

ALIEN PROPERTY CUSTODIAN

ELECTROLYTIC PRODUCTION OF MANGANESE COMPOUNDS

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This invention relates to a process for the electrolytic production of manganese compounds.

It has frequently been proposed to produce potassium permanganate electrolytically by oxidation of manganese anodes. It has hitherto not been possible to utilise these processes industrially because passivation of the anodes could not be avoided and the efficiency was too small. It was, moreover, necessary to operate with cooling.

The disadvantages hitherto prevailing are overcome according to this invention by dividing the electrolytic production of the permanganate into two stages, manganate being prepared in the first stage and the permanganate only in the second stage. It is accordingly possible to obtain either pure manganate or pure permanganate at will.

The first stage of the process of this invention, the manganate stage, consists in electrolysing anodes of manganese alloys, for example ferromanganese or silico-manganese, in concentrated solutions of alkali hydroxides or alkaline earth hydroxides. The concentration of the alkali depends on the temperature and also on the current density employed, on the distance between the electrodes and the active surface of the electrodes. The criterion for the concentration is that the electrolyte solution must be green or must turn green. As soon as this is not the case the alkali concentration must be increased until the solution becomes completely green.

An essential advantage of the process of the present invention consists in that in this first stage the operation can be carried out at high current densities and without the use of a diaphragm, without chemical passivation of the anode taking place. Apparently permanganate is first formed, which in the presence of the strong alkali decomposes into manganate and oxygen with practically no formation of manganese dioxide.

If the electrolysis in the first stage is carried out for a sufficiently long time, the manganate is precipitated in solid form. Any tendency of the anode to become coated with crystals on prolonged working can be easily overcome by temporarily immersing the anode in water or in an aqueous solution. The liquor obtained by dissolving the crystals may be employed for dissolving the solid manganate precipitated in the electrolyte.

The electrolysis in this first stage may be carried out continuously with separation of the precipitated manganate, since the concentration of the electrolyte may be maintained at the desired

value by the continuous or periodic addition of highly concentrated or even solid alkali.

The solid manganate or the manganate solution of the first stage may be employed as such.

In order to prepare permanganate either the solution of the first stage, if necessary after dilution and filtration, is oxidised in the second stage to permanganate, or the precipitated manganate is dissolved in water and very weak alkali or alkaline earth hydroxide, and this solution, after separating anode waste and ferric hydroxide, is subjected to oxidation in the second or permanganate stage. The latter method is attended with a considerable saving in heat, since less dilute liquor has to be evaporated.

Depending on the basic constituent employed in the first stage, the desired alkali or alkaline earth compound is obtained. The production of difficultly soluble manganates or permanganates may however, be facilitated by double decomposition. In this case sodium hydroxide is for example employed in the first stage and sodium manganate is produced. This sodium manganate may be converted into potassium manganate by interaction with potassium salts or it may be first converted in the second stage to sodium permanganate and only then be caused to interact with potassium salts to form potassium permanganate. The latter procedure is as a rule to be preferred, because the difference in the solubilities of the permanganates is greater than in the case of the manganates.

After separating the permanganate, the liquor poor in manganese, after simple evaporation with the addition of fresh alkali, may be re-employed in the first stage for the production of the manganate from ferro-manganese or the like.

When employing fresh or oxidised anodes it is advantageous at the beginning of the electrolysis to use a higher voltage than in the subsequent process thereof.

The following examples serve to illustrate how the process of this invention may be carried into effect:

1. A 35% potassium hydroxide solution is electrolysed at about 4 to 5 volts at room temperature with anodes of 80% ferromanganese and nickel cathodes without a diaphragm, the electrodes being spaced a few centimetres apart. The liquid is thereafter so adjusted that it contains about 85 gms. of potassium manganate and 50 gms. of potassium hydroxide, per litre. The liquid is then filtered and electrolysed in known manner to produce potassium permanganate. After thorough cooling the solid salts further pre-

precipitated are centrifuged off, the solution is evaporated down in vacuo and, if necessary, after adding potassium hydroxide, is returned to the first stage of the process.

2. 50% potassium hydroxide solution is electrolysed at room temperature with an anode of ferro-manganese (80% Mn) and a nickel cathode without a diaphragm. The voltage used is 2.6 to 4 and the distance between the electrodes a few centimetres. At the start of the electrolysis a higher voltage, for example 6 to 9 may be employed for a short time. After the electrolyte

has become saturated with manganate, solid salt is formed, which together with ferric hydroxide and anode residues collects at the bottom of the vessel. The deposit is separated from the electrolyte liquor and centrifuged and is then washed with water, for example on a filter. The manganate goes into solution and is with advantage further electrolytically oxidised to permanganate. The liquor separated from the permanganate is with advantage evaporated down to 50% of KOH.

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