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(54) **PROCESS TO MAKE HIGH-PURITY WET SALT, WET SALT SO OBTAINABLE, AND THE USE THEREOF IN AN ELECTROLYSIS PROCESS**

VERFAHREN ZUR HERSTELLUNG VON HOCHREINEM FEUCHTEM SALZ, SO ERHÄLTLICHES FEUCHTES SALZ UND VERWENDUNG DAVON BEI EINEM ELEKTROLYSEVERFAHREN

PROCEDE DE FABRICATION DE SEL HUMIDE DE GRANDE PURETE, SEL HUMIDE AINSI OBTENU, ET UTILISATION DUDIT SEL HUMIDE DANS UN PROCEDE D'ELECTROLYSE

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**US-A- 3 567 371** **US-A- 4 839 003**

- **PATENT ABSTRACTS OF JAPAN vol. 013, no. 402 (C-633), 6 September 1989 (1989-09-06) & JP 01 145319 A (JAPAN TOBACCO INC), 7 June 1989 (1989-06-07) cited in the application**
- **PATENT ABSTRACTS OF JAPAN vol. 013, no. 402 (C-633), 6 September 1989 (1989-09-06) & JP 01 145320 A (JAPAN TOBACCO INC), 7 June 1989 (1989-06-07) cited in the application**

## Description

**[0001]** The present invention relates to a process to make salt (sodium chloride) of high purity, as well as to the use of resulting high-purity, preferably wet, salt to make brine, a solution of said salt in water, for electrolysis operations, preferably the electrolysis process involving membrane cells.

**[0002]** Salt and wet-salt is long known. The conventional process to make said salt is an evaporative crystallisation of brine, followed by washing and drying steps. Said brine is typically produced by dissolving a natural source of NaCl in water. The brine will also contain K, Br, SO<sub>4</sub>, and/or Ca, which moieties are typically present in the source of NaCl. A disadvantage of the conventional process is that the salt obtained has imperfections in the crystal lattice and contains occlusions, being small pockets of mother liquor of the evaporative crystallisation process (present in cavities in the salt crystals). Due to these imperfections and occlusions, the wet salt, and a subsequent brine produced therefrom, is contaminated with compounds present in the mother liquor. In particular, the amount of K, Br, SO<sub>4</sub>, and/or Ca that is carried over is quite high. Hitherto, additional washing steps and drying steps, such as centrifuge steps, were employed, which are energy consuming, to reduce the levels of the contaminants.

**[0003]** Especially if a brine produced from the wet salt is to be used in the modern membrane electrolysis cells said contaminants are known to lead to less economic electrolysis operations.

**[0004]** For these reasons, there is a need for improved wet salt, having a lower level of contaminants, which can be produced more cost-effectively and which can be used to make a brine for electrolysis processes.

**[0005]** Surprisingly, we have now found that wet salt compositions can be produced with a reduced level of K, Br, SO<sub>4</sub>, and/or Ca and using less energy in the washing operations. The process to make such high-purity wet salt compositions is characterized in that during the evaporative crystallization process, the mother liquor contains an effective amount of a crystal growth inhibitor that is selected from oligopeptides, polypeptides, and polymers bearing two or more carboxylic acid groups or carboxyalkyl groups and optionally further phosphate, phosphonate, phosphino, sulfate, and/or sulfonate groups, such as carboxymethyl cellulose with phosphate groups, to form salt crystals with a (111) face. Said salt can be washed with a reduced amount of washing water while still containing lower amounts of K, Br, SO<sub>4</sub>, and/or Ca. A wet salt can be obtained by partially drying the salt crystals that are formed.

**[0006]** Preferably, the crystal growth inhibitor is a water-soluble polymer. More preferably, it is a water-soluble polymer bearing two or more carboxylic acid groups and optionally further phosphate, phosphonate, phosphino, sulfate, and/or sulfonate groups, such as polyacrylates. If the final salt is to be used in electrolysis op-

erations the use of peptides is less desired, since the nitrogen of the peptide can result in the formation of the highly undesired NCl<sub>3</sub> in said electrolysis process. Peptides that hydrolyze in the crystallization process to the extent that they become ineffective crystal growth inhibitors are also less preferred. However, for table salt, peptides may be acceptable. If residual crystal growth inhibitor in the final salt is undesired, then the use of hydrolyzing peptides can be preferred since the final salt, optionally after a washing step, can be free of the crystal growth inhibitor.

**[0007]** It is noted that it is known that adding certain chemicals to the evaporative process can influence the crystal form of the salt and can influence the formation of occlusions in the salt. Lead chloride, cadmium chloride, manganese sulfate and carrageen in, for instance, have been reported to reduce the amount of cavities, and consequently the amount of occlusions and occluded mother liquor, when added to the evaporative crystallizing mass. However, such chemicals are undesired. Not only can they adversely affect the electrolysis operations, they may also spill over in table-salt that is produced using the same installation, which is typically undesired.

**[0008]** The term wet salt is used to denominate "predominantly sodium chloride" containing a substantial amount of water. More particularly, it is a water-containing salt of which more than 50% by weight consists of NaCl. Preferably, such salt contains more than 90% by weight of NaCl. More preferably, the salt contains more than 92% of NaCl, while a salt being essentially NaCl and water is most preferred. The wet salt will contain more than 0.5, preferably more than 1.0, more preferably more than 1.5% by weight of water. Preferably it contains less than 10% by weight, more preferably less than 6% by weight and most preferably less than 4% by weight of water. Typically the salt will contain 2-3% of water. All of the weight percentages given are based on the weight of the total composition.

**[0009]** An effective amount of the crystal growth inhibitor is present if in the following test any crystals with a (111) face show up. More particularly, to determine whether enough crystal growth inhibitor is present, one adds a certain amount of the crystal growth inhibitor to a glass beaker of 1000ml, equipped with a magnetic stirrer bar, and containing 450 ml of demineralized water and 150 g of high-purity NaCl (pharmaceutical grade). The beaker is covered with a glass plate, but the covering is such that the gas phase inside the beaker is in direct unrestricted contact with the air. The beaker is then heated till reflux conditions (about 110°C). The heat input is selected such that within a period of 15 to 60 minutes about 2 to 10g of salt is crystallized. The crystals are separated from the mother liquor, e.g. by centrifuging, and dried. For this test the level of drying is not crucial, as long as the crystals are not (re)dissolved or altered, e.g. by mechanical forces. If analysis by means of a (light) microscope shows crystals with (111) faces,

a sufficient amount is used.

**[0010]** Preferably the amount of crystal growth inhibitor that is present in the feed of the evaporative crystallization process is less than 300 mg/kg for economic reasons. Typically more than 10 mg, preferably more than 12.5 mg, and most preferably more than 14 mg crystal growth inhibitor is used per kg of feed of the evaporative crystallization process.

**[0011]** It is noted that JP-A-01-145319 and JP-A-01-145 320 describe the use of sodium hexametaphosphate and polyacrylate, respectively, in an evaporative crystallisation process to make dried polyhedral salt with an improved flowability that can be used to improve the marketing of product to which the dried salt is fixed. Said dried salt is known to contain less than 0.5% of water. There is no disclosure that one of these chemicals can be used to make wet salt with less occlusions in a more economic way. Furthermore, the sodium hexametaphosphate was proven not to be suitable in the presently claimed evaporative crystallisation process for making wet salt due to hydrolysis of said hexametaphosphate.

**[0012]** It is furthermore noted that products like Belsperse® 164, which is a phosphino carboxylic polymer ex FMC Corporation, have been promoted for use as an anti-scaling additive in evaporative crystallizers. The product is typically used in an amount of 1-2 ppm, although a level up to 10ppm has been mentioned. However, such a concentration is not an effective amount in accordance with the present invention.

#### Experimental

**[0013]** In some test using a brine feed from our plant in Hengelo, a variety of crystal growth inhibitors, amongst which Belsperse® 164, were evaluated. Adding 25 mg/kg of Belsperse® 164 to the feed resulted in the formation of NaCl crystals with (111) faces, while at the same time K, Br, SO<sub>4</sub>, and Ca levels in the resulting crystals was lowered by more than 20%, compared to the levels in salt produced from the same feed under the same conditions, without that the Belsperse® 164 was added. Said lowering of the K, Br, SO<sub>4</sub>, and Ca levels is attributed to less occluded mother liquor and a lower amount of lattice imperfections. Also it was found that washing of the product was more efficient, so that the amount of wash water could be reduced. Furthermore, the centrifuge time to separate the wet salt from the wash water could be reduced, resulting in energy savings during washing and centrifuging of more than 1%.

**[0014]** The wet salt so obtained was preeminently suited for use in electrolysis processes since it required hardly any purification. This is of particular importance for electrolysis operations wherein membrane cells are used. Furthermore it was observed that the wet salt could be submitted to an extra drying step to make the known high-purity dried salt. Such high-purity dried salt can, for example, be used as a pharmaceutical grade salt.

**[0015]** In further tests, Belsperse® 164 was added to a conventional continuous 4 effects vacuum salt production plant in an amount of 15 g per cubic meter of brine.

**[0016]** Compared to a production run that was equal except for the Belsperse® 164 addition, the quality of the resulting wet salt (samples were taken at regular intervals from the production line) was improved as follows:

Br content	from 25 to 38 % lower
SO <sub>4</sub> content	from 30 to 60 % lower
K content	from 29 to 37 % lower
Ca content	from 27 to 50 lower.

#### Claims

1. Evaporative crystallization process to make wet salt compositions comprising more than 0.5% by weight of water that includes a step wherein a mother liquor is formed that contains an effective amount of a crystal growth inhibitor that is selected from oligopeptides, polypeptides, and polymers bearing two or more carboxylic acid groups or carboxyalkyl groups and optionally further phosphate, phosphonate, phosphino, sulfate, and/or sulfonate groups, such as carboxymethyl cellulose with phosphate groups, to form sodium chloride crystals with a (111) face.
2. Process according to claim 1 further including a washing step of the crystallized sodium chloride.
3. Wet salt comprising more than 0.5% by weight of water obtainable by the process according to claim 1 or 2, comprising sodium chloride crystals with a (111) face and traces of crystal growth inhibitor.
4. Electrolysis of a brine produced with salt resulting from the process according to claim 1 or 2.
5. Electrolysis in accordance with claim 4 wherein a membrane electrolysis cell is used.

#### Patentansprüche

1. Verdunstungskristallisationsverfahren zur Herstellung von feuchten Salzzusammensetzungen, die mehr als 0,5 Gew.-% Wasser umfassen, mit einem Schritt, bei dem eine Mutterlauge gebildet wird, die eine effektive Menge eines Kristallwachstumsinhibitors enthält, welcher ausgewählt ist aus Oligopeptiden, Polypeptiden und Polymeren, die zwei oder mehr Carbonsäuregruppen oder Carboxyalkylgruppen und gegebenenfalls weiterhin Phosphat-, Phosphonat-, Phosphino-, Sulfat- und/oder Sulfo-

natgruppen tragen, wie Carboxymethylcellulose mit Phosphatgruppen, unter Bildung von Natriumchloridkristallen mit einer (111)-Fläche.

2. Verfahren gemäß Anspruch 1, das weiterhin einen Schritt des Waschens des kristallisierten Natriumchlorids umfasst. 5
3. Feuchtes Salz, das mehr als 0,5 Gew.-% Wasser umfasst und nach dem Verfahren gemäß Anspruch 1 oder 2 erhältlich ist und Natriumchloridkristalle mit einer (111)-Fläche sowie Spuren von Kristallwachstumshemmer umfasst. 10
4. Elektrolyse einer Salzlösung, die mit Salz hergestellt ist, das aus dem Verfahren gemäß Anspruch 1 oder 2 resultiert. 15
5. Elektrolyse gemäß Anspruch 4, wobei eine Membranelektrolysezelle verwendet wird. 20

### Revendications

1. Procédé de cristallisation par évaporation pour produire des compositions de sel humide comprenant plus de 0,5 % en poids d'eau qui comprend une étape dans laquelle une liqueur-mère est formée qui contient une quantité efficace d'un inhibiteur de croissance de cristaux qui est choisi parmi des oligopeptides, des polypeptides, et des polymères portant deux ou plusieurs groupes d'acide carboxylique ou des groupes carboxyalkyles et en outre facultativement des groupes phosphates, phosphonates, phosphino, sulfates et/ou sulfonates, tels que la carboxyméthylcellulose avec des groupes phosphates, pour former des cristaux de chlorure de sodium avec une face de type (111). 25  
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2. Procédé selon la revendication 1 comprenant en outre une étape de lavage du chlorure de sodium cristallisé. 40
3. Sel humide comprenant plus de 0,5 % en poids d'eau qui peut être obtenu par le procédé selon la revendication 1 ou 2, comprenant des cristaux de chlorure de sodium avec une face de type (111) et des traces d'un inhibiteur de croissance de cristaux. 45
4. Electrolyse d'une saumure produite avec le sel résultant du procédé selon la revendication 1 ou 2. 50
5. Electrolyse selon la revendication 4 dans laquelle une cellule d'électrolyse à membrane est utilisée. 55