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ELECTROCHEMICAL PROCESS FOR PRODUCTION OF SODIUM PERCHLORATE

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1 Claim. (Cl. 204—82)

The present invention relates to the manufacture of sodium perchlorate in a relatively pure condition and free from contamination with lower oxy acids of halogens.

Sodium perchlorate is an excellent source of oxygen in explosive mixtures possessing high detonating and shattering power and, in the dry condition, is extremely useful in this connection. However, the presence of minute amounts of unconverted chlorate in the perchlorate increases the sensitivity of the perchlorate to heat and to shock.

It is an object of the present invention to manufacture pure sodium perchlorate free of halogen oxy acids or salts thereof.

It is also an object of the present invention to produce sodium perchlorate directly from sodium chlorate while, at the same time, eliminating excess of chlorate or avoiding the presence of chlorate in the perchlorate produced.

In accordance with the present invention, therefore, a cell solution of sodium chlorate is oxidized anodically, in the usual way, in a conventional oxidation cell well known for this purpose. Thus, a cell solution is prepared containing about 700 grams per liter sodium chlorate. To this solution there is added about 2 grams per liter of sodium chromate or dichromate. The purpose of the chromate is to protect the cathode and to prevent the formation in solution of reducing hydrogen, from electrolysis of the aqueous electrolyte with destruction of some of the chlorate in the cell and, therefore, at a reduced cell efficiency of output.

This solution is electrolyzed in the usual way and generally in a conventional cell cascade. The operating voltage and amperage will depend upon the construction of the cell and the movement of electrolyte therethrough. However, these are factors which are well known in the art and constitute no part of the invention herein described and claimed. In general, the temperature is permitted to rise in the last cell of the cascade and may reach 60° C. At this point, the cell electrolyte contains about 840 grams per liter sodium perchlorate. This figure may be increased to a limiting value of about 1100 grams per liter by adding additional sodium chlorate to the electrolyte from two-thirds to half way through the cascade to compensate for the sodium chlorate already converted to perchlorate. However, as the presence of unconverted chlorate in perchlorate imparts very serious and undesirable characteristics to the completed product, it is preferable to operate the cell to the lowest concentration

of chlorate that is economically feasible. The economic limit is reached when a concentration of about 1 to 5 grams per liter chlorate is reached. This is due to the fact that the high current density of 450 amperes per square foot produces excessive quantities of ozone by reason of electrolysis of the aqueous electrolyte, thus lowering the cell efficiency.

The perchlorate cell solution at the end of the conversion is, in accordance with the present invention, already at a relatively elevated temperature, namely, in the neighborhood of about 60° C. To this solution, removed from the cell, a substance is added having the power of selectively reducing any residual chlorate and chromate. The reducing material selected must possess, in addition to this selective reducing power, the characteristic of ready removability from the solution. Sulfur dioxide provides an excellent reducing substance for the purpose intended, since this material may be bubbled through the electrolyzed cell solution, destroying the residual chlorate which is normally present at this point to the extent of about one gram per liter, and reducing any portion of the chromate not already reduced at the cathode. The chlorate is reduced to chloride, and the chromate to chromic compounds.

The sulfur dioxide treatment is continued until such time as the cell solution gives no further test for the presence of chlorate ion. To this end, the electrolyzed cell solution is added to a test indicator made of one gram per liter indigo carmine. The test is made by mixing one milliliter of the indigo carmine with 5 milliliters of concentrated hydrochloric acid, and the mixture heated to boiling. To this boiling mixture, 5 milliliters of the reduced cell solution are added. Five parts per million of chlorate will cause a sharp decoloration of the indicator, and one part per million can be detected. Sulfur dioxide does not interfere with this procedure. Sulfur dioxide is, therefore, added to this solution until a test made with the indigo carmine indicator shows the presence of less than one part per million of chlorate, that is, the elimination of substantially all of the chlorate and any other halogen oxy acids.

Excess sulfur dioxide is eliminated from the treated solution by heating the solution to boiling and bubbling air therethrough to sweep out such excess. Sulfur dioxide may be tested for by permitting the evolved vapors to act upon 1/1000 N potassium permanganate solution.

The acidity of the treated solution is then ad-

justed to a pH of about 7. To this end, sodium carbonate solution or other mild alkali may be employed. The chromic ion is precipitated as chromic hydroxide and may be removed.

The cell solution thus purified is evaporated to dryness and the sodium perchlorate dried carefully and slowly at about 160° C. The material may be dried in any suitable or conventional fashion by the employment of conventional pulverizing and drying equipment and, in general, the time required to dry the material will be dependent directly upon the efficiency of the drying equipment.

An analysis of the dried sodium perchlorate gave the following composition:

	Percent
Sodium perchlorate -----	98.70
Sodium sulfate -----	1.00
Sodium chloride -----	0.04
Sodium carbonate -----	0.32

The present invention provides a method of purifying electrolyzed sodium chlorate and the

production of sodium perchlorate free of deleterious chlorate whereby the sodium perchlorate may be used directly as a compounding agent in explosive materials without the necessity of changing the perchlorate to the potassium or ammonium salt as has been done heretofore.

What is claimed is:

The method of manufacturing solid sodium perchlorate uncontaminated with chlorate, which comprises anodically oxidizing an aqueous solution of sodium chlorate containing a water soluble salt of hexavalent chromium with the production of perchlorate contaminated with chlorate, treating the oxidized solution with sufficient sulfur dioxide to reduce chromates to chromic salts and the residual chlorate to chloride, adding mild alkali to adjust the pH of the solution to about 7 to precipitate chromic hydroxide, removing the precipitated chromic hydroxide, and thereafter evaporating and drying the relatively purified solution to recover the sodium perchlorate.

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