

Next Generation Anticaking Agent for Edible Salt

Salt production

Keywords: Anticaking agent, bio-based material, iron tartrate, edible salt

Abstract

The new anticaking agent, a complexation product of sodium tartrates and iron (III) chloride (in short iron tartrate) patented by AkzoNobel, has been accepted for use in edible salt in Europe, USA, and China. The recommended maximum dosage level is 106 mg iron tartrate per kg of salt (= 12 ppm calculated as Fe). This anticaking agent is bio-based, biodegradable and free of ferrocyanide, whilst having an effective anticaking function.

In this work, the anticaking mechanism and performance of iron tartrate for edible salt are presented.

Iron tartrate is found to effectively inhibit crystal growth of sodium chloride. The experimental result shows that 6 ppm iron tartrate (calculated as Fe) inhibited crystal growth by 83%, which was about the same as the traditional anticaking agent ferrocyanide (YPS) at 2.5 ppm (calculated as $\text{Fe}(\text{CN}_6)^{4-}$). 12 ppm iron tartrate inhibited crystal growth even further to 98%. Accordingly, the anticaking mechanism of iron tartrate is the inhibition of the recrystallization process of salt crystals.

The anticaking performance of iron tartrate in salt was first tested on the lab scale. A caking energy method using a rheometer was developed to quantify the caking behavior of salt containing various dosage levels of iron tartrate. It was found that iron tartrate had a strong anticaking effect at a dosage level ≥ 3 ppm.

To evaluate the anticaking performance of iron tartrate in (iodized) edible salt in practical situation, a long-term storage test was carried out. Salt containing 5 ppm iron tartrate packaged in bags and carton boxes was stored indoors without climate control. The performance of iron tartrate in terms of anticaking and compatibility with iodized salt was evaluated after 3, 6, 12, 18, and 24 months of storage. The test result shows that at a dosage level of 5 ppm iron tartrate was sufficient to prevent caking of (iodized) edible salt for at least 24 months.

1 Introduction

Edible salt primarily composed of sodium chloride is an essential compound for life of humans and other animals. Salt is a crystalline material. When left untreated, salt crystals have a strong tendency to agglomerate and form lumps. This process is called caking, which makes it difficult to handle salt in transport and storage. The major caking mechanism is the bridges formation between crystals, as illustrated in Figure 1. Such bridges are formed by dissolution and subsequent recrystallization in contact areas. This is mainly caused by the variations of relative humidity and/or temperature of environment.

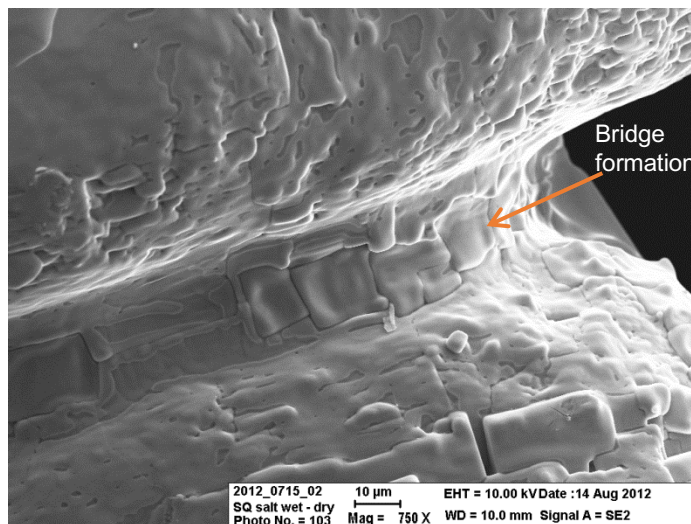


Figure 1: Caking caused by bridge formation between salt crystals.

Usually, anticaking agents are added to salt to make it free flowing. Ferrocyanide, a synthetic complex with sodium or potassium, is the most commonly used anticaking agent for edible salt. It is also known as yellow prussiate of soda (YPS). It has a strong anticaking effect on salt because it effectively inhibits sodium chloride dissolution and crystal growth.^[1]

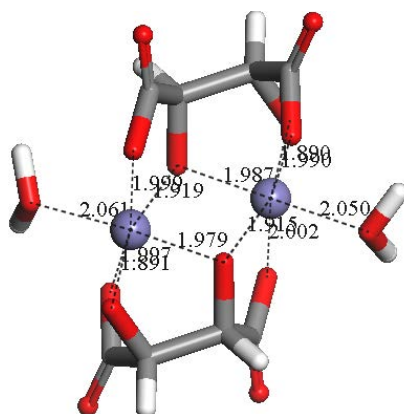


Figure 2: Structure of Fe (III) and meso-tartrate complex from molecular modelling. The binuclear complex contains 2 iron atoms, 2 meso-tartrate and 2 water molecules.^[2]

Recently, a complexation product of sodium tartrates (D-, L-, and meso-tartrate) and Fe (III) chloride (iron tartrate) was introduced by AkzoNobel as a new anticaking agent for salt.^{[2][3]} Iron tartrate is based on tartrate derivatives originating from the wine industry. It is bio-based, biodegradable and free of ferrocyanide. The key functional component is the complex of Fe (III) and meso-tartrate (Figure 2). Iron tartrate has been accepted for use in edible salt in Europe, USA, and China. It is applied at levels up to 106 mg iron tartrate per kg of salt (= 12 ppm calculated as Fe). In this paper, its anticaking mechanism and performance for edible salt are described.

2 Experimental section

2.1 Effect of iron tartrate on salt crystal growth

The effect of iron tartrate on salt crystal growth was investigated in cooling crystallization. The applied temperature profile is shown in Figure 3. Brine solution with the saturation temperature at 80 °C was prepared by adding 189.5 g of salt (pharmaceutical grade) to 500 mL demineralized water. The solution was kept under stirring at a temperature 5 °C higher than the saturation temperature until all the crystals dissolved. Then, the brine solution was cooled down to 80 °C. To the saturated brine, iron tartrate solution and 10 g of salt as seed were sequentially added. The reason of applying seeding was to prevent the statistical variation of nucleation in crystallization experiments. The concentration of iron tartrate in brine was varied to be 20, 90, 180, 270, and 360 ppm (calculated as Fe). These concentrations in brine are equivalent to 0.75, 3, 6, 9 and 12 ppm iron tartrate in salt (calculated as Fe), by assuming that dry salt adsorbs 2.5% water and iron tartrate complex stays only in the saturated brine around salt crystals.

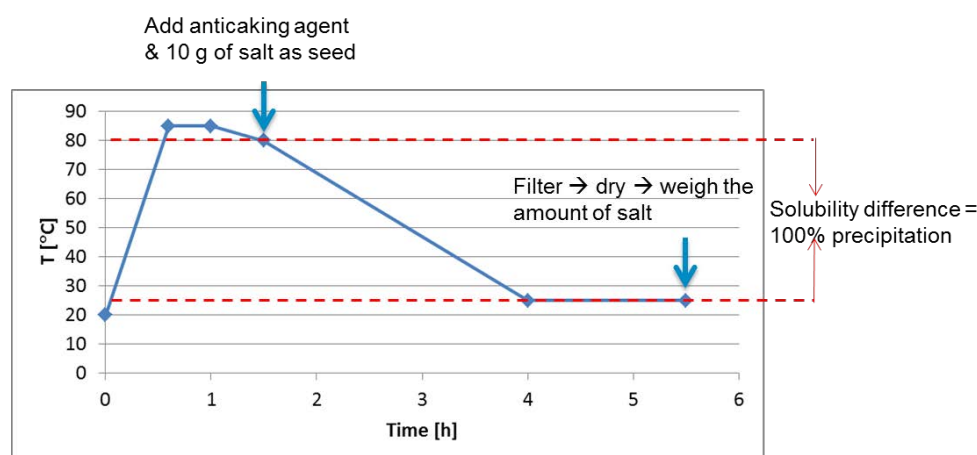


Figure 3: Temperature profile applied in cooling crystallization experiments.

After adding seeds, the brine was cooled down to 25 °C in 2.5 hours and then kept at a constant temperature for another 1.5 hours. Salt crystals precipitated due to cooling. The obtained salt was finally filtered out, dried at 50 °C for 12 hours, and weighed. The solubilities of sodium chloride at 80 and 25 °C are 379.3 and 359.6 g/L-water, respectively. The solubility difference is 19.7 g/L-water. In these experiments 500 mL water is used. Therefore, when 9.85 g of salt crystal is obtained, excluding the 10 g of seeding crystals, the precipitation percentage is 100%. The precipitation percentage P is calculated using the following equation:

$$P = \frac{C}{C_0} \times 100\%$$

where C is the amount of obtained salt crystals excluding 10 g of seeding crystals, and C_0 is the amount of salt crystals obtained from the solubility difference between 80 and 25 °C.

Moreover, the influence of iron tartrate on salt crystal shape was studied using the same cooling crystallization with the exception that seeding was not used. In this way, crystals were crystallized via both nucleation and crystal growth induced by cooling. The concentration of iron tartrate in brine was 20 ppm in this test. During cooling a droplet of brine was immediately moved to a glass stage positioned under the microscope. A sequence of microscopic images was taken, recording the appearance and growth of crystals under the influence of iron tartrate.

2.2 Anticaking effect of iron tartrate on salt caking

A caking energy method using a rheometer (Stable Micro Systems) was developed to quantitatively measure salt caking status. In this method, caking is prompted by the evaporation of water from salt. The rheometer measures the force required to turn a twisted blade through (caked) salt while slowly moving downward, forcing the salt to flow in a reproducible manner. The caking energy (in mJ) of salt sample is calculated from the integral of the force (in N) versus travelling depth into the salt (in mm). This caking energy represents the energy required to break the (caked) salt sample.

1.75 kg of food grade dry salt (no anticaking agent) from AkzoNobel was used in this test. An identical particle size distribution for all samples was assured by homogeneously splitting this amount of salt to 7 portions (250 g / portion). Salt sample of each portion was put in a plastic bag, to which 2% of water and iron tartrate solution were sequentially added and mixed. The dosage level of iron tartrate was varied from 1 – 12 ppm (calculated as Fe).

A salt portion was further divided into 4 cylinders (50 ± 0.05 g salt per cylinder). The salt in the cylinders was compressed by applying a 1-kg weight on the top. The salt samples were further dried by dry air for 2.5 hours to ensure that water in salt was completely evaporated. Finally, the caking energy of salt was measured using the rheometer. The average value of caking energy measured from the 4 cylinders was used for each sample condition.

Sample code	Salt	Iron tartrate [ppm]	KI [ppm]	KIO ₃ [ppm]
a.	Food grade	5	/	/
b.	Food grade	5	118	/
c.	Food grade	5	/	34

Table 1: Salt compositions for a long-term storage test.

2.3 Storage test of edible salt containing iron tartrate

2.3.1 Preparation of salt samples and storage condition

A long-term storage test has been carried out since March 2015. Food grade dry salt (no anticaking agent) from AkzoNobel was used. Three types of salt, salt containing iron tartrate, iodized salt (KI) containing iron tartrate and iodized salt (KIO₃) containing iron tartrate, were prepared according to the compositions given in Table 1. Salt and additives were homogeneously

mixed using a ploughshare mixer (Lödige). After mixing, the moisture content of salt was about 0.05%.

In each batch, about 20 kg of salt was produced, split into 500 g portions, and packaged in perforated PE bags and non-laminated carton boxes. Salt samples were stored indoors without climate control. Salt in bags were stored under pressure achieved by stacking 2 bricks (~ 5 kg each) on top of a pair of bags. Figure 4 gives an impression of salt samples and storage condition.



Figure 4: Salt samples and storage condition in a long-term storage test.

2.3.2 Evaluation method

Bags were carefully cut and gently moved to a 2-mm sieve. Flowability of salt was evaluated using sieving with maximum sieving time of 60 seconds at amplitude of 0.2 mm. When salt was not completely through the sieve after 60 seconds, the remaining salt was sieved again for another 60 seconds at amplitude of 0.5 mm. Flowability of salt in bags was differentiated to be 5 levels.

- Level 1: Excellent flowability. Completely through after sieving for < 15 seconds at amplitude 0.2 mm.
- Level 2: Good flowability. Completely through after sieving for 15 - 60 seconds at amplitude 0.2 mm.
- Level 3: Reasonable flowability. Completely through after sieving for 60 seconds at amplitude 0.2 mm & 0 - 15 seconds at amplitude 0.5 mm.
- Level 4: Limited flowability. Completely through after sieving for 60 seconds at amplitude 0.2 mm & 15 - 60 seconds at amplitude 0.5 mm.
- Level 5: Poor flowability. Remaining salt left on the sieve after sieving for 60 seconds at amplitude 0.2 mm & 60 seconds at amplitude 0.5 mm.

Carton boxes were open from the perforated opening and gently placed on a sample holder in an angle of 45°. The time needed for emptying a box was recorded. When salt flowing was stopped by caked salt, the box was shaken manually and intensively for 5 times and then measured again. This shaking procedure was used maximally twice. Flowability of salt in carton boxes was differentiated to be 5 levels.

- Level 1: Excellent flowability. Completely flow out without shaking, < 20 seconds.
- Level 2: Good flowability. Completely flow out without shaking, 20 – 60 seconds.
- Level 3: Reasonable flowability. Completely flow out after 1st shaking procedure.
- Level 4: Limited flowability. Completely flow out after 2nd shaking procedure.
- Level 5: Poor flowability. Remaining salt left in box after 2nd shaking procedure.

3 Results and discussion

3.1 Effect of iron tartrate on salt crystal growth

Inhibiting crystal growth is one of the main mechanisms that anticaking agents prevent salt from caking.^[4] Usually, anticaking agents that are crystal growth inhibitors can also act as crystal shape modifiers. This is because molecules of an anticaking agent might be adsorbed differently on various facets of a crystal. Consequently, it changes the relative growth rates of various crystal facets that determine crystal shape. In this way, crystal shape can be changed by crystal growth inhibitors.^{[4][5][6]} For instance, the most commonly used anticaking agent for salt, YPS, inhibits crystal growth strongly. Besides, it changes salt crystal shape from cubic to dendritic.^[1] To understand the anticaking effect and mechanism of iron tartrate, experiments were conducted to study its influence on crystal growth and crystal shape of salt.

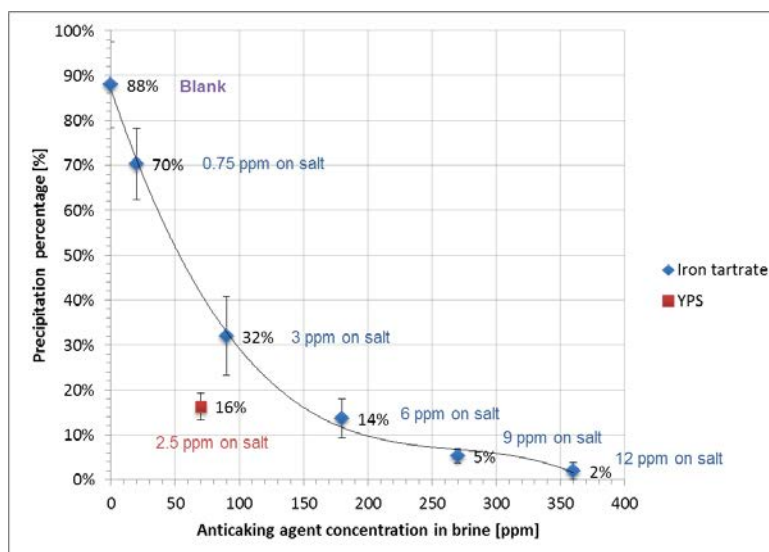


Figure 5: Effect of iron tartrate on salt crystal growth. Solid line is a guide to the eye.

Figure 5 shows the experimental result of crystal growth. In the blank experiment (no anticaking agents), after 4-hour cooling, most of the salt crystallized from the brine. The precipitation percentage P was around 88%. When the brine containing 20 ppm iron tartrate (≈ 0.75 ppm in salt), the amount of salt crystallized was reduced, $P \approx 70\%$. A further increase of iron tartrate concentration dramatically decreased salt precipitation. When iron tartrate in brine increased to 180 ppm (≈ 6 ppm in salt), only 14% of salt crystallized, which was about the same level as YPS at 70 ppm in brine calculated as $\text{Fe}(\text{CN}_6)^{4-}$ (≈ 2.5 ppm in salt). Using the amount of salt precipitated in the blank experiment as a reference, 180 ppm iron tartrate in brine inhibited crystal growth about 83%. When iron tartrate increased to 360 ppm (≈ 12 ppm in salt), only 2% of salt crystallized after 4-hour cooling. In other words, salt fraction inhibited to crystallize was as high as 98%.

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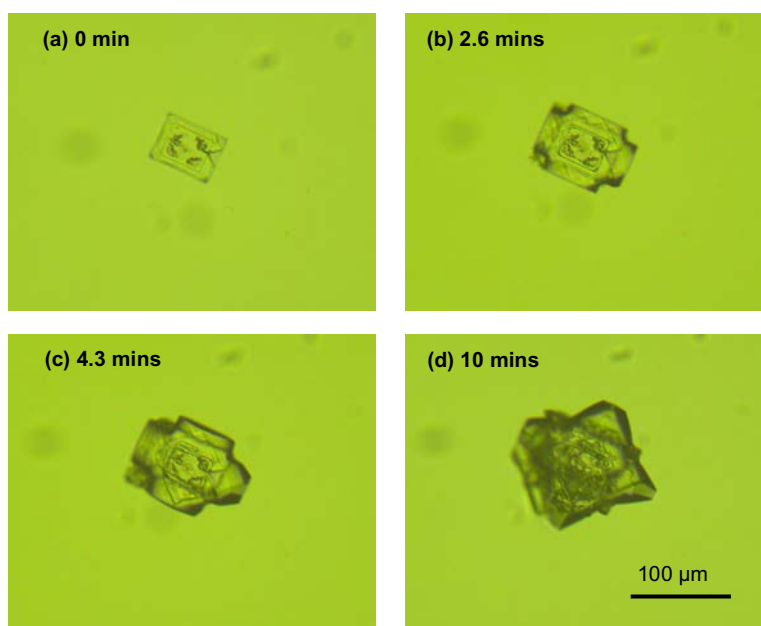


Figure 6: A sequence of microscopic images showing the change of salt crystal shape under the influence of iron tartrate.

With the aid of optical microscopy, the effect of iron tartrate on salt crystal shape was observed. A sequence of microscopic images in Figure 6 illustrates the appearance and growth of a salt crystal under the influence of iron tartrate at 20 ppm in brine. Image (a), taken just after the detection of this salt crystal, shows that it had a rectangle shape. During growing crystal shape completely changed, as shown in images (b) – (d). Finally, the salt crystal became four-angle star shape instead of cubic shape.

The experimental result clearly shows that, like the anticaking agent YPS, iron tartrate effectively inhibited salt crystal growth and changed crystal shape.

3.2 Effect of iron tartrate on salt caking

The effect of iron tartrate on salt caking is presented in Figure 7, where the dosage level of iron tartrate in salt varies from 1 to 12 ppm and a blank sample containing no anticaking agent is a reference for comparison. Each data point is an average value of 4 measurements. The blank salt sample caked most seriously, while the addition of iron tartrate effectively reduced salt caking. The caking energy of salt was decreased by 32% at 1 ppm of iron tartrate. The anticaking effect of iron tartrate increased obviously with an increase of its dosage level. At 3 ppm of iron tartrate, the caking energy of salt was reduced by 72%. Raising the dosage level further did not result in significantly better anticaking effect. At 6 and 12 ppm of iron tartrate, the caking energy of salt was reduced by 81%.

The experimental result shows that iron tartrate effectively prevents salt from caking at a dosage level of 3 ppm. In this test method, however, salt caking is prompted by fast evaporation of water from salt, resulting in relatively weak caking. 3 ppm iron tartrate is thus sufficient to prevent salt from caking. In practice, edible salt is often stored under pressure for a long time. Salt crystals experience many times of dissolution and recrystallization due to the variation of storage

condition, resulting in strong caking. Therefore, the recommended dosage level of iron tartrate in salt is up to 12 ppm.

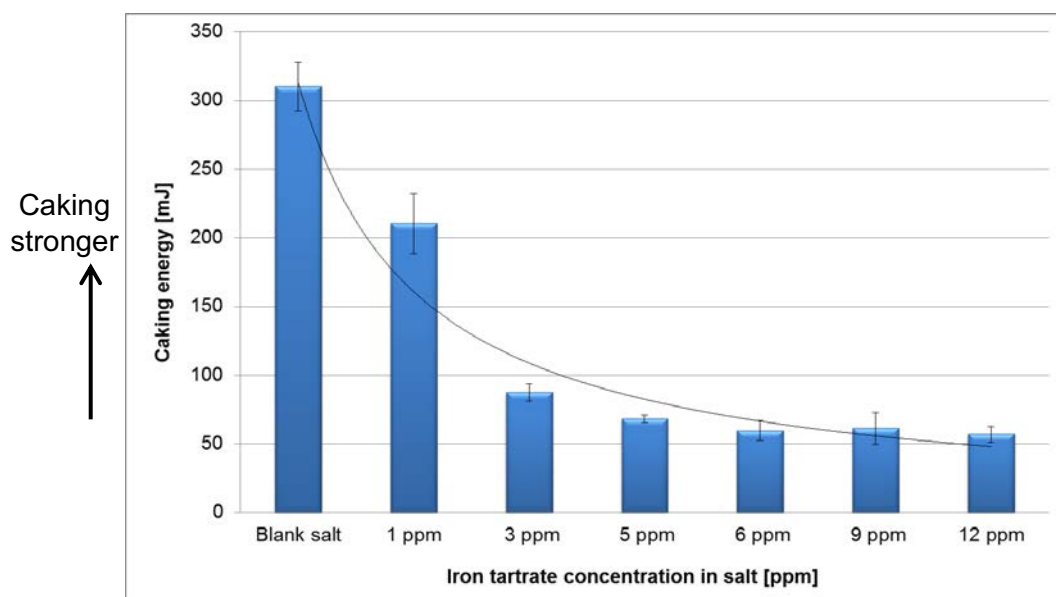


Figure 7: Effect of iron tartrate on salt caking. Solid line is a guide to the eye.

3.3 Storage test of edible salt containing iron tartrate

Anticaking performance of iron tartrate in edible salt was evaluated in a long-term storage test, where 5 ppm of iron tartrate was used. The evaluation result of 3, 6, 12, 18 and 24 months of storage is given in Table 2. Levels 1 – 5 are used to distinguish the flowability of salt samples. The explanation of each level is given in section 2.3.2.

Sample code	Salt type	Package type	3 months	6 months	12 months	18 months	24 months
a.	Salt + 5 ppm iron tartrate	Bag	1	1	1	2	2
		Box	1	1	3	3	3
b.	Iodized salt (KI) + 5 ppm iron tartrate	Bag	1	1	2	1	1
		Box	1	1	1	1	1
c.	Iodized salt (KIO ₃) + 5 ppm iron tartrate	Bag	2	2	2	3	3
		Box	3	2	3	3	3

Table 2: Result of long-term storage test of (iodized) edible salt containing iron tartrate.

For bag package, salt containing 5 ppm iron tartrate showed excellent flowability after 12-month storage. After 24 months, salt slightly caked but its flowability was still good. Iron tartrate showed approximately the same good anticaking performance in iodized salt (KI) in 24 months. While, it

seems that flowability of salt containing both iron tartrate and KIO_3 was slightly worse than that of the other two samples. However, it still had good flowability after 12-month storage and reasonable flowability after 24-month storage.

For carton box package, salt containing 5 ppm iron tartrate showed excellent flowability after 6-month storage. After 12-month storage, salt slightly caked. The lumps were easily broken by shaking the boxes. The caking status after 24 months was comparable to that of 12-month storage. Iodized salt (KI) containing iron tartrate performed best. It showed excellent flowability up to 24-month storage. Similarly to sample c packaged in bags, iron tartrate had less anticaking effect in sample c packaged in boxes. But its flowability was still acceptable. The test result indicates that the anticaking performance of iron tartrate was slightly affected by KIO_3 . A study is being carried out to understand its influence and mechanism. In addition, a seasonal effect on salt caking was also observed in this test. For instance, sample c packaged in boxes caked stronger in 3 months of storage than in 6 months of storage.

According to the result of long-term storage test, iron tartrate is an effective anticaking agent for (iodized) edible salt in practical situation. At the dosage level of 5 ppm, iron tartrate was sufficient to effectively reduce salt caking for at least 24 months. Depending on different types of package, storage conditions, and storage time, a higher dosage level of iron tartrate in salt might be needed. It should be noted that the maximum dosage level of iron tartrate in edible salt is 12 ppm.

4 Conclusions

Iron tartrate, a bio-based and biodegradable product, was recently introduced by AkzoNobel as a next generation anticaking agent for edible salt. The anticaking mechanism of iron tartrate was studied by understanding its effect on crystal growth and crystal shape of sodium chloride. It was found that iron tartrate effectively inhibited salt crystal growth. At the dosage level of 6 ppm (calculated as Fe), iron tartrate inhibited crystal growth by 83%, which was about the same as YPS at the dosage level of 2.5 ppm (calculated as $\text{Fe}(\text{CN}_6)^{4-}$). 12 ppm iron tartrate inhibited crystal growth even more effectively, reaching to 98%. In addition, like the traditional anticaking agent ferrocyanide (YPS), iron tartrate is a crystal shape modifier. Under the influence of iron tartrate, salt crystallized from brine had a four-angle star shape.

Next to that, the anticaking effect of iron tartrate in salt was tested in lab. The experimental result shows that iron tartrate effectively prevented salt from caking at 3 ppm. Salt caking energy was reduced by 72%, compared to the blank salt sample. However, edible salt is often stored under pressure for a long period of time in practice, resulting in strong caking. Therefore, a long-term storage test was carried out, in which the dosage level was increased to 5 ppm. Iron tartrate was added to edible salt and iodized edible salt containing KI or KIO_3 . Samples were packaged in bags and carton boxes and stored indoors without climate control. The performance of iron tartrate in terms of anticaking and compatibility with iodized salt were evaluated after 3, 6, 12, 18, and 24 months of storage. The test result shows that 5 ppm iron tartrate was sufficient to effectively reduce caking of (iodized) edible salt for at least 24 months in practical situation.

It is therefore concluded that iron tartrate at ppm level is an effective anticaking agent for edible salt. Its anticaking mechanism is the inhibition of the recrystallization process of salt crystals.

5 References

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