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(54) **METHOD FOR MAKING ANHYDROUS SODIUM PERCHLORATE**

(76) Inventor: **Jean-Michel Bossoutrot**, F-69630 Chaponost (FR)

Correspondence Address:
HUNTON & WILLIAMS
INTELLECTUAL PROPERTY DEPARTMENT
1900 K STREET, N.W.
SUITE 1200
WASHINGTON, DC 20006-1109 (US)

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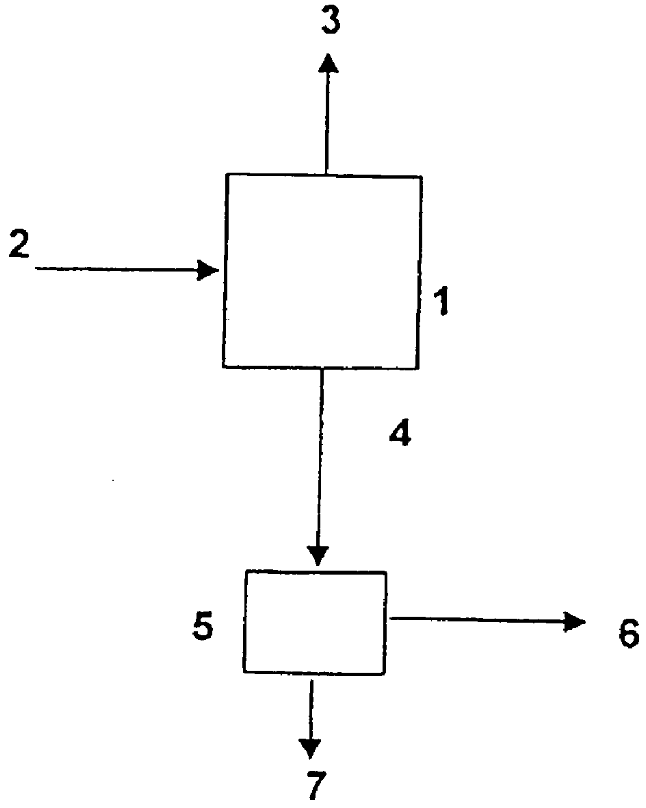
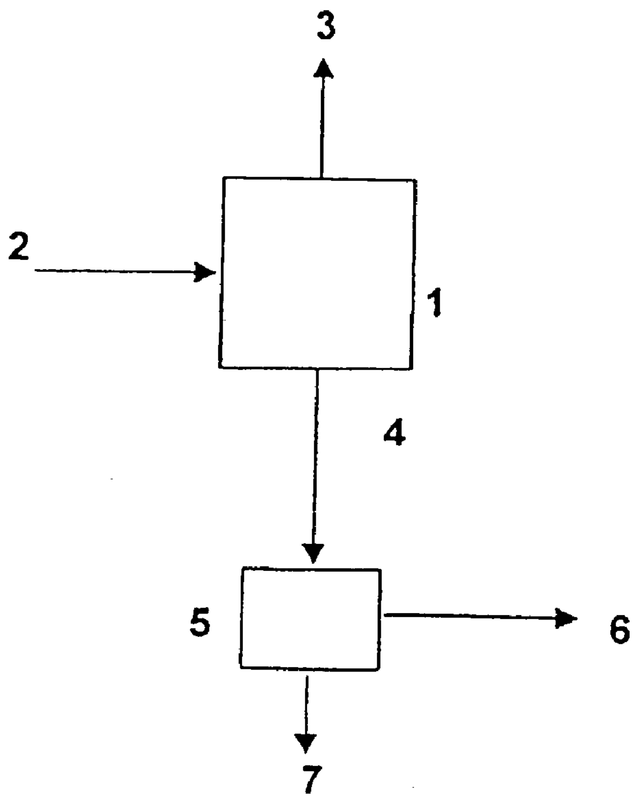
(57) **ABSTRACT**

The invention concerns a method for making anhydrous sodium perchlorate whereby an aqueous sodium perchlorate solution, directly derived from electrolysis of an aqueous sodium chlorate solution, is subjected to vacuum evaporation. The invention also concerns anhydrous sodium perchlorate crystals which preserve good pourability and methods for making them.



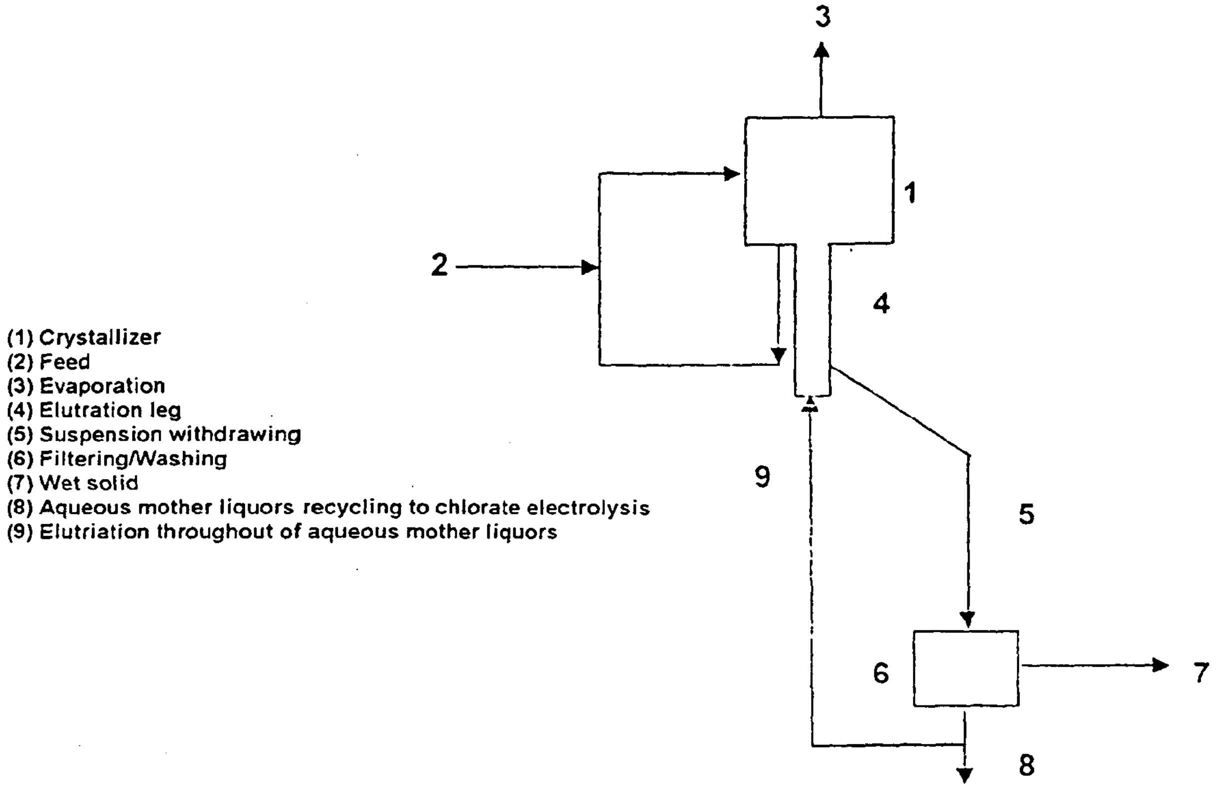
Laboratory Diagram



(1) Crystallizer
(2) Feed
(3) Evaporation
(4) Suspension withdrawing
(5) Filtering/Washing
(6) Wet solid
(7) Aqueous mother liquors

Fig. 1/2 Laboratory Diagram

Fig. 2/2 Industrial process



(1) Crystallizer
(2) Feed
(3) Evaporation
(4) Elutration leg
(5) Suspension withdrawing
(6) Filtering/Washing
(7) Wet solid
(8) Aqueous mother liquors recycling to chlorate electrolysis
(9) Elutriation throughout of aqueous mother liquors

METHOD FOR MAKING ANHYDROUS SODIUM PERCHLORATE

[0001] The present invention relates to a process for the manufacture of anhydrous sodium perchlorate.

[0002] It is known to manufacture sodium perchlorate by electrolysis of an aqueous chlorate solution of the said metal in a single electrolytic stage or a succession of individual electrolytic stages. Reference may be made, on this subject, to Patents EP 368 767, U.S. Pat. No. 3,518,180 and U.S. Pat. No. 3,475,301.

[0003] Thus, Patent EP 368 767 discloses a continuous process for the manufacture of sodium perchlorate by electrolysis in a single stage of an electrolyte (liquid comprising sodium chlorate and sodium perchlorate in the dissolved state) kept uniform with a stationary composition, which composition is chosen so that it can directly deposit, by cooling, perchlorate crystals in a monohydrate, dihydrate or anhydrous form.

[0004] It is also indicated that, on conclusion of the electrolysis stage, the aqueous sodium perchlorate solution is crystallized by cooling or evaporation of water.

[0005] In Example 2 of U.S. Pat. No. 3,518,180, the electrolytic cell fed with a solution comprising 300 g/l of sodium chloride and 700 g/l of sodium perchlorate produces, at the outlet, a solution comprising 80 g/l of sodium chlorate and 1100 g/l of sodium perchlorate. After settling in an intermediate tank, this solution is subsequently evaporated to result in a suspension of crystals which is then centrifuged to give perchlorate crystals. No information is given regarding the nature of the perchlorate or the evaporation conditions.

[0006] Furthermore, the process for the manufacture of sodium perchlorate by oxidation of sodium chlorate, disclosed in U.S. Pat. No. 3,038,782, is carried out in the presence of lead dioxide in a reaction medium comprising sulphuric acid. After the electrolysis stage, the aqueous perchlorate solution is freed from lead-based compounds by filtration at approximately 90-100° C. and then evaporated at 150° C. and subsequently the concentrated aqueous solution comprising 1.32 mol of sodium perchlorate, 2.96 mol of perchloric acid, 0.12 mol of sulphuric acid and 8.45 mol of water is cooled to 25° C. to give, after filtration, 0.92 mol of sodium perchlorate crystals accompanied by 0.08 mol of perchloric acid and 0.15 mol of water. The perchloric acid is subsequently removed by neutralization to finally give anhydrous sodium perchlorate comprising approximately 3.3% by weight of water, which, after drying at 105-100° C., results in dry anhydrous sodium perchlorate.

[0007] The Applicant Company has now found that the crystallization of anhydrous sodium perchlorate under specific conditions makes it possible to obtain crystals with a high degree of purity.

[0008] A first subject-matter of the present invention is a process for the manufacture of anhydrous sodium perchlorate, according to which an aqueous sodium perchlorate solution, originating directly from an electrolysis stage or from a succession of individual electrolytic stages on an aqueous chlorate solution of the said metal, is subjected to vacuum evaporation at a temperature of between 52 and 75° C., preferably of between 60 and 70° C. The absolute pressure is preferably between approximately 1500 and 7000 Pa.

[0009] The aqueous sodium perchlorate solution is advantageously chosen so that the anhydrous sodium perchlorate can be isolated directly by crystallization, that is to say a solution which deposits the anhydrous sodium perchlorate by evaporation of water or by cooling; reference may be made, on this subject, to the work published under the direction of Paul Pascal, Nouveau Traité de Chimie Minérale [New Treatise on Inorganic Chemistry], 1966, Volume II, Part 1, p. 353 and FIG. 37, which shows the $NaClO_4$—$NaClO_3$—H_2O ternary diagram.

[0010] The composition of this aqueous solution is preferably that which lies within the region of the $NaClO_4$—$NaClO_3$—H_2O ternary diagram delimited by the points: A: 58 g of $NaClO_3$, 270 g of $NaClO_4$; B: 87 g of $NaClO_3$, 295 g of $NaClO_4$, C: 280 g of $NaClO_4$ and D: 300 g of $NaClO_4$ per 100 g of water.

[0011] The aqueous sodium perchlorate solution, originating from the electrolysis of an aqueous sodium chlorate solution, can be obtained by keeping the concentration of the sodium chlorate and of the sodium perchlorate constant in the single electrolysis stage by continuous addition of sodium chlorate and water simultaneously, each in an amount equal respectively to the amount of sodium chlorate and to the amount of water which, in the free state or in the combined form, are withdrawn continuously from the said stage.

[0012] Sodium bichromate can be added to the electrolytic solution to inhibit cathodic side reactions, such as, for example, the reduction of hypochlorite and chlorate ions.

[0013] The temperature of the electrolysis is generally between 40 and 90° C. and the pH of the electrolytic solution is between 6 and 10.

[0014] Platinum-based anodes are advantageously used.

[0015] After the evaporation stage, the suspension of anhydrous sodium perchlorate crystals is filtered and then the crystals can subsequently be washed with water to remove the residual impurities.

[0016] The Applicant Company has noticed that, when the aqueous wash liquor is brought to a temperature of between 55 and 80° C., preferably of between 55 and 65° C., the washed crystals are composed essentially of anhydrous sodium perchlorate (devoid of sodium perchlorate monohydrate) and exhibit good flowability. In addition, the degree of purity of the anhydrous sodium perchlorate is improved.

[0017] The anhydrous sodium perchlorate crystals, thus filtered and washed, generally comprise 1 to 2% by weight of water.

[0018] A simplified diagram of a specific embodiment of the invention is given in **FIG. 1**. A crystallizer **1**, fed with aqueous sodium perchlorate solution originating directly from the electrolysis of sodium chlorate **2**, is placed under vacuum and then heated to a temperature of between 52 and 75° C. The evaporated water **3** leaves the crystallizer and a suspension of anhydrous sodium perchlorate crystals is withdrawn via **4**. This suspension is subsequently filtered in **5** and wet anhydrous sodium perchlorate crystals are recovered in **6** and the filtrate is recovered in **7**. According to an alternative form, after filtering, the anhydrous sodium perchlorate crystals can be washed with water brought to a temperature of 55-80° C.

[0019] According to another specific embodiment of the invention (**FIG. 2**), a crystallizer **1** equipped with an elutriation leg **4** is fed continuously with aqueous sodium perchlorate solution originating directly from the electrolysis of sodium chlorate **2**. The crystallizer, placed under vacuum, is heated to and maintained at a temperature of between 52 and 75° C. The suspension of the anhydrous sodium perchlorate crystals is subsequently withdrawn in **5** and then filtered in **6**.

[0020] The wet anhydrous sodium perchlorate crystals are recovered in **7** and can optionally be washed. The aqueous filtration solution **8** can be recycled to the electrolysis and can optionally be injected into the crystallizer in **9**.

[0021] The choice of the throughput of the loop for recirculation of the aqueous sodium perchlorate solution of the crystallizer and that of the elutriation throughput injected in **9** make it possible, by regulating the amount of water evaporated in **3**, to obtain the desired size of the crystals.

[0022] Another aim of the invention is the production of anhydrous sodium perchlorate crystals which retain good flowability over time. This aim can be achieved by subjecting the filtered (washed or unwashed) anhydrous sodium perchlorate crystals to a drying stage until a residual water content of less than 0.1% by weight and preferably of less than or equal to 0.05% by weight is obtained.

[0023] The drying stage can be carried out at a temperature of between 60 and 150° C. and for a period of time of between 10 minutes and 1 hour.

[0024] Fluidized bed drying is preferred and the temperature is preferably between 100 and 150° C. for a period of time of between 15 and 45 minutes in a batchwise process.

[0025] It is also possible to operate with continuous drying.

[0026] The Applicant Company has also noticed that the addition of a sufficient amount of finely divided silica to the filtered (washed or unwashed) anhydrous perchlorate crystals, preferably the crystals obtained after filtering and washing, makes it possible to obtain anhydrous sodium perchlorate crystals which retain good flowability over time.

[0027] These anhydrous perchlorate crystals have good flowability even after storage for a few months.

[0028] The amount of silica charged generally depends on its nature. An amount of silica of between 0.05 and 0.5% by weight with respect to the anhydrous sodium perchlorate crystals has given highly advantageous results.

[0029] Although it is possible to use silica with a hydrophilic nature, it is generally preferable to use hydrophobic silica. The specific surface area of the silica is advantageously between 100 and 300 m^2/g.

[0030] The addition of the silica to the anhydrous sodium perchlorate crystals can be easily carried out in a mixer, for example a rotary mixer.

[0031] The present invention also relates to the anhydrous sodium perchlorate crystals thus obtained.

Experimental Part

EXAMPLE 1

[0032] A crystallizer with a capacity of one litre is fed, with a throughput of 300 cm^3/h, with an aqueous solution comprising 1100 g/l of sodium perchlorate and 115 g/l of sodium chlorate originating directly from a sodium chlorate electrolytic cell.

[0033] The crystallizer is placed under an absolute pressure of 5000 Pa and brought to and then maintained at a temperature of 65° C. Under these conditions, to maintain a constant level in the crystallizer, 70 g/h of water are evaporated and a suspension is withdrawn comprising 20 to 30% by weight of anhydrous sodium perchlorate crystals in the form of slightly agglomerated rods with a size of 500×100 μm.

[0034] The suspension is subsequently filtered and then the filter residue is washed with water brought to 65° C.

[0035] After filtering, the anhydrous sodium perchlorate crystals comprise 0.8% by weight of sodium chlorate and, after washing, the sodium chlorate content in the crystals is less than 0.2%.

[0036] Residual water is present at approximately 2% by weight.

EXAMPLE 2

[0037] A 20 m^3 crystallizer, maintained under an absolute pressure of 4000 Pa and at a temperature of 65° C., is continuously fed, via the recirculation loop, with an aqueous sodium perchlorate solution originating from a stage of electrolysis of sodium chlorate and comprising 1110 g/l of perchlorate and 124 g/l of chlorate.

[0038] The throughputs for feeding with aqueous sodium perchlorate solution, for evaporating water and for withdrawing suspension via the elutriation leg are adjusted so as to obtain a level of solids of approximately 15% by weight in the crystallizer and 30% by weight in the elutriation leg.

[0039] The composition of the aqueous solution in the crystallizer is 295 g of sodium perchlorate and 34 g of sodium chlorate per 100 g of water.

[0040] A residence time of the solid in the crystallizer of 5 to 6 h and that of the liquid of approximately 10 h makes it possible to produce approximately 1.2 t/h of dry anhydrous sodium perchlorate.

[0041] The suspension withdrawn from the elutriation leg is subsequently filtered and then the filtered residue is washed with water brought to 65° C. The Cr^{3+} content in the crystals after filtering is 7 ppm and, after washing, this content is reduced to less than 1 ppm.

[0042] The chlorate (ClO_3^-) content present in the crystals after filtering is 0.3% by weight and that after washing is less than 0.05% by weight.

[0043] The residual water content in the washed crystals is approximately 1 to 1.5% by weight.

[0044] The anhydrous sodium perchlorate crystals have a particle size of 800 μm in the elutriation leg.

EXAMPLE 3

[0045] The processing is carried out as described in Example 2 but with an aqueous wash liquor brought to 35° C. The result of this is that the crystals set solid during the washing, which even results in the filtration device becoming blocked.

EXAMPLE 4

[0046] The processing is carried out as in Example 1 but while maintaining the crystallizer at 32° C. and at an absolute pressure of 500 Pa. Under these conditions, sodium perchlorate monohydrate crystals are obtained.

EXAMPLE 5

[0047] 700 g of anhydrous sodium perchlorate crystals originating from Example 1 are introduced into a fluidized bed maintained at 140° C. After 40 minutes, the residual water content is only 0.05% by weight. This product retains very good flowability after storage for one month.

EXAMPLE 6

[0048] Drying is carried out under the same conditions as those described in Example 5 but with 50 kg of anhydrous sodium perchlorate crystals originating from Example 2.

[0049] A residual water content of approximately 0.05% by weight is obtained.

EXAMPLES 7-11

[0050] 50 kg of sodium perchlorate crystals prepared according to Example 2 are charged to a rotary mixer, they are then stirred for 1 hour and then silica is added over 10 to 15 minutes. Stirring is maintained for 30 to 40 minutes after the addition.

[0051] Finally, the resulting solid is packaged in a polyethylene bag and then enclosed in a 50 kg keg for 6 months.

[0052] After 3 or 6 months, on opening the keg, the solid retains perfect flowability (see Table I).

EXAMPLE 12

[0053] The sodium perchlorate crystals prepared according to Example 2 and bagged up directly, then enclosed in a keg, set solid after storage for three months.

EXAMPLE 13

[0054] The processing is carried out as in Example 7 except that, instead of the silica, 200 ppm of triethanolamine, in the form of an aqueous solution prepared beforehand by dissolution of 10 g in 150 g of water, are added over 10 to 15 minutes.

[0055] After opening the keg after storage for three months, the solid has set solid.

EXAMPLE 14

[0056] The processing is carried out as described in Example 13 except that 200 ppm of sodium dodecyl sulphate are added instead of triethanolamine.

[0057] After storage for three months, it is observed, on opening the keg, that the product has set solid.

TABLE I

Example	Silica	Amount % by weight	Storage time (months)	Observations
7	Degussa C600	0.3	3	Very good flowability
	"	0.3	6	"
8	"	0.2	3	"
	"	0.2	6	"
9	"	0.05	3	Very good flowability but a few lumps in the keg
10	Degussa D22S	0.2	3	"
	"	0.2	6	"
11	"	0.05	3	Surface crusting and lumps in the keg
	"	0.05	6	"

1. Process for the manufacture of anhydrous sodium perchlorate, according to which an aqueous sodium perchlorate solution, originating directly from an electrolysis stage or from a succession of individual electrolytic stages on an aqueous chlorate solution of the said metal, is subjected to vacuum evaporation at a temperature of between 52 and 75° C., preferably of between 60 and 70° C.

2. Process according to claim 1, characterized in that the absolute pressure is between 1500 and 7000 Pa.

3. Process according to claim 1 or **2**, characterized in that the aqueous sodium perchlorate solution is chosen so that the anhydrous sodium perchlorate can be isolated directly by crystallization.

4. Process according to claim 3, characterized in that the composition of the aqueous sodium perchlorate solution lies within the region of the $NaClO_4$—$NaClO_3$—H_2O ternary diagram delimited by the points:

A: 58 g of $NaClO_3$, 270 g of $NaClO_4$

B: 87 g of $NaClO_3$, 295 g of $NaClO_4$

C: 280 g of $NaClO_4$

D: 300 g of $NaClO_4$ per 100 g of water.

5. Process according to any one of claims 1 to 4, characterized in that, on conclusion of the evaporation stage, the suspension of the anhydrous sodium perchlorate crystals is filtered and then the crystals are optionally washed with water.

6. Process according to claim 5, characterized in that the temperature of the aqueous wash liquor is between 55 and 80° C., preferably between 55 and 65° C.

7. Process according to claim 5 or **6**, characterized in that the filtered anhydrous sodium perchlorate crystals are subsequently subjected to a drying stage until a residual water content of less than 0.1% by weight and preferably of less than or equal to 0.05% by weight is obtained.

8. Process according to claim 5 or **6**, characterized in that a sufficient amount of finely divided silica is added to the filtered anhydrous sodium perchlorate crystals.

9. Process according to claim 8, characterized in that the amount of silica added is between 0.05 and 0.5% by weight with respect to the anhydrous sodium perchlorate crystals.

10. Process according to claim 8 or **9**, characterized in that the silica is a hydrophobic silica.

11. Process according to any one of claims 8 to 10, characterized in that the specific surface area of the silica is between 100 and 300 m^2/g.

12. Anhydrous sodium perchlorate crystals which are capable of being obtained according to any one of claims 7 to 11.

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