

UNITED STATES PATENT OFFICE.

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DEPOLARIZING AGENT FOR DRY BATTERIES AND PROCESS OF MAKING SAME.

1,358,626.

Specification of Letters Patent.

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No Drawing.

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To all whom it may concern:

Be it known that I, CARLETON ELLIS, a citizen of the United States, and a resident of Montclair, in the county of Essex and State of New Jersey, have invented certain new and useful Improvements in Depolarizing Agents for Dry Batteries and Processes of Making Same, of which the following is a specification.

This invention relates to a process of making manganese dioxid substantially or entirely free from manganites thereby yielding a product suitable as a depolarizing agent for dry batteries of the Leclanche type and relates particularly to a finely-divided black precipitate of manganese dioxid containing relatively small amounts of water of hydration or being entirely free therefrom which may be prepared in the manner set forth below.

In the oxidation of many of the compounds of manganese in the manganous condition only a partial conversion of manganese dioxid is secured ranging in some cases from 40 or 50% to 70 or 80% under other conditions. Often a portion of the manganese dioxid unites with some of the manganous material to form a manganous manganite which is quite resistant to further oxidation so that if the conditions are such that the product is formed even very drastic oxidation treatment does not yield a product of a high percentage of manganese dioxid.

According to the present invention a product containing at least 95% of manganese dioxid and normally 98 to 99% is obtained. This product is preferably secured by simultaneously reacting on a manganous compound with two or more oxidizing agents, for example, nitric acid and hypochlorous acid or sodium hypochlorite and nitric acid. A mixture especially suited for such reaction is manganous nitrate and sodium hypochlorite which when heated to boiling in fairly concentrated solution yield a black precipitate of manganese dioxid substantially free from manganites and which contains about 95% MnO_2 .

Manganous nitrate when heated alone produces manganous dioxid but not in so pure a state as that obtained by the joint action of hypochlorite. While it is not necessary to have one oxidizing agent com-

bined with the manganous base it is preferable and manganous nitrate, chlorate and the like is suitable for this purpose.

An illustration of one method of carrying out the invention is as follows:

5 parts by weight of manganous nitrate ($6H_2O$) was dissolved in 20 parts of water and 10 parts of a 30% solution of sodium hypochlorite was added. This mixture was heated to boiling and an abundant precipitate of black manganese dioxid containing over 95% MnO_2 (a small amount of water of hydration was present) was obtained. In another case the hypochlorite was added in successive portions, and the manganese dioxid formed was filtered off after each addition. The product contained approximately a like content of MnO_2 . A portion of the dioxid obtained by this process was boiled for a few minutes with a 10% solution of sulfuric acid. Practically no manganese was dissolved. The product exhibited medium conducting properties.

In another case manganous nitrate (hydrated) was melted in its own water of hydration until it began to decompose forming manganese dioxid or a body containing the latter. A concentrated solution of sodium hypochlorite was added slowly, the rate of addition being such as to keep the volume of the solution constant. The reaction was very violent. The manganese dioxid produced was filtered off and was found to be of high purity.

Some of the material obtained in this manner exhibits a peculiar lag or hysteresis of electrical conductivity.

If a column of manganese dioxid prepared according to the present invention is connected in series with a lamp and a source of potential, a considerable time will elapse before the current through the circuit rises to its full value, as indicated by the fact that the lamp will light (a sufficient potential being employed) but only after a lapse of time. If commercial hydrated manganese dioxid of approximately the same degree of purity is tested in a similar way, it may also indicate a slight lag in conductivity, but in the case of the material heretofore known, the lag, measured in seconds, will be less than one-third of that exhibited by my novel product, according to measurements which have been made. In some

cases, the lag of the prior products is only one-twentieth as much as with the herein-described product, but in general, it is about one-twelfth as great.

- 5 The product obtained by such powerful oxidation or effect of this duplex oxidizing agent may, if desired, be treated in some cases by extraction with an acid such as dilute nitric acid to remove any residue of
10 acid soluble material, iron, etc., or successive extraction with nitric and then with sulfuric acid may be employed. The product is then well washed and dried. The drying may take place at 100° C. or higher in order
15 to eliminate as far as possible any free or combined water.

The invention involved herein embraces a new product, namely a depolarizing agent consisting of or comprising a higher oxid
20 of manganese compound or material preferably in the form of a black precipitate containing at least 95% MnO_2 in a slightly hydrated condition and of medium conductivity for the electric current and in the
25 preferred form manifesting a slight lag or hysteresis of conductivity which is different from ordinary mineral manganese dioxide (pyrolusite) or artificial normally-hydrated artificial manganese dioxide which conduct
30 the electric current without noticeable lag.

What I claim is:

1. The process of making manganese di-
oxid substantially free from manganites
which comprises heating manganous nitrate
35 in the presence of sodium hypochlorite.
2. The process of making manganese di-
oxid substantially free from manganites
which comprises heating manganous nitrate
in the presence of a hypochlorite.
- 40 3. The process of making manganese di-
oxid which comprises heating a compound
of manganese and nitric acid in the pres-
ence of a hypochlorite.
4. The process of making manganese di-
45 oxid substantially free from manganites
which comprises reacting on manganous
nitrate with sodium hypochlorite.
5. The process of making manganese di-

oxid material containing at least 95% MnO_2 , which comprises boiling a solution 50
of manganous nitrate with an added oxidiz-
ing agent.

6. The process of making manganese di-
oxid containing over 95% MnO_2 , which
comprises boiling a solution of manganous 55
nitrate and sodium hypochlorite, in collect-
ing the precipitate, washing and extracting
the residue with dilute nitric acid and finally
washing the acid extracted residue with
dilute sulfuric acid.

7. The process of making manganese di-
oxid which comprises boiling a solution of
manganous nitrate and sodium hypochlo- 60
rite, in collecting the precipitate, washing
and extracting the residue with dilute nitric
acid.

8. The process of making manganese di-
oxid which comprises boiling a concentrated
solution of manganous nitrate and sodium
hypochlorite, in collecting the precipitate 70
and washing the latter.

9. The process of making manganese di-
oxid which comprises adding to a boiling
solution of manganous nitrate successive
portions of sodium hypochlorite, and col- 75
lecting and washing the precipitate.

10. As a new product higher oxid of man-
ganes depolarizing material, a finely-di-
vided black precipitate containing at least
95% MnO_2 and possessing a substantially 80
greater conductivity lag than pure hydrated
manganese dioxide depolarizers heretofore
used.

11. A depolarizing agent comprising pre-
cipitated slightly hydrated manganese ma- 85
terial containing over 95% MnO_2 , and pos-
sessing a conductivity lag at least three
times as great as the ordinary pure hydrated
manganese depolarizer.

12. A depolarizing agent comprising pre- 90
cipitated slightly hydrated manganese ma-
terial containing over 95% MnO_2 , and pos-
sessing a conductivity lag of a greater order
of magnitude than ordinary pure hydrated
 MnO_2 depolarizer.

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