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METHOD OF MANUFACTURING ARTIFICIAL BIOXIDES OF MANGANESE

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This invention relates to a Method of Manufacturing Artificial Bioxides of Manganese, the principal object of the invention being to provide a method whereby manganese bioxides of high quality may be produced by electrolysis, without having any tendency to adhere to the anodes and in commercially practicable quantities.

Because of the superior chemical and galvanic activity of products obtained by the use of artificial manganese bioxides as compared with the natural manganese bioxides, numerous efforts have been made to produce artificial manganese bioxides. One of the more simple of the methods employed consisted in subjecting a solution of manganese sulfate to electrolysis. However, this method presents so many disadvantages that its industrial application is impractical. By following the modus operandi described by Nichols, "Trans. of the Electro-Chemical Society," vol. LXII,1932, p. 392, that is to say, by the use of a perceptibly neutral medium a bioxide of suitable quality is obtained, but it adheres to the anode so tenaciously that it is extremely difficult to detach it, which characteristic renders the process pretty nearly impracticable. It is possible to avoid this difficulty by maintaining the electrolyte more or less acid. The techniques of this method are described in French Patent No. 323,916 and German Patent No. 163,813. However, in carrying out that method, another serious difficulty presents itself, namely, beside the bioxide there are formed from the manganic sulfate and the bioxide, products of a higher degree of oxidation, and it is well known that the separation of the bioxide from such a mixture involves considerable technical difficulties.

Applicant has found that artificial bioxides of manganese may be obtained without encountering any of the difficulties or inconveniences mentioned above and in sufficient quantity to make it commercially practicable, by subjecting to electrolysis, not a solution of a manganese salt, but a suspension of an insoluble or only slightly soluble manganese compound of a degree of oxidation lower than the bioxide in a solution of an alkaline halide. As examples of insoluble or slightly soluble compounds may be mentioned manganese hydroxide, carbonate, borate, phosphate, silicate. It is to be understood, however, that the invention is by no means limited to these compounds.

In case the insoluble or slightly soluble compound is obtained by precipitating a solution of manganese chloride in a medium of a base or an alkaline salt, the final reaction mixture may be subjected to electrolysis without other treatment. The invention is applicable in particular to products resulting from the treatment by an acid and then by a base, of natural or artificial manganese compounds at least partially soluble in acids, and more particularly to the product obtained by treating by an acid and then by a base, of the sesquioxide of manganese resulting from the roasting reducer of a natural bioxide.

The applicant has further found that it is possible to influence or control the structure of the final product by modifying in the course of the electrolysis, the pH of the medium by addition of basic or acid substances.

The isolation of the reaction product of the medium in which it has been formed presents no difficulty, as it can be accomplished by any of the known means, such as decantation, filtration, etc. The product obtained constitutes a hydrated manganese oxide in which practically all the manganese is in the quadrivelent condition.

Example 1.—50 liters of brine containing in suspension 2 Kg. 500 of carbonate of manganese precipitate are electrolysed for 7 hours, with 200 amperes at about 80–90°. At the end of the time, the bioxide obtained is separated by filtration and is washed and dried. An article made with 5 grs. of this product gives a period of discharge of 6 to 7 hours.

Example 2.—3 Kg. 500 of Mn_2O_3, natural or resulting from reducer roasting of pyrolusite, are treated by suspension in water to which hydrochioric acid has been added to produce weak permanent acidity, then by sodium carbonate for re-precipitating the manganese in solution. On completion of these operations, the electrolysis of this suspension is proceeded with as in Example 1 and a product of analogous properties is obtained.

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