PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improved Process for Reducing the Caking Tendency of Sodium Chloride

We, N. V. KONINKLIJKE NEDERLANDSCHE ZOUTINDUSTRIE, a Company organized and existing under the Laws of the Kingdom of The Netherlands, of Boortorenweg, Hengelo, Province of Overijsel, Holland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

When sodium chloride is stored after a longer or shorter period, just as with many other substances, agglomeration usually called caking tends to occur, which often proceeds to such an extent that the entire mass can be reconverted into a manageable, granular, and free-flowing product only with great difficulty and at great expense. This caking is to be attributed to different mechanisms, which are difficult to separate. These different mechanisms are affected by a number of exterior circumstances, such as variations in moisture content, duration of the storage, temperature, and pressure.

The physical or crystallographic nature of the salt affects the extent of the caking. Thus it has long been known that an increase of the size of the grains or crystals and a reduction of the differentiation in the crystal size reduce the caking tendency, and also that ground mine salt as well as so-called pan salt and sea salt, which have formed on the surface of brine, show less caking tendency than cubic salt formed in solutions.

In order to counteract the caking tendency deliberately, a large number of measures have been proposed, all of which amount to the addition of foreign compounds.

The numerous compounds employed for this purpose include, for example, poorly soluble compounds which either are capable of binding water, such as calcium sulphate or silicagel, or produce a film on the crystal, as a result of which moistening or contact with other crystals is reduced, such a magnesium carbonate, calcium phosphate, or aluminium stearate. Salt which has been treated in this way generally does not give clear solutions; sometimes also the rate of dissolution becomes so low that the saline taste is reduced. Other water-insoluble compounds counteracting the caking tendency are, for example, mineral or organic oils or fats, which have the same drawbacks.

For the said purpose use has also been made of certain water-soluble compounds for which the cause of the effect has not always been established, such as magnesium chloride, sorbitol, and calcium lactate. Upon being treated with $MgCl_2$, however, the salt remains more or less moist, while the addition of sorbitol and of calcium lactate is comparatively costly and its effect leaves much to be desired. The recommended amounts of these soluble compounds are generally between 0.1 and 5% of the salt; in a few cases a minimum amount of 0.02% is mentioned.

Finally it may be mentioned that according to Specification 667,101 salt has been made in the form of highly branched dentrites. Such salt is obtained by adding to the brine a compound capable of causing the sodium chloride to crystallize in the form of three-dimensional dendrites and of keeping the liquor moving so slightly that the crystals forming remain intact. The following substances have been stated to produce the above-mentioned effect: compounds with octahedrally coordinated complex ions (e.g. potasisum ferro- and ferri-cyanides which may be added in amounts as low as 0.00005%), water-soluble salts of mono- or polycarboxylic acids having no more than 20 carbon atoms (e.g. soaps), and compounds which are highly soluble in water to form solutions of 35 to 80%, in which common salt is generally only soluble to 1—2% and which are highly viscous. This dendritic form has been made in order to give the salt a low bulk density (at most 0.7 g/cm³). Additionally it has been mentioned that salt thus crystallized does not, upon exposure to the air, cake together, as do cubic salt crystals. If during this salt production the brine should be agitated more violently, the dendrites would break and the bulk density would become higher. It is not known that salt consisting of

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broken dendrites has less caking tendency than ordinary salt.

Now it has been found that the caking tendency of sodium chloride can be considerably reduced by adding a soluble ferro- or ferricyanide or a soluble cadmium salt to solid sodium chloride, which may be suspended in its mother liquor after the termination of the evaporation, in amounts of less than 0.05%, and preferably of 0.02 to 0.00002%, all these percentages being referred to the solid sodium chloride.

Upon further investigation it was found that for the effect of the addition there is an optimum percentage which is far below the percentage in which the known soluble anti-caking agents are generally used for addition to salt which has already been separated. Their effect, however, far exceeds that of any known anti-caking agents. For the agents investigated, when added to common salt with a grain size of about 0.4 mm, these optimum percentages are usually between 0.0001 and 0.002%. Percentages of 0.05 or higher do not enter into consideration as under normal conditions these amounts offer no advantage over lower amounts, while the costs of the treatment and the quantity of impurities in the salt would become unnecessarily high. On the other hand, with even smaller amounts, e.g. 0.00002%, a marked effect is produced, which may be sufficient when the conditions during storage are favourable or the demands are less rigorous. It is, however, explicitly stated here that the above-mentioned percentages apply to the case where the compound added is carefully distributed over the salt; if the distribution is defective, the percentages lower than 0.01 in particular will have a less favourable effect, and it will then be necessary to add amounts of 0.01 to less than 0.05%.

Since the caking is correlated with the size of the surface per unit weight, it is evident that the percentage to be used depends on the grain size of the salt or, in other words, that the amount of the foreign compound to be used would be more effectively expressed in grams per m^2 of salt surface, or in the thickness in molecules of the layer of this agent, if it were uniformly distributed over the salt surface. When this thickness is calculated, it is found that sometimes the addition of an amount which is insufficient to produce a monomolecular layer on the salt already has an effect which is close to the optimum obtainable. In several cases coversion of the amount of the foreign compound added gave layer thicknesses between 0.3 and 2 molecules at the maximum reduction of the caking tendency. When it is borne in mind that the distribution over the salt surface is naturally very imperfect, it appears from this that only a part of this surface need be covered.

The optimum percentages mentioned above apply to salt with an average grain size of 0.4 mm; for finer or coarser salt they are to be increased or decreased proportionately in order to attain a similar effect.

In the process according to the invention it is therefore desirable to provide for good distribution of the foreign compound on the salt. It is thus advantageous to add the said compound in dissolved condition. Preferably a comparatively dilute solution of the compound is atomized on the salt. Thereupon the salt is mixed thoroughly.

Another suitable method of treatment, resulting in excellent distribution, comprises the addition of the compound to be used to a suspension of sodium chloride in its mother liquor; the salt adsorbs a large portion of the compound and can be separated in a centrifuge or filter and subsequently dried.

The compound may be added to dry as well as moist salt, irrespective of whether it is subsequently dried or not; the effect is independent of this, provided good distribution is ensured.

The greatest advantage of the present process is that with the right dosage the effect is much greater than with any known agent. No universal methods exist for a quantitative estimation of the caking tendency. There is frequently no correlation between the results of laboratory scale experiments and the behaviour during large scale storage. Up to the present no numerical evaluation is therefore possible. Wherever evaluations have been given in the above about the improvements obtained, these refer to a comparison with the best compound known to applicants for counteracting the caking tendency under practical conditions that have been carefully standardized.

Other advantages consist in that the compounds to be added are soluble so that the salt treated gives a clear solution, and that, because the amounts of the additions are so small, the contamination of the salt is negligible and is even extremely difficult to detect analytically.

With regard to the process of British Patent 667,101 described above, which aims at salt having a low bulk density it has been stated as an additional advantage that the dendritic salt produced does not cake together, as do cubic salt crystals. Since the caking was thus correlated exclusively with the crystal form of the product, it could not be inferred from this statement that the foreign compounds used according to the invention would be capable of reducing the caking tendency when added to solid salt of normal bulk density.

Naturally the addition of the foreign compounds according to the invention may be combined with known expedients, e.g. the addition of magnesium carbonate in order to keep table salt free-flowing.

EXAMPLE I.

On a stream of 30 tons of solid sodium

chloride per hour having a moisture content of 0.08%, a temperature of 45° C. and a grain size between 0.2 and 0.8 mm, 5 litres per hour of a solution containing 2% of sodium ferrocyanide are atomized by means of compressed air. The salt subsequently passes through a mixing screw, where thorough mixing takes place.

Upon being stored in a silo this salt remains perfectly loose and causes no appreciable transport difficulties, in sharp contrast with untreated salt deposited in the silo with the same moisture content and at the same temperature.

When packed in bags and stored under unfavourable conditions (great variations in the humidity of the air and in the temperature), the treated salt does not show any caking tendency, whereas salt which has been treated with the optimum amount of one of the best known anti-caking agents is transformed into a lump which cannot be crushed by hand.

EXAMPLE II.

Solid sodium chloride, originating from a strainer and having a grain size between 0.30 and 0.45 mm, falls in a stream of 6 tons per hour from a height of 1 metre. On this stream, 1½ litres per hour of a solution containing 5% of cadmium nitrate are atomized: the salt is thoroughly mixed in a mixing screw which at the same time conveys it to a storage or packing space. It shows the same qualities as those mentioned in Example I

EXAMPLE III.

From an evaporation plant a mixture of 40 tons of solid sodium chloride and 30 m³ of mother liquor is discharged per hour. To this paste are added 200 g. of potassium ferricyanide per hour; the conduit through which the suspension flows is so constructed that through mixing takes place. The salt is subsequently separated from the mother liquor in a centrifuge. The salt which leaves the centrifuge and still another contains 2½% of mother liquor is dried. It shows the same qualities as those mentioned in Example I.

What we claim is:—

1. Process for reducing the caking tendency of sodium chloride by adding foreign compounds to the solid salt, characterized in that as a foreign compound a soluble ferro- or ferricyanide or a soluble cadmium salt is added to solid sodium chloride, which may be suspended in its mother liquor after the termination of evaporating, in amounts, referred to the solid sodium chloride, of less than 0.05% and preferably of 0.02 to 0.00002%.

2. Process according to claim 1, characterized in that the foreign compound is added in a dissolved condition.

3. Process according to claims 1 or 2, characterized in that a solution of the foreign compound is atomized on the solid sodium chloride.

4. Process according to any one of the claims 1—3, characterized in that the foreign compound is added to a sodium chloride suspension and that the sodium chloride is subsequently separated from the mother liquor.

5. Sodium chloride of normal bulk density, which contains one or more of the foreign compounds mentioned in claim 1 in an amount therein specified.

6. A process for reducing the caking tendency of sodium chloride substantially as hereinbefore described.

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