UNITED STATES PATENT OFFICE.

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PROCESS FOR MAKING ALKALINE PERMANGANATES, CHLORATES, AND HYDROGEN.

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To all whom it may concern:

Be it known that I, THEODORE J. BREWSTER, a citizen of the United States, residing at New York, in the county of New York and State of New York, have invented certain new and useful Improvements in Processes for Making Alkaline Permanganates, Chlorates, and Hydrogen, of which the following is a specification.

The object of my invention is to so improve the present known manner of making permanganates of the alkaline metals, and to provide a method of making them so that commercial use may result of the process.

Alkaline permanganates have previously been made by heating manganese ore with an alkali, sometimes with the addition of an oxidizing agent to increase the yield, thus forming the manganate of the metal in question. This manganate would then be oxidized to permanganate either by boiling with water which causes a precipitation of manganese dioxid, or by oxidation by means of the electric current. Other means of converting manganates to permanganates include treatment with chlorin. These various processes for making the manganates and permanganates are open to the objection that they do not fit into the chemical industrial conditions well enough so that a cheap product can be made.

My invention provides for the utilization of cheap raw materials, and provides for the return to the process of all products intermediate to the production of permanganates and the production of valuable by-products as well, so that permanganate of potash or soda may be made economically.

The process starts with muriate of potash, which is available in large quantities, or with common salt, in the case that the permanganate of soda is wanted. The chlorid of the alkali metal is dissolved in water and subjected to the action of electricity in the well known manner, whereby chlorin and the hydroxid of the alkali metal is formed. I then evaporate the product of the electrolytic action which consists of a caustic alkali containing some undecomposed chlorid, whereby the most of the chlorid separates out from solution and is returned to the process. The caustic solution, which may be caustic soda or potash is then mixed with oxids of manganese, preferably well ground to a fine powder, and I then heat the mixture until dry.

As the material forms some lumps in this process, I grind the product to as fine a powder as possible, then heat it to a temperature best suited for the reaction, which usually is above 360 degrees but under a red heat, allowing air to be in contact with the powder, so that oxidation to the manganate can take place to the best advantage. Mixing while calcining is beenficial. I calcine until a sample taken from time to time and analyzed shows that there is being formed no more manganate.

The powder is then cooled, and leached with water. This solution consists of the caustic alkali and manganate together with a small amount of chlorid. This solution is then treated with an excess of chlorin in such a way that the chlorin is in excess continually, and the solution is preferably hot. This manner of treating results in the production of little or no hypochlorite, but on the contrary the caustic alkali is converted into chlorid and chlorate, and the manganate is converted into permanganate.

The reactions are practically quantitative in both cases. For example, one molecule of alkaline manganate reacts with one atom of chlorin forming one molecule of alkaline chlorid and one molecule of alkaline permanganate. In the case of the caustic alkali, six molecules of this react with six atoms of chlorin, forming five molecules of alkaline chlorid and one of alkaline chlorate. When the chlorination is complete, the solution contains an alkaline chlorid, chlorate, and permanganate besides a trace of chlorin.

The latter is boiled off or otherwise disposed of, and the solution is concentrated and the separation into its constituents made by means of fractional crystallization by well known methods. The alkaline chlorid is returned to the process, the alkaline chlorate and permanganate are ready for sale.

All of the manganese oxids are not consumed in the calcining operation with the formation of manganate, but remain after the calcined powder has been leached with water. These oxids are returned to the process and used in place of fresh raw material.

These oxids may be in any degree of oxidation and still be used so long as they con-

tain manganese in sufficient quantity to make the operation pay. When oxids of a lower degree of oxidation than the dioxid are used, it usually requires a longer period of calcining to obtain a good result, but otherwise the operation is the same as when the dioxid is used. Practically the whole of the manganese can be converted into permanganates.

The electrolysis of the alkaline chlorid produces hydrogen as well as chlorin. This hydrogen can be used for many purposes, such as the hydrogenation of oils, ketones, manufacture of ammonia, cyanamid, etc. It is produced in more or less high purity according to the type of electrolytic cell used, and the care in the process. Usually it can be had ninety-five per cent. (95%) pure or better.

The following example shows how the process may be worked: Ten parts of muriate of potash is dissolved in thirty parts water, and if the muriate of potash contains any lime, enough carbonate of potash is added to precipitate the lime as carbonate, and the solution is filtered and fed into an electrolytic cell at the best speed suitable for the operation of the cell. The action of the electrolytic current is to decompose the muriate of potash into the alkali metal and chlorin. In a well constructed cell, it is possible to remove the chlorin as it forms ninety (90) to ninety-eight per cent. (98%) pure, and from the cathode, the alkali metal unites with water as soon as formed with the formation of caustic alkali and hydrogen.

The latter escapes also ninety (90) to ninety-nine per cent. (99%) pure, according to the conditions. In this case, caustic potash is formed and is removed in the solution that flows from the cell. This solution will contain some undecomposed chlorid, as it is not customary to operate the cell in a manner that all of the chlorid is converted into caustic. The solution may have the following composition, for example: six parts caustic potash, two parts chlorid of potash, and thirty parts water.

This is evaporated until there remains six parts water, whereupon practically all of the chlorid separates out during the operation, and is returned to the process.

The strong potassium hydroxid solution containing six parts caustic potash is mixed with nine parts of finely ground oxids of manganese, and heated until dry. Any lumps are broken up during the drying, and when the whole is dry, the product is ground as finely as possible in a mill, and then heated while being exposed to the action of air until a sample withdrawn from time to time and analyzed shows that no more manganate of potash is being made.

The heating usually of one to four hours is enough, and the temperature usually should be between 360 degrees and 450 degrees. These temperatures and periods are merely suggestive, and I do not limit myself to them.

The calcined product is then cooled and all soluble matter is dissolved out with water. This solution contains caustic potash, magnanate of potash, and some chlorid of potash. The solution is then treated with chlorin in a manner that there is continually an excess of chlorin, thereby avoiding the formation of hypochlorites. The chlorination of the solution results in the formation of permanganate of potash, chlorid of potash, and chlorate of potash. Any excess chlorin which may be dissolved in the solution is removed by boiling or other means, and the potash salts are separated from each other by means of fractional crystallization, the methods of which are well known. The chlorate of potash and permanganate are now finished products, while the chlorid of potash is returned to the process.

In some cases it is desirable to form the permanganate with a minimum amount of chlorate, since the separation of these products presents some difficulties. In this case, the manganate solution which contains also a caustic alkali is treated with only the amount of chlorin necessary to oxidize to the permanganate. This is easily done on a manufacturing scale by measuring the chlorin by passing it through a meter into an analyzed solution of the manganate, where it is absorbed. In this reaction, a portion of the chlorin reacts with the caustic alkali forming a hypochlorite, while the balance oxidizes directly the manganate to the permanganate. If this solution is then carefully neutralized with hydrochloric acid, the hypochlorite is decomposed with liberation of chlorin and the unoxidized manganate is then converted into permanganate without appreciable amounts of chlorates being formed. The resulting solution will contain practically nothing but the chlorid and permanganate of the alkali metal, the separation of which is easily performed by means of fractional crystallization by well known methods.

There are cases where it is desirable to begin the process with a caustic alkali instead of an alkaline chlorid, and in this case it is desirable to recover the excess caustic alkali for re-use. To accomplish this result, it is desirable to use caustic potash instead of caustic soda, and to prepare the manganate in the manner given. The manganate solution, which contains caustic alkali, may be converted into the permanganate form by either of two methods, the choice of which is made according to local conditions.

The first method consists of diluting the manganate solution to about five (5) to ten per cent. (10%) strength and boiling, where-

by the manganate is converted into permanganate according to the following reaction:

$$3K_2MnO_4+2H_2O=2KMnO_4+MnO_2+4KOH.$$

The manganese dioxid is filtered off and returned to the process, and the permanganate solution is evaporated and crystallized in the regular manner. The mother liquor of the crystallization contains much caustic alkali and is returned to the process to be used in place of fresh materials in the preparation of the calcined product.

The second method of conversion of manganate to permanganate consists of subjecting the manganate to the action of the electric current in an electrolytic cell. In this operation practically the whole of the manganate can be converted into permanganate according to the reaction:

$$2K_2MnO_4+H_2O+O=2KMnO_4+2KOH.$$

This electrolytic oxidation is preferably performed using a graphite anode and an iron cathode, and using a low current density at the anode (four to six square inches per ampere) and a high current density at the cathode.

Due to the large anode surface exposed to the solution, the nascent oxygen produced at the anode oxidizes the manganate to permanganate, whereas at the cathode, the high current density causes most of the hydrogen to be evolved in the molecular form, and its reducing action is minimized. The addition of a small amount of permanganate before starting the operation is advisable. The electrolysis may thus be performed in a simple cell without the use of a diaphragm. The product of the electrolytic action consisting of an alkaline solution of permanganate is concentrated and crystallized in the regular way, the mother liquor of the crystallization being returned to the process.

Having thus described my invention, what I claim as new and desire to secure by Letters Patent is:

1. A process of making alkaline manganates consisting of mixing oxids of manganese with an alkali solution, evaporating to dryness, grinding, calcining in presence of air or oxygen, and leaching the calcined product, substantially as described.

2. A process of making alkaline permanganates consisting of mixing oxids of manganese with a solution containing an alkali, evaporating to dryness, grinding, calcining in the presence of air or oxygen, leaching the product with water, and treating the solution with chlorin, substantially as described.

3. A process of making alkaline permanganates and chlorates consisting of mixing oxids of manganese with a solution containing an alkali, evaporating to dryness, grinding, calcining in the presence of air or oxygen, leaching the product with water, and treating the solution with chlorin, substantially as described.

4. A process of making alkaline permanganates consisting of mixing a solution of a caustic alkali with manganese oxids, evaporating to dryness, grinding, calcining in the presence of air or oxygen, leaching the calcined product with water, and treating the solution with chlorin and hydrochloric acid, substantially as described.

5. A process of making alkaline permanganates consisting of mixing oxids of manganese with an alkali solution, evaporating to dryness, grinding, calcining in the presence of air or oxygen, leaching the calcined product with water, boiling the solution, and crystalizing, substantially as described.

6. A process of making alkaline permanganate consisting of mixing oxids of manganese with an alkali solution, evaporating to dryness, grinding, calcining in the presence of air or oxygen, leaching the calcined product with water, subjecting the resulting solution to electrolysis, boiling the solution and crystallizing, substantially as described.

In testimony whereof I have signed my name to this specification in the presence of two subscribing witnesses.

THEODORE J. BREWSTER.

Witnesses:
ISABEL LEVINSON,
M. SINGER.