

# Sodium Ferrocyanide as an Anticaking Agent for Sodium Chloride

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## ABSTRACT

*Bulk sodium chloride has a natural tendency to harden and cake when exposed to varying conditions of temperature and/or humidity. Thus, rock salt or evaporated salt stored in outdoor stockpiles, open air sheds, or even in closed buildings will progressively harden with time unless the temperature and humidity are held constant. This caking characteristic of sodium chloride has imposed severe restrictions on its use as a bulk commodity in industrial processes. Evaporated salt, for example, is subject to such severe caking that its industrial use has been limited to the bagged product.*

*This paper describes the mechanism of the caking process and the effectiveness of sodium ferrocyanide in preventing caking. The technique of application, the physiological characteristics, and the usage as a food additive are discussed. Also included in this paper is the subject of patent coverage of anti-caking additives for sodium chloride.*

## PROBLEMS CAUSED BY SALT CAKING

Bulk sodium chloride has a natural tendency to harden and cake when exposed to varying conditions of temperature and/or humidity. Thus, untreated rock salt or evaporated salt stored in outdoor stockpiles, open air sheds, or even in closed buildings will progressively harden with variations in temperature and humidity. This caking characteristic has imposed severe restrictions on the use of sodium chloride as a bulk commodity in industrial processes. For example, untreated evaporated salt would normally cake so severely in storage that its industrial use has been limited in many cases to the bagged product.

Great quantities of rock salt are used for deicing streets and highways during the winter season. When this rock salt is stockpiled in bulk, the normally changing conditions of temperature and humidity cause the salt to cake and form a very hard crust in the outer layers of the pile. Prolonged exposure could result in the entire pile solidifying. Salt thus exposed and caked would have to be crushed and rescreened to permit its use in highway maintenance spreading equipment. Cake salt can be extremely hard; pressures in excess of 5,000 pounds per square inch may be required to fracture specimens of caked salt. One industrial salt consumer actually used dynamite to reclaim the bulk rock salt that had been stockpiled for several years as an emergency supply.

## CONDITIONS CAUSING CAKING

The first step in the development of caking of salt is adsorption of moisture from the atmosphere. Daily cycling of temperature and the natural variations in humidity cause moisture to be alternately adsorbed and evaporated from the surface of the salt granules. The adsorbed moisture forms a film of saturated brine which collects by capillary action at the points of contact between the individual granules of salt. If the atmospheric humidity drops or the temperature rises, some

of the moisture in the saturated brine film is evaporated, causing recrystallization of salt in the brine, and these new crystals produce a solid bridge, effectively bonding together the salt granules.

When the partial pressure of water vapor in air that is in contact with salt is greater than the vapor pressure of the saturated brine, water will be absorbed from the air into the brine which coats the surface of the salt crystal. The brine film will thus continue to absorb water until it is diluted to the point where its vapor pressure equals the partial pressure of the water vapor in the air. In this manner moisture is adsorbed into the salt mass. Conversely, water will be evaporated from the brine when the brine film is in contact with air having a relative humidity low enough that its partial water vapor pressure is less than the vapor pressure of the brine.

If chemically pure salt crystals come in contact with air that has a relative humidity in excess of 75%, water will be adsorbed onto the crystal surfaces. If the relative humidity of the air is less than 75%, the crystals will remain dry or any existing brine film will evaporate. This 75% relative humidity is the critical humidity of the salt. Since the relative humidity of air varies considerably from day to day, there are periods when water is adsorbed and periods when it is evaporated, and, as previously noted, this cycling process causes caking.

The bonding, or caking, action is illustrated in Fig. 1. The saturated brine, which has collected between adjacent salt granules 1, forms a solid crystalline bridge 2 upon evaporation. Freezing temperatures will also cause solidification due to the formation of a bridge of solid sodium chloride dihydrate.

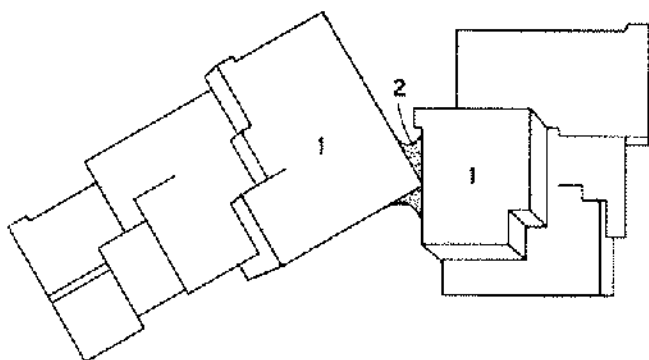


Figure 1

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#### EFFECT OF SODIUM FERROCYANIDE IN PREVENTING CAKING

In 1953 May and Scott (1) demonstrated that sodium ferrocyanide and certain other compounds could be used as an additive to produce dendritic salt of low bulk density. In 1962 Kaufmann (2) demonstrated the use of sodium ferrocyanide as an anticaking agent for sodium chloride. It is this latter process which is the subject of this paper.

Two events may occur to reduce the free-flowing characteristics of salt: The salt can absorb moisture and become sticky and wet; and the wet salt can then dry out and cake. Either occurrence is undesirable. Additives which tend to keep the salt free-flowing, despite absorption of moisture, are in the class of insoluble talclike powders, called fillers. Included in this group of additives are: magnesium carbonate, calcium silicate, calcium phosphate, sodium aluminosilicate, and calcium stearate, none of which prevent caking. However, they do enhance free-flow under moisture conditions which would otherwise cause salt to remain sticky.

If sodium ferrocyanide, also known as yellow prussiate of soda (YPS), is present in minute quantities in the salt, it will dissolve in the adsorbed moisture and therefore be present in appreciable concentration in the saturated brine film which covers the individual salt crystals. This brine will collect by capillary action at the points at which the crystals contact each other. As shown in Fig. 2, salt crystallizing from this brine will take on a skeletal structure instead of the normal cubic habit. These delicate,

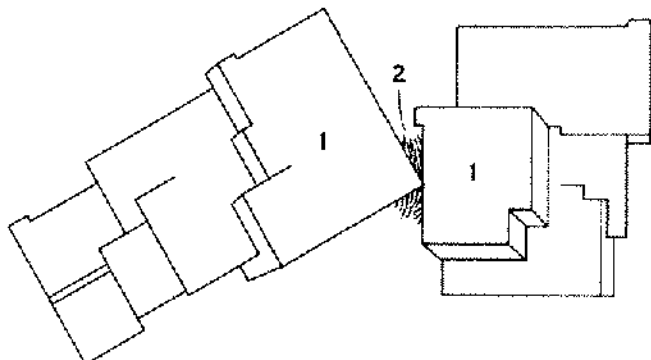


Figure 2

fragile crystals 2 have no mechanical strength, and crystal bonding does not take place between the salt granules 1.

Saratovkin (9) defines skeletal crystals as those with "...well-developed edges and corners, but with the faces replaced by deep, stepped holes. The growth pyramids are not...filled with crystalline material, but are empty. The corners and edges are there, but not the faces." "Crystallographers often term skeletal crystals those which metallographers call dendritic. The converse also applies between metallographers and minerologists." "Dendritic forms are characterized by branches which are attached to one another." The skeletal structure is without branches.

#### EFFECT OF VARIOUS YPS CONCENTRATIONS ON CRYSTAL GROWTH FROM SALT BRINE

Figures 3 through 7 demonstrate the effect of YPS on crystal growth from saturated salt brine. Saturated solutions of sodium chloride brine containing various concentrations of YPS were placed in open petri dishes and allowed to evaporate. Photographs were taken after 2, 4, 6, 24, and 48 hours of exposure to ambient atmospheric conditions.

As shown in Fig. 3, crystallization started with two hours in the blank, the brine solution containing no YPS. Crystals in the blank were cubic, somewhat transparent, and fairly small at this stage of their development. In the solutions containing varying quantities of YPS, no crystallization had developed at this stage.

After four hours, as shown in Fig. 4, crystallization progressed further in the blank, and some crystals developed in the solution containing five parts per million of YPS. No crystal development had taken place in the other specimens. The crystals in the YPS-treated sample were

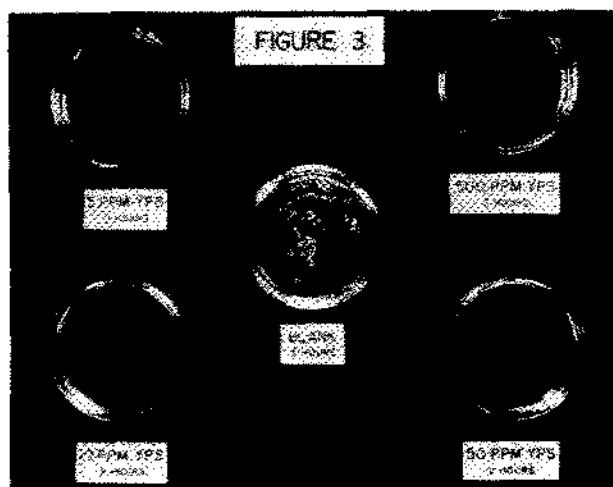


Figure 3

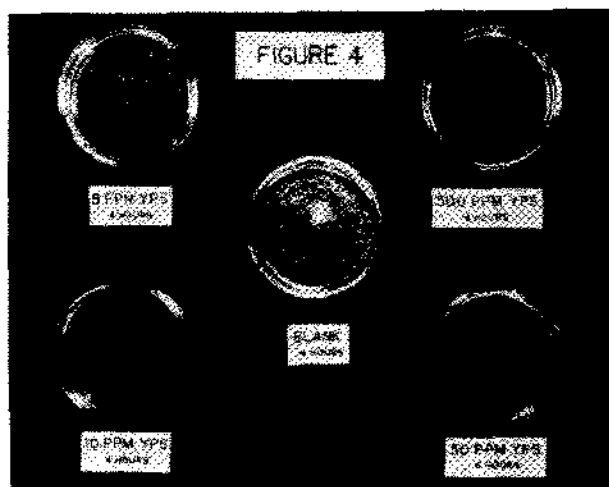


Figure 4

smaller and more numerous than in the blank. Figure 5 shows the same effect after six hours. Some crystals were evident in the sample containing 10 ppm, and none developed in the samples containing 50 and 500 ppm of YPS. The crystals decreased in size with increasing YPS concentration. Also they increased in number with increasing YPS concentration.

Figure 6, taken after 24 hours of evaporation, shows development of crystals in all of the samples. Note the sample containing 500 ppm of YPS has solidified to approximately a 50% slurry, while in the other dishes the crystallization has developed to a much lesser degree, with approximately half of the original mother liquor still present in the dishes. In the operation of this experiment, crystallization took place not only on the bottom of the dishes, but as a film on the top of the brine solution. We attempted to illustrate the development of the crystals at the bottom of

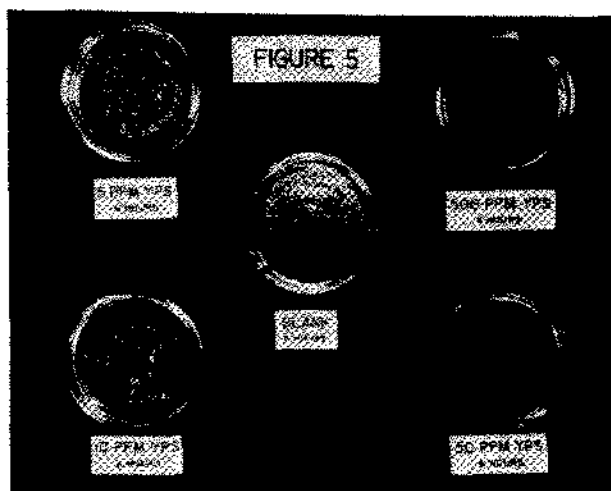


Figure 5

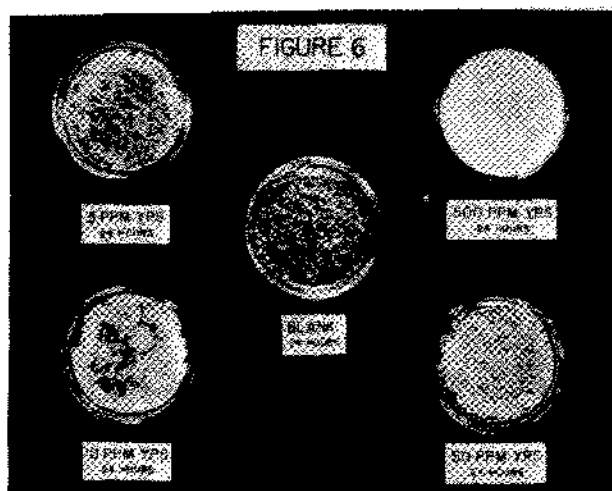


Figure 6

the dish only, and skimmed the grainier type crystals from the surface of the dishes. Thus, to the best of our ability, the illustrations show the subsurface crystal development rather than including the sheets of crystals which formed at the surface. In this particular illustration, some of the surface-formed crystals are evident in the sample containing 10 ppm of YPS.

Figure 7 shows the continued development of the crystals after 48 hours. The sample containing 500 ppm of YPS has completely dried out due to the development of the skeletal crystals of vastly increased surface area.

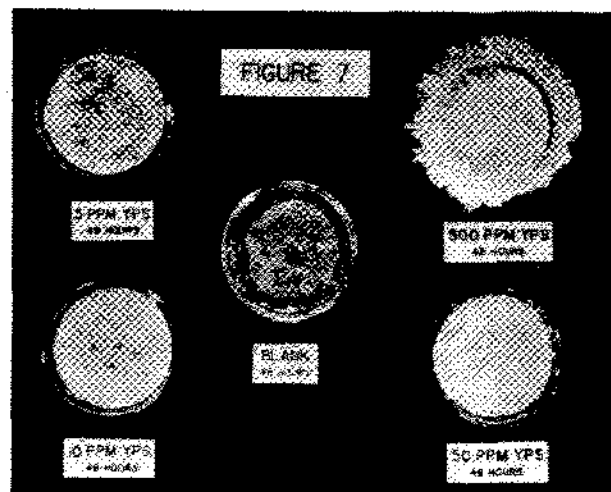


Figure 7

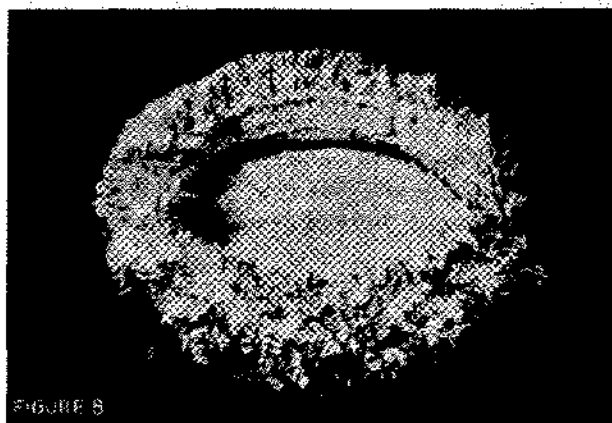


Figure 8

Figure 8 shows a close-up of this crystal structure. These crystals are very delicate and collapse at the slightest touch.

The following conclusions may be drawn from these tests:

1. YPS retards the development of crystals from saturated brine. In effect, it promotes supersaturation.

2. The crystals which develop from brine treated with YPS are smaller in size and greater in number than those from untreated brine.
3. YPS concentrations at least as low as 5 ppm in brine are enough to affect the crystallization characteristics of sodium chloride.

### RECOMMENDED YPS CONCENTRATIONS

As was shown in Figs. 3 through 7, as little as 500 ppm of YPS in the brine assures complete crystal modification to the skeletal structure. If we assume that as little as 0.2% moisture in untreated salt is enough to cause caking, then the 500 ppm of YPS in the brine is equivalent to 1 ppm of YPS in the salt. Field experience has demonstrated that in evaporated salt 5 ppm of YPS in the salt is a more practical dosage level to provide adequate distribution in the salt and assure freedom from caking.

When rock salt is stockpiled and exposed to weather, the YPS, being quite soluble, leaches from the pile with rainfall. To provide extended anticaking action for this exposure and to compensate for the larger size of the salt crystals, the YPS dosage must be greatly increased. A treatment of 200 to 250 ppm, equivalent to 0.4-0.5 lbs. per ton, has proven to be a good economic choice for protection against both leaching and caking.

The use of 5 ppm of YPS (calculated as the anhydrous material) for use as an anticaking agent in salt has been approved by the Food and Drug Administration of the Department of Health, Education, and Welfare. Notice of this approval appears in section 121.1032, subpart D, Part 121, Title 21, Code of Federal Regulations. The same reference permits the use of 13 ppm of YPS when used as an adjuvant in the production of dendritic crystals of salt. Toxicological studies have indicated that 50,000 to 100,000 times this amount of YPS have no adverse effects of any kind.

### METHODS OF APPLYING YPS

It is quite impractical to add 5 ppm of YPS dry to evaporated salt and expect distribution complete enough to obtain freedom from caking. Standard operating procedure is to apply the YPS in solution form by spraying the salt as it passes on a conveyor belt. A preferred location for this application may be just prior to the drying stage in the refining process. In order to improve the stability of the YPS, the pH of the stock solution may be raised to about 11 by the addition of 8.5 grams per liter of soda ash to the stock solution. The strength of the stock solution and the rate of feed to the salt are adjusted to minimize the moisture addition and provide 5 ppm of YPS in the salt.

YPS treatment of rock salt may be accomplished either wet or dry. Spraying of a YPS stock solution on a stream of salt on a conveyor belt is common practice. It is also quite effective to add the YPS dry, with half of the YPS dosage applied to the stream of salt on a conveyor belt and the balance added as a cap to the salt in the storage pile. Rainfall distributes this "capping." Additional capping may be applied as required to replenish YPS lost by leaching.

Various schemes have been tried to minimize the susceptibility of YPS to leaching. United States Patent 3,009,775 describes the use of a wax-treated YPS for bulk rock salt anticaking purposes. United States Patent 3,174,825 describes the pretreatment of the YPS crystals with tetramethyl cyclotetrasiloxane to achieve a 50% reduction in rate of leaching. Semipermeable coatings have been applied to the YPS crystals to obtain controlled release of the soluble ferrocyanide. The cost of these anti-leaching treatments generally is sufficiently high that it is more economical to replenish the YPS as needed on the pile. In addition, if heat is required for the coating treatment it usually decomposes the YPS decahydrate into the anhydrous material, with major degradation of the YPS crystal. The powder thus formed is subject to loss through wind action.

### LABORATORY EVALUATION OF ANTICAKING AGENT

The effectiveness of YPS as an anticaking agent may be demonstrated by a simple laboratory testing procedure. To the prepared sample, 2% moisture is added and the wetted salt molded into a cylinder approximately four inches tall by one inch in diameter. This cylinder is oven dried at

105°C overnight, allowed to cool, and then tested for compressive strength in a (Carver) hydraulic press. Untreated evaporated salt will withstand a pressure of upwards of 500 psi (pounds per square inch) before fracture. YPS-treated salt will usually fracture at less than 50 psi. The effectiveness of YPS as an anticaking agent, compared to several free-flowing agents, is illustrated in Fig. 9.

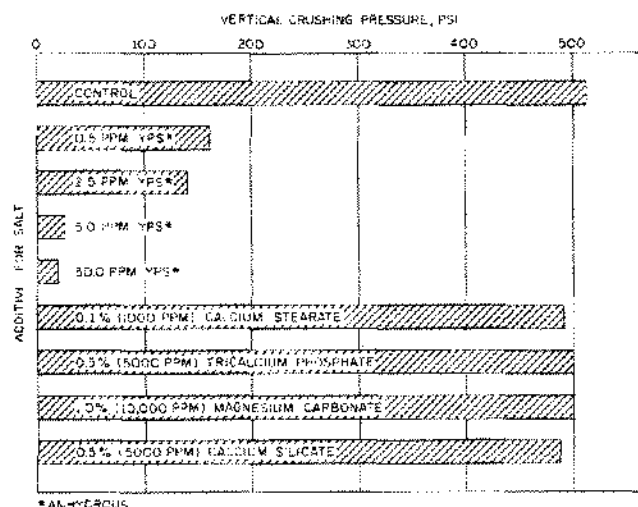


Figure 9

Using this test procedure, eight test briquets of each of the following salt samples were tested for hardness of caking:

1. Control sample, consisting of untreated salt.
2. Salt containing 0.5 ppm YPS.\*
3. Salt containing 2.5 ppm YPS.\*
4. Salt containing 5.0 ppm YPS.\*
5. Salt containing 50.0 ppm YPS.\*
6. Salt containing 0.1% calcium stearate.
7. Salt containing 0.5% tricalcium phosphate.
8. Salt containing 1.0% magnesium carbonate.
9. Salt containing 0.5% calcium silicate.

The average pressure for each of the YPS concentrations was as follows:

0.5 ppm YPS	164 psi
2.5 ppm YPS	145 psi
5.0 ppm YPS	28 psi
50.0 ppm YPS	22 psi

The New York City Department of Sanitation conducted a series of silo storage tests in 1958 to determine the effectiveness of 0.5-1.0% of three additives as anticaking agents in rock salt: silica gel, another desiccant, called Micro-Cel E, and 0.025% of YPS. The rock salt treated with

\* Calculated as the anhydrous material.

these additives was placed in cylindrical silos measuring four feet by eight feet and having a capacity of about 3.5 tons of salt. The silos were capped with a metal lid and allowed to stand. After two years, inspection was conducted by removing the lids and examining the nature and thickness of the crust in each silo. The free-flowing properties were observed by removing shear gates from the bottom of the silos. When the salt failed to flow freely from the silo, a crane lifted the silo off the salt so that its condition could be determined with accuracy.

The results of these tests again demonstrated the superiority of YPS. The only salt samples that were free-flowing after the two years' exposure were those treated with YPS. The other samples were caking, and the salt had become quite wet and mushy at the gate opening.

First domestic commercial deliveries of YPS-treated evaporated salt were made in 1961 to a major chemical corporation. In this instance, bulk evaporated salt was shipped in hopper cars a distance of some 500 miles. This company reported as follows:

"This will confirm our observations regarding the anticaking agent, yellow prussiate of soda, which \_\_\_\_\_ is employing in its bulk shipment of industrial evaporated salt to our plant at \_\_\_\_\_.

"We understand that 5 ppm YPS is added to the salt before loading. All salt so treated has been found to flow freely from the bottom hoppers of the railroad cars without difficulty and delay, even though the cars may have been on the road for a week or more. We know from experience that untreated salt will cake severely in the cars and be costly to unload. Our use of this salt does not allow the presence of conditioning agents such as magnesium carbonate, calcium silicate, etc. Therefore, we feel that your development of the salt treatment with yellow prussiate of soda has solved a major problem for us."

#### NONTOXICITY OF YPS ADDITIVE

To confirm the nontoxicity of YPS as an anticaking additive in salt, Food and Drug Research Laboratories, Inc. were retained to perform independent subacute toxicological studies.

The summary and conclusions of the FDRL report relates that feeding studies were conducted, in which weanling albino rats were fed 0.05% (500 ppm), 0.5% (5,000 ppm), and 5.0% (50,000 ppm) of the test compound (YPS) in the diet for a period of 90 days. Observations were made of growth, appearance, physical condition, food utilization, hematology, blood chemistry, and survival. Gross autopsies were performed and extensive histopathological examinations were included.

Results reported that at the 0.05% YPS level, no adverse effects were observed. At the 0.5% YPS level, equivalent to 500,000 ppm in salt normally used for seasoning, the only adverse finding was a minimal degree of tubular damage. At the 5.0% YPS level, equivalent to five million ppm in salt, anemia resulted after 12 weeks of feeding, and marked tubular damage was seen in the kidneys.

The use of YPS as an anticaking agent in evaporated salt is also common practice in Europe. Normal dosage is 10 ppm for salt for human consumption, and may run as high as 50 ppm for industrial usage, including salt for use in mercury cell chlor-alkali operations.

In Australia the Food Additives Committee of the National Health and Medical Research Council has approved the use of 50 ppm of sodium ferrocyanide in salt used in the food industry.

#### RELATED PATENTS

In addition to the May and Scott and the Kaufmann patents previously cited, the following patents have issued and may be of interest:

United States Patent 3,090,756(3) describes the use of ferrocyanide-treated salt as an anti-freezing agent for coal, ore, limestone, and other granular material.

British Patent Number 752, 582(4) describes the use of sodium ferrocyanide or cadmium nitrate to reduce salt caking.

British Patent Number 818, 385(5) describes the use of complex anticaking compounds, among which are cobalt and iron cyanides.

United States Patent 2, 947, 603(6) describes a noncaking rock salt composition adapted for outdoor storage, comprising crushed rock salt interspersed with pellets formed of a mixture of sodium chloride and water-dispersible alkali metal ferrocyanide. It is claimed that using the additive in pellet form improved uniformity of distribution and reduced loss through leaching.

United States Patent 2, 965, 444(7) provides for the use of insoluble ferric ferrocyanide salts as anticaking agents impervious to leaching. Potassium ferric ferrocyanide (Prussian blue) is one of the complex ferrocyanide additives claimed.

United States Patent 3, 174, 825(8) claims the use of unique coating materials, liquid organic siloxanes, to reduce the loss of anticaking agents through leaching. The noncaking additive, usually a soluble ferro- or ferricyanide is coated with a liquid organosilicon compound (siloxane) which upon contact with moisture reacts to form a water-resistant polymeric film. Solution of the additive is greatly retarded by this film, but enough is dissolved to provide ample noncaking action.

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