Aug. 26, 1952 A. L. FOX 2,608,531

ELECTROLYTIC PREPARATION OF MANGANESE DIOXIDE

Filed Nov. 2, 1949 2 SHEETS—SHEET 1

Relation Of Current Efficiency To Pressure Of Compacting Of Titanium Anodes

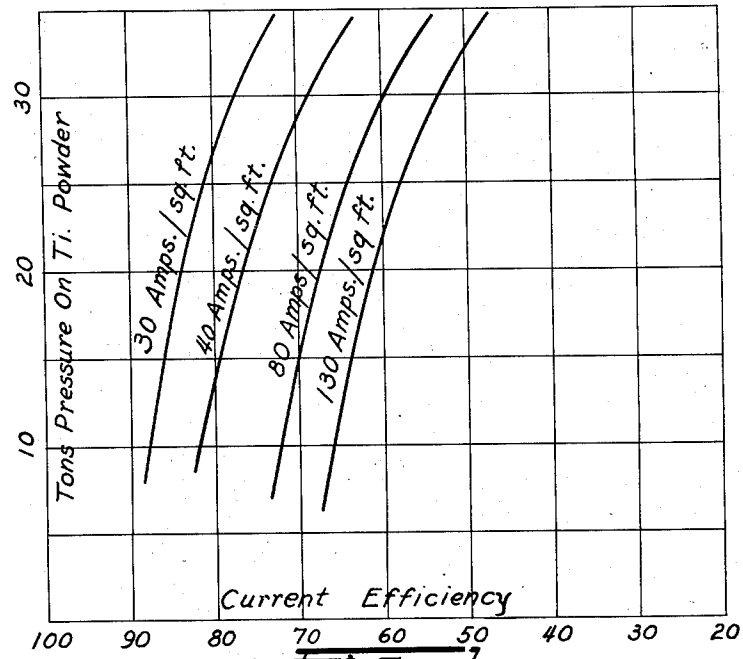
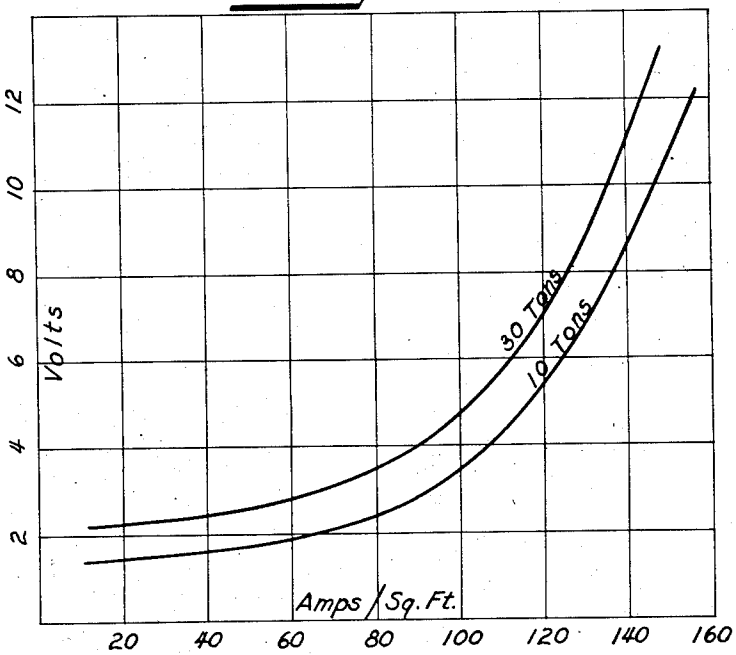


Fig. 1



Voltage-Current Density Relationship For Ti. Anodes

Fig. 2

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ELECTROLYTIC PREPARATION OF MANGANESE DIOXIDE

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Relationship of MnO_2 Content to Current Density For MnO_2 — Made On Titanium Anodes

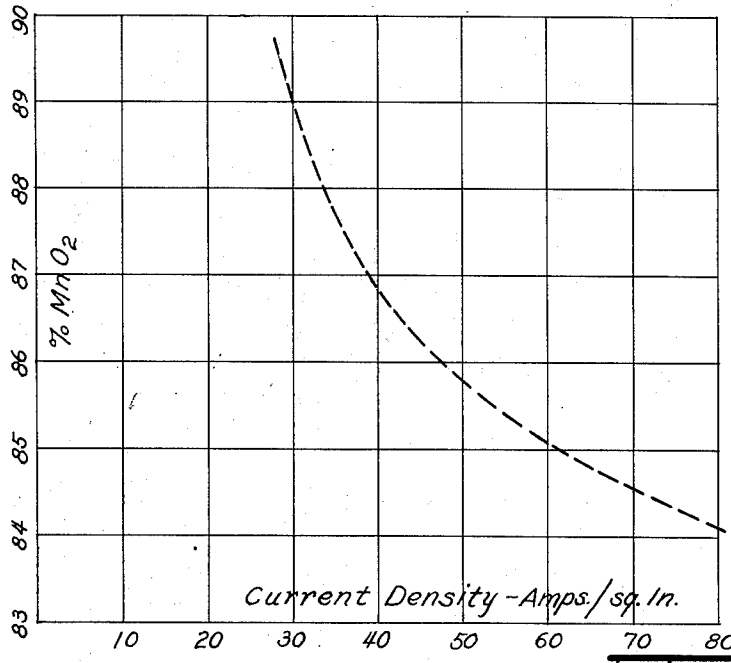
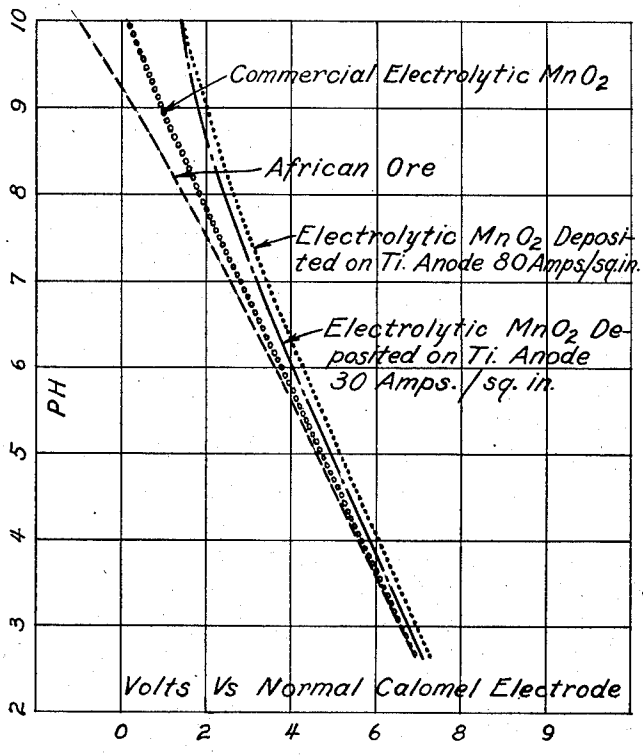


Fig. 3



Analysis of MnO_2

30 Amps. - 89.0 MnO_2
40 Amps. - 86.8 MnO_2
80 Amps. - 84.2 MnO_2

Fig. 4

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ELECTROLYTIC PREPARATION OF MANGANESE DIOXIDE

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7 Claims. (Cl. 204—83)

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This invention relates to the electrolytic preparation of manganese dioxide. It relates particularly to improved anodes to be used in the production of manganese dioxide by electrolysis of solutions containing manganese sulphate and sulphuric acid.

It is well known in the art to produce electrolytic manganese dioxide having valuable properties as a depolarizer for primary cells and for other purposes by the electrolysis of solutions containing about 50 grams per liter of manganese as sulphate and 25 grams per liter of sulphuric acid. This electrolysis has been carried on commercially using graphite anodes and either graphite or lead cathodes. This combination has been open to a considerable number of practical objections. In order to obtain current efficiency above 70% it has been necessary to carry on the electrolysis within a fairly limited range of acidity. It has likewise been necessary to maintain the temperature around 90° C. and to use a low current density, namely, from 10 to 20 amperes per square foot. The close control of these conditions has been rendered necessary not only by the effect of the mentioned variables upon the quality of the product but because the graphite anodes deteriorate rapidly when higher acidity or higher current densities are used.

Other materials for anodes have been suggested, such as platinum and various alloys of lead and other metals. These anodes, however, have all been unsatisfactory either because of cost or the quality of the product produced. It is the aim of the present invention to provide an anode for the production of electrolytic manganese which permits a wider choice of the other variables, such as solution temperature, acidity and current density, without a deterioration of the quality of the manganese dioxide produced to any such extent as has been heretofore known in the art.

I have found that anodes may be formed principally of titanium in accordance with my copending application, Serial No. 109,061, filed August 6, 1949, which give excellent results. It is not satisfactory, however, to use massive titanium of either the ductile or cast variety. All such solid forms of titanium which I have tried are not satisfactory as anodes for the deposition of manganese dioxide. The voltage required for deposition on such anodes is prohibitively high and the current efficiency poor. I have found, however, that if the anode be fabricated from titanium chips, entirely satisfactory results may be obtained.

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I prefer to use titanium chips which are made by the mechanical disintegration, such as cutting with a lathe tool of the product formed by the reaction of molten magnesium on titanium tetrachloride. The chips made from such a reduction product are conveniently purified from magnesium and magnesium chloride by leaching with dilute hydrochloric acid. Such chips contain a certain amount of hydrogen which appears to be actually advantageous to the production of anodes for the practice of my invention.

Titanium chips prepared in the manner described and having a sieve size up to 35 mesh are compacted under a suitable pressure and in a suitable die for the production of the anodes of my invention. The pressure used for the production of these anodes has a definite relationship to the behavior of the electrolytic process in which they are used. In Figure 1, I have shown the relationship between pressure used to compact the titanium chips and the current efficiency for several different current densities. In every case illustrated in this figure the cell was operated at 90° C. It will be seen that, in general, the lower the pressure used to compact the chips into the anode and, therefore, the more porous the anode, the better will be the current efficiency at any particular current density. The low limit for the pressure used to compact the chips into the anode is, of course, determined by the necessary mechanical strength of the anode and its tendency to disintegrate during the electrolysis. I have found that pressures as low as 10 tons per square inch give an anode with satisfactory properties in this respect. Lower pressures may be used with some sacrifice in anode strength and life.

The results given are for the preferred form of titanium for my invention, namely, the chips made from the reduction product of titanium tetrachloride with magnesium, which chips have been subsequently leached with acid. Increased mechanical strength can be obtained in anodes formed in this way by sintering in vacuum or in an inert atmosphere. Such increase in strength, however, is accompanied by a decrease in the value of such anodes for my invention. As an example, I heat an anode made by compacting the titanium chips at 20 tons per square inch to 800° C. for one hour in vacuum. The resulting anode gives approximately the same result in the electrolytic cell as would be obtained had the chips been compressed at 50 or 60 tons per square inch.

Titanium chips made in other ways can be used for the practice of my invention and tita-

titanium particles compacted into a coherent but incompletely consolidated porous mass having a large surface area whereby to form a deposit of electrolytic MnO_2 on the anode, and separating the deposited MnO_2 from the anode.

2. Process as defined in claim 1, in which the titanium of the anode contains hydrogen.

3. Process as defined in claim 1, in which the anode consists essentially of particles of titanium produced by reducing a halide of titanium with magnesium, said particles having a size not greater than 35 mesh, compressed into a coherent body at a pressure of from 10 to 50 tons per square inch.

4. Process as defined in claim 1, in which the anode consists essentially of particles of hydrogen-containing titanium, having a size not greater than 35 mesh, compressed into a coherent body at a pressure of from 10 to 50 tons per square inch.

5. Process as defined in claim 1, in which the anode is partially coated with a film of graphite.

6. Process as defined in claim 1, in which the electrolysis is carried out at a temperature between atmospheric and 100° C.

7. The method of claim 1, further characterized by the electrolysis being carried out at a current density of from 30 to 80 amperes per square foot.

ABRAHAM L. FOX.

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

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