganese dioxide with a high concentration of α-modification therein, it is necessary to use an electrolyte containing between 18 and 26 grams/liter of potassium ions and between 75 and 90 grams/liter of sulfuric acid.

The presence of normal proportions of ordinary contaminants in the electrolyte, such as barium, calcium, magnesium, sodium or ammonium, or mixtures thereof, could not be found to affect the process of the present invention.

The α-modification is formed during the electrolysis, conditional upon the incorporation of potassium ions into the manganese dioxide lattice. Conditional upon the extent to which potassium ions are incorporated thereinto, there is obtained a final product of which the X-ray diagram shows the reflexes of either the γ-modification or α-modification, or the reflexes of the two modifications together (cf. FIG. 1 of the accompanying diagrams). The α-modification component in the overall electrolytic mangenese dioxid is approximately proportional to the potassium concentration in the manganese dioxide, as has been established by the quantitative evaluation of a series of tests (cf. FIG. 2 of the accompanying diagrams).

The influence which the concentration of sulfuric acid has on the precipitation of manganese dioxide in its α-modification is not easy to define. We have found, however, that the acid is required to be used in a certain minimum concentration so as to initiate the incorporation of appreciable amounts of potassium into manganese dioxide, and that the quantity of potassium incorporated is a function of the concentration in which the sulfuric acid is actually used. We have further found that electrolytic manganese dioxide contained potassium in percentages which were the higher, the higher the concentration of sulfuric acid, for a given concentration of potassium ions. This is shown in FIG. 3 of the accompanying diagrams. FIG. 4 of the accompanying drawings inversely shows the influence which an increasing concentration of potassium ions in the electrolyte has upon the potassium concentration in electrolytic manganese dioxide, for a constant concentration of sulfuric acid.

On evaluating these results it is possible to produce electrolytic manganese dioxide of which the X-ray diagram shows the reflexes of the α- and γ-modifications in any desired ratio of intensity.

These α,γ-electrolytic manganese dioxides may be made with the use of electrolytes, such as those commonly employed in the commercial production of γ-electrolytic manganese dioxide. These electrolytes often contain manganese sulfate and sulfuric acid together with considerable proportions of mangesium sulfate (e.g. 60 grams/liter) and calcium sulfate (e.g. 2 grams/liter) as well as minor porportions of contaminants. Ammonium ions may also be present therein. All these compounds and ions could not be found to affect the efficiency of the potassium ions added to the electrolyte, nor could they be found to affect the additional efficiency of the sulfuric acid concentration relative to the formation of the α-modification of manganese dioxide.

The manganese dioxides made by the process of the present invention, which contain predetermined proportions of α-modification, are suitable for use as depolarization masses in galvanic primary cells, and offer beneficial effects over depolarization masses made of pure γ-manganese dioxide, especially in the event of high current intensity discharges. By the appropriate selection of the α-component it is possible to provide an optimum combination of various beneficial properties. A cell made by the paper-lined system with the use of electrolytic γ-manganese dioxide was found after 130 hours discharge time through 130 ohms to have a voltage of 1 volt, while the same cell, save that it was made with the use of α,γ-manganese dioxide with about 50% α-component, had a voltage of 1.3 volts, under identical conditions. Intermittent discharge through 5 ohms showed that a cell made with the use of α,γ-manganese dioxide enable substantially 20 percent more current to be taken therefrom until the test limit was reached, than a comparative cell made wih the use of pure γ-manganese dioxide. A "paper-lined cell" is a cell in which the "bobbin" together with the depolarizer mass is enveloped in paper.

EXAMPLE 1

An electrolyte containing, per liter, 40 grams of Mn in the form of manganese sulfate, 72 grams of H_2SO_4 and 18 grams of K in the form of potassium sulfate was subjected to electrolysis in an electrolytic cell suitable for compact precipitation of electrolytic manganese dioxide, at temperatures of between 95 and 98° C. and a current density of about 1 ampere per square decimeter. Electrolytic manganese dioxide, which contained 1.9% of potassium, substantially 50% of α-modification and 50% γ-modification, was found to precipitate in compact form.

EXAMPLE 2

The electrolyte contained, per liter, 30 grams of Mn in the form of manganese-II-sulfate, 8 grams of Mg in

the form of mangesium sulate, 0.5 gram Ca in the form of calcium sulfate, 24 grams of K in the form of potassium sulfate and 85 grams of sulfuric acid. It was subjected to electrolysis at 95° C. and a current density of about 1 ampere per square decimeter. Manganese dioxide, which contained 3.3% of potassium and 90% of α-modification, was found to precipitate in compact form on the anode.

EXAMPLE 3

An electrolyte containing, per liter, 40 grams of manganese, 8 grams of magnesium, 0.5 gram of calcium and 12 grams of potassium—in the form of sulfates—and 70 grams of sulfuric acid was subjected to electrolysis at 80° C. and a current density of substantially 1 ampere per square decimeter. Manganese dioxide, which contained 1.6% of potassium and 45% of α-modification, was found to precipitate.

We claim:

1. A process for the electrolytic production of manganese dioxide from an electrolyte substantially consisting of manganese-II-sulfate solutions in sulfuric acid, which comprises using an electrolyte containing potassium ions in a concentration of 1 gram/liter up to the saturation concentration and free sulfuric acid in a concentration of between 20 and 150 grams/liter and maintainig these concentrations during electrolysis with the resultant formation of manganese dioxide of which between 5 and 100% is α-modification of MnO_2, the balance being γ-modification.

2. The process as claimed in claim **1**, wherein the electrolyte contains the potassium ions in a concentration of between 4 and 40 grams/liter.

3. The process as claimed in claim **1**, wherein the electrolyte contains between 60 and 90 grams/liter of free sulfuric acid.

4. The process as claimed in claim **1**, which comprises making manganese dioxide with a low concentration of α-modification therein with the use of an electrolyte containing between 4 and 10 grams/liter of potassium ions and between 60 and 70 grams/liter of free sulfuric acid.

5. The process as claimed in claim **1**, which comprises making manganese dioxide with a high concentration of α-modification therein with the use of an electrolyte containing between 18 and 25 grams/liter of potassium ions and between 75 and 90 grams/liter of sulfuric acid.

6. The process as claimed in claim **1**, wherein the electrolyte contains as a further constituent as least one contaminant selected from the group consisting of compounds of barium, calcium, magnesium, sodium and ammonium.

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