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CATALYST PREPARATION

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1 Claim. (Cl. 204—40)

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This invention relates to catalyst preparation and, more particularly, it relates to the production of a catalyst structure comprising manganese dioxide.

It is an object of this invention to produce a new and improved catalyst structure comprising manganese dioxide.

It is another object of this invention to produce a solid catalyst structure comprising an outer coating of manganese dioxide.

It is still another object of this invention to produce a manganese dioxide catalyst which has particular utility in the decomposition of hydrogen peroxide.

Other objects of the invention will appear hereinafter.

The objects of this invention may be accomplished, in general, by electrodepositing black manganese dioxide on a cathode from an aqueous electrolytic solution containing potassium carbonate, potassium permanganate, and potassium manganate.

The manganese dioxide may be directly electrodeposited on a metal supporting structure, for example, a supporting structure of iron, steel, nickel, aluminum, or manganese. It is preferred, however, to first electrodeposit manganese on an iron or steel support and then electrodeposit manganese dioxide on said support.

In order to obtain a particularly desirable form of catalyst structure, a foraminous supporting structure of iron or steel is used. This structure may be a section of wire-mesh screen having a mesh size between $\frac{1}{32}$ inch and $\frac{1}{4}$ inch or it may be perforated iron or steel sheeting having a comparable size of openings. Wire-mesh screen of this type can be obtained as plain screen without protective coating or as an unlacquered-galvanized or lacquered-galvanized screen. When the screen structure contains no protective coating or when it contains a lacquer coating, it is preferably first cleaned with an alkaline cleaning solution, for example, an aqueous solution containing 8 to 16 ounces per gallon of caustic soda. The screen may be cleaned in such solution by immersing it in the solution having a temperature of 90° C. to 100° C. for a period of ten minutes and then spray-rinsing the same with water. Other alkaline cleaning solutions commonly used in the arts for such purposes can be used as well.

The screen, whether or not it is previously cleaned in an alkaline bath, is preferably subjected to acid pickling, for example, in an aqueous solution of sulfuric acid containing 3% to 5% acid and having a temperature around 20° C. to 30° C.

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The screen may be immersed in the acid pickling bath for a period of three to ten minutes, or as much longer as necessary to remove the galvanizing (zinc) therefrom and produce a clean steel surface. Any other acid pickling bath which will produce a clean steel surface can, of course, be used.

The clean steel screen may next be subjected to plating with manganese, or alternatively, manganese dioxide may be electrodeposited directly on the steel surface. Preferably, the steel supporting structure is first plated with manganese. This may be done by any known manganese plating process. Particularly good results have been obtained by plating from an aqueous solution containing manganese acetate, $(Mn(C_2H_3O_2)_2 \cdot 4H_2O)$, ammonium acetate, and ammonium hydroxide. Good results have also been obtained by plating from an aqueous solution containing manganese sulfocyanate $(Mn(CNS)_2 \cdot 3H_2O)$, ammonium sulfocyanate, and ammonium hydroxide.

Plating manganese from an acetate solution may be carried out as follows:

The clean steel supporting structure is made the cathode in an aqueous plating bath containing 200 to 300 grams per liter manganese acetate quadrihydrate $Mn(C_2H_3O_2)_2 \cdot 4H_2O$, 150 to 210 grams per liter ammonium acetate and 1.5 to 3.0 grams per liter ammonium hydroxide. This solution may be made up by dissolving 40 to 65 parts by weight of metallic manganese (electrolytic grade) in 220 to 300 parts by weight of 100% acetic acid and 400 to 600 parts by weight of water. When all the manganese has dissolved, add 150 to 200 parts by weight of ammonium hydroxide, and add sufficient more ammonium hydroxide to produce a pH of 7 to 8.

The plating is carried out with graphite anodes, preferably with cotton bags around the anodes. The total anode area should be as large as possible. The anode current density is preferably maintained between 10 and 30 amperes per square foot, and the cathode current density between 60 and 150 amperes per square foot, depending upon the temperature of the plating bath. If the plating bath has a temperature between 20° C. and 30° C. a cathode current density of 60 to 75 amperes per square foot is preferred, and if the bath has a temperature of 40° C. to 50° C. a current density of 135 to 150 amperes per square foot will be preferred. The lower temperature range and lower cathode current density gives the best results. An E. M. F. of 6 to 9 volts is preferred. Plating for one to two hours will produce a desir-

able deposit. This solution may be replenished by additions of electrolytic manganese to the solution.

Manganese may be plated from a sulfocyanate solution as follows:

A manganese sulfocyanate plating solution is made up by placing 40 to 65 parts by weight of metallic manganese (electrolytic grade) in an aqueous solution containing 200 to 300 parts by weight of ammonium sulfocyanate and 600 to 1000 parts by weight of water. The mixture is boiled until the manganese is dissolved. The solution should contain about 200 to 250 grams per liter manganese sulfocyanate

$$(Mn(CNS)_2 \cdot 3H_2O)$$

about 75 to 125 grams per liter ammonium sulfocyanate and sufficient ammonium hydroxide to produce a pH of between 7.5 and 9.0.

The plating is carried out with graphite anodes at current densities, bath temperatures, and E. M. F. similar to the operating conditions above referred to with reference to plating from a manganese acetate solution. This bath may be replenished by addition of electrolytic manganese and ammonium sulfocyanate as required to maintain the bath contents within the ranges above described. A sufficiently thick deposit will be obtained after one or two hours of plating.

The manganese plated steel structures may be rinsed with water and the manganese dioxide electrodeposited thereon. However, if desired, the steel supporting structure may be subjected to electrodeposition of manganese dioxide without first electrodepositing manganese thereon. It is of advantage to first deposit manganese on the steel because the electrodeposited manganese dioxide is otherwise rapidly removed from the steel supporting structure when used in the decomposition of 27% to 100% H_2O_2. An undercoat of manganese is, therefore, highly desirable so that the hydrogen peroxide decomposition reaction can be maintained for extended periods.

The cathodic electrodeposition of manganese dioxide on the steel or the manganese-coated steel is carried out in an aqueous solution containing potassium carbonate, potassium permanganate and potassium manganate. This solution may be produced by first dissolving between 100 and 140 grams per liter potassium carbonate and 8 to 30 grams per liter potassium permanganate in water, and reducing the permanganate by passing an electric current through said solution with iron anodes and cathodes for about one to three hours at about 10 ampere hours per gallon. The bath is then ready for cathodic electrodeposition of manganese dioxide on the supporting structure. Sheet steel anodes are employed with an anode current density of 10 to 40 amperes per square foot. Preferably, the bath is maintained at 20° C. to 30° C. Sufficient anode area in the bath to give a ratio of anode area to cathode area of about 2 to 1 is preferred. A cathode current density of 25 to 50 amperes per square foot is desirable. A 30-minute operation of electrodeposition will produce a satisfactory coating of manganese dioxide. The manganese dioxide will, under the above conditions, be deposited at the

rate of about 0.04 gram per ampere hour. The bath may be replenished by adding about one pound of $KMnO_4$ for every 1000 ampere hours of operation.

The manganese dioxide catalyst structures produced in accordance with the present invention are particularly useful as decomposition catalysts for hydrogen peroxide solutions containing between 27% and 100% H_2O_2 by weight. These catalysts may, however, be used wherever manganese dioxide has a useful function as a catalyst. When use is made of the catalytic structure of the present invention for the decomposition of hydrogen peroxide, it is only necessary to immerse the same in the aqueous peroxide solution.

Reference in the specification and claims to parts, proportions and percentages, unless otherwise specified, refers to parts, proportions and percentages by weight.

Since it is obvious that many changes and modifications can be made in the above-described details without departing from the nature and spirit of the invention, it is to be understood that the invention is not to be limited to said details except as set forth in the appended claim.

What is claimed is:

The process of producing a catalytic structure particularly suitable for the decomposition of hydrogen peroxide which comprises cathodically electrodepositing manganese on an iron support by plating for a period of one to two hours with graphite anodes from an aqueous plating bath containing 200 to 300 grams per liter manganese acetate quadrihydrate, 150 to 210 grams per liter ammonium acetate and 1.5 to 3.0 grams per liter ammonium hydroxide, and then cathodically electrodepositing manganese dioxide on said manganese surface by plating for a period of at least 30 minutes with steel anodes from an aqueous electrolytic plating solution prepared by dissolving 100 to 140 grams per liter potassium carbonate and 8 to 30 grams per liter potassium permanganate in water, and passing an electric current for a period of one to three hours through said solution with iron anodes and cathodes to produce potassium manganate in the solution.

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REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
476,639	Haswell	June 7, 1892
1,352,208	Lovelace	Sept. 7, 1920
1,524,937	Keeler	Feb. 3, 1925
1,776,787	Ergang	Sept. 30, 1930
1,907,710	Bass	May 9, 1933
1,975,239	Angelank et al.	Oct. 2, 1934
2,320,773	Fink et al.	June 1, 1943

OTHER REFERENCES

Transactions of the Electrochemical Society, vol. 73, (1938), pp. 327–335.