PROCESS FOR THE ELECTROLYTIC PRODUCTION OF SODIUM PEROXODISULFATE

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References Cited
UNITED STATES PATENTS
880,599 3/1908 Teichner et al...................... 204/82

FOREIGN PATENTS OR APPLICATIONS
81,404 5/1895 Germany............................ 204/82
205,069 12/1908 Germany............................ 204/82

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ABSTRACT
Sodium peroxodisulfate is produced by direct electrolysis by electrolyzing, at 0.3 to 1.2 amperes per square centimeter, a solution containing sodium sulfate and sulfuric acid in such quantity that the solubility of the sodium peroxodisulfate formed amounts to less than 0.6 mole per liter, and maintaining the concentration of sodium sulfate and sulfuric acid substantially constant during the electrolysis.

12 Claims, 1 Drawing Figure
3,915,816

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PROCESS FOR THE ELECTROLYTIC PRODUCTION OF SODIUM PEROXODISULFATE

This invention relates to the production of sodium peroxodisulfate. More specifically, the invention relates to a novel process for the production of this material by direct electrolysis.

A number of attempts at the production of sodium peroxodisulfate (hereinafter referred to simply as sodium persulfate) by direct electrolysis have been described in the past. However, the processes involved have not been successfully applied in practice. In the electrolysis of sodium hydrogen sulfite solutions, for example, relatively high current yields of about 80% and more are achieved at the beginning of the electrolysis, but it is soon observed, i.e., within several hours, that the current yield rapidly diminishes, and may drop to negative values, mathematically speaking. Various measures which have been described in the literature, such as the use of mercury as cathode, have not produced useful results. This discouraging situation has been interpreted in part as being due to the action of the Na⁺ ion on the anodic oxidation process. Therefore, the prevailing view has been that direct electrolysis for the production of sodium persulfate from sodium sulfite is technically impossible or uneconomical.

Consequently, a four-step process is used for the technical production of sodium persulfate, which may be described by the following equations:

\[(\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{SO}_4 \rightarrow (\text{NH}_4)_2\text{SO}_4\text{aq} + \text{H}_2\text{O}\]  

(1)

By electrolysis, an ammonium persulfate solution is formed from ammonium bisulfite solution with current yields averaging 70 percent, plus hydrogen and oxygen. The electrolytic cells used for this purpose require means at the cathode, such as an asbestos cord wrapping or the like, to combat the ad-diffusion of the anions so that the reduction of the persulfate ions may be limited or prevented. A precipitation of \((\text{NH}_4)_2\text{S}_2\text{O}_8\) in this case is generally undesirable and leads to a considerable increase in the cell voltage and hence in the energy requirement.

From the ammonium persulfate solution produced in accordance with Equation (1), as free of acid as possible, the salt is obtained in crystalline form by evaporation or precipitation:

\[(\text{NH}_4)_2\text{S}_2\text{O}_8\text{aq} \rightarrow (\text{NH}_4)_2\text{S}_2\text{O}_8\text{cryst.} + \text{aq}\]  

(2)

The salt is separated by suitable separating units and then dried. Then it is reacted with sodium hydroxide or caustic soda solution in accordance with:

\[(\text{NH}_4)_2\text{S}_2\text{O}_8\text{cryst.} + 2\text{NaOH} \rightarrow \text{Na}_2\text{S}_2\text{O}_8 + 2\text{NH}_3 + 2\text{H}_2\text{O}\]  

(3)

This reaction must be performed at reduced pressure with the consumption of heat, \(\text{NH}_3\) and \(\text{H}_2\text{O}\) having to be removed as gas and vapor, respectively. The ammonia that forms must finally be absorbed in an \(\text{H}_2\text{SO}_4\) receiver.

\[2\text{NH}_3 + \text{H}_2\text{SO}_4\text{aq} \rightarrow (\text{NH}_4)_2\text{SO}_4\text{aq}\]  

(4)

and be recycled to the electrolysis process.

The balanced equation of this process may thus be represented as follows:

\[2\text{NaOH} + 2\text{H}_2\text{SO}_4\text{aq, anodic} \rightarrow \text{Na}_2\text{S}_2\text{O}_8\text{cryst.} + \text{H}_2 + 2\text{H}_2\text{O}\]  

(1-4)

Caustic soda solution and sulfuric acid serve as raw materials in this technical process. In addition to the electrolysis apparatus required for step (1) of the process, a considerable amount of apparatus is required for the remaining steps, mainly for the combined processes (3) and (4). During the process, certain conditions, mainly with regard to temperature and pressure, must be maintained precisely. A transformation of 95 to 98 percent is achieved in step (3), i.e., the losses of active oxygen are economically acceptable. In this step, every precaution must be taken to see that there are no decomposition catalysts present in the solution. The presence of such materials results in reductions of yield and also in a hazardous condition: in an extreme case, catalytic decomposition would result in explosion with catastrophic consequences for personnel and equipment.

The invention provides a process for the direct electrolytic production of sodium persulfate suitable for use on a large commercial scale in which the product formed is recoverable without a thermal crystallization process, i.e., in which a major drawback of prior art processes is overcome.

Essentially, the process of the invention comprises the direct electrolytic production by electrolyzing, at 0.3 to 1.2 A/cm², a solution containing \(\text{Na}_2\text{SO}_4\) and \(\text{H}_2\text{SO}_4\) in such quantity that the solubility of the sodium peroxodisulfate that is formed will be less than 0.6 mole per liter and the concentration of \(\text{Na}_2\text{SO}_4\) and \(\text{H}_2\text{SO}_4\) is kept constant during the electrolysis.

The process of the invention may be represented by the following equation:

\[\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4 \rightarrow (\text{NH}_4)_2\text{S}_2\text{O}_8\text{cryst.} + \text{H}_2\text{O}\]  

(5)

The knowledge that the concentration of the sodium persulfate dissolved in the electrolyte must be kept as low as possible in order to limit losses through reduction of \(\text{S}_2\text{O}_8^{2-}\) at the cathode (reversal of Equation 5) has proven to be essential to the successful performance of the electrolytic process of Equation (5). On the other hand, the anodic oxidation of the sulfuric acid at high \(\text{HSO}_4^-\) ion concentrations (schematically in accordance with

\[2\text{HSO}_4^- \rightarrow 2\text{H}^+ + \text{S}_2\text{O}_8^{2-} + 2\text{e}^-\]  

(6)

is promoted; surprisingly, however, under the conditions in accordance with the invention, the anticipated negative effect of the \(\text{H}^+\) ions formed in accordance with Equation (6) in the sense of a hydrolysis of the persulfate ion as follows:
$3\text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{HSO}_4^- + \text{HSO}_3^- \tag{7}$

is hardly perceptible.

For the performance of the electrolysis process a solution is used which contains

2.6 to 3.1 moles Na$_2$SO$_4$ per liter and

2.8 to 3.5 moles H$_2$SO$_4$ per liter. In this electrolyte, Na$_2$S$_2$O$_8$ has a solubility of 0.2 to 0.6 mole. During the electrolysis the feedstocks must be added constantly in such measure that the concentration of acid, sulfate and sodium ions will remain as constant as possible. Then, after the saturation limit is reached in the start-up phase of the electrolysis, newly formed sodium persulfate immediately precipitates in crystallized form and is thus removed from any further reactions. It can best be separated continuously in a partial stream by means of suitable separating units. After washing and drying, a very pure salt is obtained.

To achieve an optimum yield, it has proven desirable to limit the total amount of dissolved sodium persulfate, since the amount of persulfate that is exposed to hydrolysis in accordance with Equation (7) and which is lost to the process will remain relatively small. Accordingly, the amounts of electrolyte used in an electrolysis apparatus are not to exceed approximately 200 liters per kA with reference to the installed current intensity. Preferably, the operating range is 80 to 160 kA.

The preferred anode material is pure platinum in the form of sheets, wires or bands, or in the form of a coating on suitable supports. These supports will also serve as a conductor of current to the platinum which alone has the electrochemical action.

The anodic current density necessary for the anodic oxidation of the hydrogen sulfate ion amounts to at least 0.3 A/cm$^2$; it may be increased up to 1.2 A/cm$^2$ if provision is made for sufficient cooling. The electrolyte temperature may amount to as much as about 28°C, or even more for short periods. The best yields are obtained if the temperature is not substantially more than 22°C. The addition of polarization-increasing compounds, such as chloride, borate, cyanide, rhodanide, etc., is preferred for optimum results. If such compounds are added it is desirable to keep their concentration constant, too.

The process of the invention will be further explained with the aid of the following examples and the drawing:

**EXAMPLE 1**

An electrolyte, consisting of 3.0 moles Na$_2$SO$_4$ per liter, 3.3 moles of H$_2$SO$_4$ per liter and 0.5 g NaCl + 0.8 g NaCN per liter, was pumped by means of a pump (5) through the electrolysis cell (1) where the chemical process of Equation (5) took place, was separated in container (2) from the electrolysis gas mixture (3) and was recycled into container (4). From the latter a partial stream was fed to the saturation tank (6) where the raw materials (8) were continuously metered in at a rate corresponding to the electrochemical transformation. The electrolysis was performed in a flow-through cell with a current density of 0.5 A/cm$^2$ at a current drain of 60 A; the time of stay of the electrolyte in the cell was 0.37 seconds, and its temperature was 20°C; the electrolyte volume was 8 liters. After about 6 hours of operating time, crystallized Na$_2$S$_2$O$_8$ began to precipitate out of the electrolyte, while a steady current yield of 62 percent established itself. The current percentage eliminated for the oxygen formation was 10 percent. After another 6 hours of continued electrolysis the persulfate salt (7) was separated by centrifugation.

**EXAMPLE 2**

In the same system as described in Example 1, an electrolyte consisting of 2.8 moles of Na$_2$SO$_4$ per liter, 3.1 moles of H$_2$SO$_4$ per liter and 0.4 g of NaSCN per liter, was electrolyzed at 0.6 A/cm$^2$. Steady current yields of about 60 percent were produced over the 6-day course of the experiment. The cell voltage was 5.1 volts. This shows an electrolysis power requirement of about 1.9 kWh per kg of sodium persulfate.

For comparison, 1.5 to 2.0 kWh/kg must be reckoned for the technical electrolysis processes known or commonly used at the present time for the production of ammonium persulfate. To this must be added the power required for the reactions of Equations (3) and (4), so that the total consumption amounts to 3 kWh/kg. The process of the invention, therefore, not only involves substantially simpler procedures but also makes possible a very appreciable reduction of power consumption. Furthermore, the invention dispenses with the vacuum apparatus required in the known chemical process and the elevated temperatures in the stage corresponding to Equation (3). From the safety standpoint, too, therefore, it represents an advance in relation to this known technical process.

It will be understood that the specification and examples are illustrative but not limiting of the present invention and that other embodiments within the spirit and scope of the invention will suggest themselves to those skilled in the art.

What is claimed is:

1. Process for the direct electrolytic production of sodium persulfate from (sodium hydrogen sulfate) a solution containing Na$_2$SO$_4$ and H$_2$SO$_4$, which process comprises electrolyzing in a cell, at a current density of from 0.3 to 1.2 amperes per square centimeter, an electrolytic solution containing said Na$_2$SO$_4$ and H$_2$SO$_4$ in such quantity that the solubility of the sodium persulfate formed amounts to less than 0.6 mole per liter, and maintaining the concentration of Na$_2$SO$_4$ and H$_2$SO$_4$ constant during the electrolysis.

2. Process as claimed in claim 1 wherein said solution contains from 2.6 to 3.1 moles of sodium sulfate per liter and contains at least 0.1 molar excess of sulfuric acid over sodium sulfate.

3. Process as claimed in claim 1 wherein said solution contains from 2.8 to 3.5 moles of sulfuric acid per liter and contains at least 0.1 molar excess of sulfuric acid over sodium sulfate.

4. Process as claimed in claim 1 wherein the current density is from 0.4 to 0.7 amperes per square centimeter.

5. Process as claimed in claim 1 wherein said solution also contains potential-increasing material, the concentration of which is maintained constant.

6. Process as claimed in claim 5 wherein said potential-increasing substance is a chloride, borate, cyanide or rhodanide.

7. Process as claimed in claim 1 wherein the electrolyte solution is cycled into and out of the cell.
8. Process as claimed in claim 7 wherein the average residence time of a electrolyte solution in the cell is 1.0 second or less.

9. Process as claimed in claim 6 wherein dispersed solid sodium peroxodisulfate is separated from the electrolytic solution while being cycled outside of the cell.

10. Process as claimed in claim 1 wherein the temperature of the electrolyte solution is maintained at below 28°C.

11. Process as claimed in claim 10 wherein said temperature is maintained between 16°C and 22°C.

12. Process as claimed in claim 1 wherein the volume of the electrolyte solution does not exceed about 200 liters per kA of installed current intensity.
UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,915,816
DATED : October 28, 1975
INVENTOR(S) : Erwin Rossberger

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 4, Claim 1, lines 2 and 3, cancel "(sodium hydrogen sulfate)".

Signed and Sealed this Twenty-fourth Day of August 1976

[SEAL]

Attest:

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