

Stabilizing Ammonium Nitrate against Crystalline Change

Marion L. Brown, Albert W. Green, and Ladelle Blanton

Ammonium nitrate undergoes volume expansion and contraction as it passes through its crystal transition temperatures, causing prills and granules to break down into fine particles or dust. The effect of various chemical additives on the physical breakdown at the transition temperatures has been studied. A mixture of boric acid, diammonium phosphate, and ammonium sulfate was found to be

the most effective for stabilizing ammonium nitrate against physical breakdown as ammonium nitrate cycles through its transition temperatures. A commercially proved process has been developed for producing greatly improved granular and prilled ammonium nitrate, and mixed fertilizers containing ammonium nitrate.

Both producers and users of ammonium nitrate are troubled by serious product quality problems—namely, caking and physical breakdown of prills and granules to dust or fine particles. As a result, producers must recycle large amounts of their production and make frequent plant shutdowns for equipment cleaning. Producers and users of granular and prilled ammonium nitrate and ammonium nitrate-containing fertilizers experience serious product deterioration in storage.

This paper reports a new patented (Brown *et al.*, 1967) method which has solved these problems by using less than 0.5% of an inorganic additive composition.

Numerous patented processes (Dieckmann *et al.*, 1965; Griffith and Stites, 1964; Guth, 1962; McFarlin and Stites, 1962; Stengel and Brodhacker, 1953) have sought to overcome the problems. Potassium nitrate (Campbell and Campbell, 1946; Janecke *et al.* 1932; Whetstone, 1948), magnesium nitrate, and nucleating agents (Russo, 1966) are being used commercially for this purpose. Nucleating agents are silicates, clay, talc, and naturally occurring silica materials. None of the processes, however, appears to solve the problems and most create additional problems. For example, although magnesium nitrate increases the resistance of ammonium nitrate to breakage at the transition points, it increases hygroscopicity and the prills are subject to "sugaring," a breakdown of prills to fine particles resembling sugar granules. In addition, the authors' tests indicate magnesium nitrate lowers the 90° F. transition. This means prills are likely to cycle through the transition point even more often. It also causes a change in crystal structure as moisture is absorbed or as moisture migrates in prills. Both phenomena cause prill breakdown during long storage. Potassium nitrate and the nucleating additives give only limited resistance to transition breakage. Prills and granules containing these additives fail to retain their hardness.

Because of the limitations of the available processes, goals were set on developing a process capable of producing prills (or granules) which would be highly resistant to breakage during production and, for at least one year's storage, to breakage by impact, grinding, and handling; breakage by thermal expansion and contraction as storage

temperature cycles; sugaring; moisture absorption; caking caused by moisture absorption and migration; and decline in hardness.

This paper presents a new patented method for producing ammonium nitrate prills which retain their hardness and which are much harder with high resistance to breakage by physical shock; extremely stable to transition temperature breakdown; not subject to sugaring; less hygroscopic than ammonium nitrate without additives or with previously reported additives; and much more resistant to caking.

By adding less than 0.5% of a mixture of boric acid, DAP (diammonium phosphate), and ammonium sulfate to ammonium nitrate melt prior to prilling or to granulating, an extremely stable product can be produced. Fines and dust production in both high and low density plants is reduced sharply. Prills of unprecedented hardness, which are completely stable to over 1400 90° F. transitions, are produced. Major increases in storage stability of both low and high density prills are observed.

A brief review of ammonium nitrate crystal transitions should be helpful in explaining the approach to the problem. Table I shows the volume change at each transition. As ammonium nitrate passes through the transition points and changes from one crystal form to another, significant volume changes take place. Prills and granules develop stress cracks because of these volume changes. The stress cracks permanently weaken prills and granules so that they break into pieces with slight handling. Repeated passage through the transitions will shatter the prills to dust, usually leading to caking.

Ammonium nitrate passes through one or more of the transition points during production as well as in storage. Both production operating conditions and storage conditions, therefore, affect product stability. In warehouse

Table I. Crystalline Transition Changes

Transitions	Temperature, °F.	Volume Change
I-II	257.4	2.1
II-III	183.6	1.3
III-IV	89.8	3.6
IV-V	-0.4	2.9
II-IV	113-123.8	

Source: Hendricks *et al.* (1932).

storage, the 90° F. transition normally causes the most trouble. A 3.6% volume shrinkage occurs when the temperature drops below 90° F., while a 3.6% volume expansion occurs when the temperature exceeds 90° F. In most production plants, ammonium nitrate solution is sprayed at temperatures up to 360° F. into air which cools the drops, causing them to freeze into prills. As ammonium nitrate cools from 360° to 89° F., it passes through the first three transition points (Table I). With rapid cooling as practiced in many plants, ammonium nitrate may pass directly from phase II to phase IV crystal form, skipping phase III. This "skip phase" transition causes as many cracks and stresses to form in prills as does the 90° F. transition. Passing through the 183° F. transition also causes severe stresses.

Formation of stresses during manufacture greatly amplifies prill breakage caused by passing through the transition in storage. Prill moisture absorption and migration increase as prills crack, causing additional crystalline changes. These crystalline changes result in formation of small crystals or granules. Under certain conditions, these crystals will be in the form of fines. Under other conditions, they will cement together to cause caking.

Lowering the 90° F. transition, as apparently done by some additives, can result in even more severe storage problems because prills will then cycle through the transition even more often.

To produce a superior product, it is necessary to eliminate most of the stresses created when prills pass the transitions during production as well as in storage. A research and development program was initiated to study these problems.

Procedures were developed for making prills in the laboratory and for testing prill resistance to moisture, thermal shock, and mechanical shock. With these procedures, new ideas were tested.

MATERIALS

Materials used for making the mixture containing the 0.2% H_3BO_3 , 0.2% $(NH_4)_2HPO_4$, and 0.01% $(NH_4)_2SO_4$ mixture are: technical grade orthoboric acid, powdered or granular; diammonium phosphate prepared from furnace grade phosphoric acid; and industrial grade ammonium sulfate.

PROCEDURE

90° F. Transition Tests. Two different tests are used to determine the resistance of prills to repeated passage through the transitions. In the first test, 25 prills are heated for 2 hours in an oven at 110° F., then cooled to 78° F. for 2 hours. After each cycle, the percentage of unbroken prills is recorded.

In another test, prill cracking due to phase II-phase IV transitions is determined by 2-hour cycles between 200° and 110° F.

Hygroscopicity. Moisture absorption tests are run by placing four portions of each sample on watch glasses. These watch glasses are placed on a perforated shelf 2 inches above the water level in a water bath, controlled at 90° F. After the samples are placed on the shelf, the bath is covered. Portions of each sample are then removed

after 5-, 10-, 15-, and 20-minute intervals and the moisture is determined by Karl Fischer titration.

Hardness Index. To determine relative hardness, 100 grams of screened sample (-8 mesh, +10 mesh) are placed on a 12-mesh screen with 120 $\frac{3}{8}$ -inch stainless steel balls. The screen is placed on the Ro-Tap machine and shaken for 30 minutes. The screen is then removed from the Ro-Tap machine and material left on the 12-mesh screen is weighed. The hardness index denotes the percentage of prills left on the 12-mesh screen.

Accelerated Caking Tests. For comparison of caking properties of various samples, accelerated caking tests are used. Portions of each sample are placed in a cylinder and weights are placed on top of the granules to simulate the weight of the bottom bag when 20 100-pound bags are stacked. Saturated air at 98° F. is passed through the granules for 1 hour. Dry air at 95° F. is then passed through the granules for 1 hour. The saturated air step is repeated, followed by passing dry air through the granules for 30 minutes. This procedure usually cakes the granules.

After the cylinder of caked material is gently removed and placed on a hydraulic press, the pressure is gradually increased until the cake breaks. The breaking pressure gives an index of the degree of caking. The higher pressures indicate a higher degree of caking in storage. From the results, predictions can be made of expected storage time without caking. Good correlation is obtained between this test and warehouse storage.

Determination of Transition Temperatures. Ammonium nitrate prill samples are ground and placed in a calorimeter. By programming the heating or cooling rate of the samples, it is possible to obtain a plot of temperature *vs.* time. Each time a crystal transition occurs, there is a sharp increase in temperature, the direction depending upon whether the sample is being heated or cooled. Heating rates of 5° C. per minute were used.

DISCUSSION OF RESULTS

Transition Stability. Prills can pass through the 90° F. transition as many as 200 times in a calendar year in southern locations. If as little as 4 to 6% of the prills crack, dust formation and caking occur, seriously affecting product quality. Since large tonnages of prills may remain in storage over 1 year, prills should develop less than 4% cracks after 400 transitions.

Table II shows the improved transition stability of the sample containing H_3BO_3 , $(NH_4)_2HPO_4$, and $(NH_4)_2SO_4$. The sample containing no additive has 10% of the prills broken after only 10 transitions and 100% broken after only 40 transitions. Potassium nitrate improves prill stability somewhat, but 4% of the prills are broken after only 20 transitions, and breakage progresses rapidly after 20 transitions. Although magnesium nitrate improves initial stability, breakage progresses rapidly after 20 transitions. Breakage reaches 6% after only 30 transitions, and 100% after only 60 transitions. The nucleating agent stabilizes the product for only 10 transitions. In striking contrast, the sample containing H_3BO_3 , $(NH_4)_2HPO_4$, and $(NH_4)_2SO_4$ shows no breakage after 1400 transitions.

From the data, the samples containing H_3BO_3 , $(NH_4)_2HPO_4$, and $(NH_4)_2SO_4$ could be expected to withstand ex-

Table II. Effect of Additives on Prill Breakage from Thermal Shock at 90° F. Transition
 % Prills Cracked from Thermal Shock
 Additive Type

No. of Transitions	None	(NH ₄) ₂ HPO ₄	KNO ₃	Mg(NO ₃) ₂	Nucleating Agent	H ₃ BO ₃ , (NH ₄) ₂ HPO ₄ , (NH ₄) ₂ SO ₄
	0	0.6	2.0	1.2	2.2	0.2, 0.2, 0.01
10	10	0	0	0	0	0
20	52	0	4	0	8	0
30	96	2	12	6	10	0
40	100	6	20	24	12	0
50		6	26	60	16	0
60		8	38	100	20	0
70		10	54		20	0
80		16	76		20	0
90		26	100		20	0
100		34			20	0
200		100			24	0
300					32	0
400					56	0
500					100	0
600						0 ^a

^a This sample passed through over 1400 transitions without any breakage.

tre storage conditions for 2 years or longer. Warehouse storage tests have verified this conclusion.

The results of the phase II-IV transition tests are equally striking. Although prills pass through this transition four times, at most, in production, the ability of the prills to withstand repeated passage through this transition point without cracking gives an accurate indication of the resistance of prills to thermal and mechanical stress. It also gives an excellent indication of the reduction in dust and broken prill formation one would expect in production of prills. In this severe test also, the H₃BO₃, (NH₄)₂HPO₄, and (NH₄)₂SO₄ stabilized prills withstand more than 600 transitions without a single prill cracking.

Hygroscopicity. Figure 1 shows the samples containing H₃BO₃, (NH₄)₂HPO₄, and (NH₄)₂SO₄ absorb much less moisture than the other samples. Note that during the first 10 minutes of exposure, moisture absorption on this sample is zero. This indicates a higher relative humidity is required for the sample containing H₃BO₃, (NH₄)₂HPO₄, and (NH₄)₂SO₄ to absorb moisture. The prills containing magnesium nitrate, potassium nitrate, or nucleating agent absorb most of the moisture on the surface, causing the prills to become sticky.

Another test is run by placing portions of each sample in open beakers in a room at 75° F. and 70% relative humidity. When the moisture content reached 0.6%, the sample containing magnesium nitrate became extremely soft whereas the other samples remained hard.

Hardness. For good handling and storage properties, an initial hardness of 50 or higher is desirable. Even more important, the prills should retain a hardness of at least 50 in storage. If the hardness index is below 50, prills will be crushed in field applicators. Dust segregates to the bottom of the applicator, causing plugging. Also, much of the dust blows away.

Table III shows prill hardness after aging. The sample containing the nucleating agent has a very low initial hard-

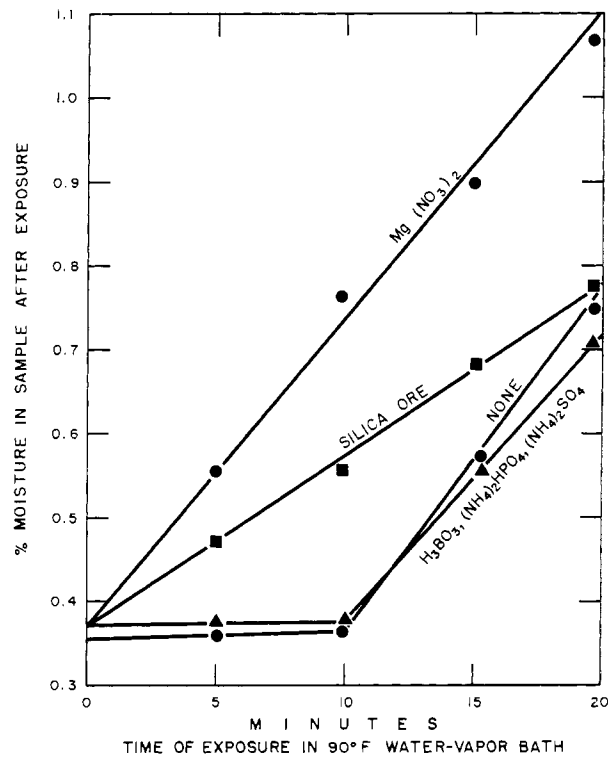


Figure 1. Effect of additives on moisture absorption

ness. Although hardness improves somewhat during the first three weeks of aging, rapid decline follows. The sample containing magnesium nitrate has a high initial hardness, but rapid decline occurs, even at storage temperatures below 90° F. The low density sample containing H₃BO₃, (NH₄)₂HPO₄, and (NH₄)₂SO₄ has a high initial hardness. Even more important, this sample retains its hardness with

Table III. Hardness Index with Aging

Type	Additive		Prill Density	Period of Aging, Months				
	Type	%		0	3	6	12	24
None		0	High	35	50	25		
Mg(NO ₃) ₂		1.2	High	81	65	9	0	
Nucleating agent ^a		2.2	High	17	15	13		
H ₃ BO ₃ , (NH ₄) ₂ HPO ₄ , (NH ₄) ₂ SO ₄		0.2, 0.2, 0.1	High	70	75	80		
H ₃ PO ₄		1.0	High	70	0			
None		0	Low	45	30	...	0	
H ₃ BO ₃ , (NH ₄) ₂ HPO ₄ , (NH ₄) ₂ SO ₄		0.2, 0.2, 0.01	Low	70	70	70	70	70

^a This sample showed an increase in hardness to 35 after 2 months, but hardness declined sharply thereafter.

aging even after 24 months. The high density samples have a hardness index of 80 or higher and also retain their hardness.

Warehouse storage tests of samples containing magnesium nitrate show inability to retain hardness. After 6 to 12 months of storage, most of the samples had a hardness index of zero.

Caking. Normally, caking of ammonium nitrate results from crystal growth on the surface of the granules. As the granules absorb moisture, ammonium nitrate goes into solution. As the granules dry, ammonium nitrate recrystallizes, cementing adjacent granules together.

The data in Table IV compare the effectiveness of various additives in retarding caking. If the samples flow freely when removed from the cylinder, a zero caking index is assigned. Samples containing H₃BO₃, (NH₄)₂HPO₄, and (NH₄)₂SO₄ have a caking index of 315 p.s.i., while the sample containing magnesium nitrate has a caking index of 325. High density prills without additive

have a caking index of 360. In sharp contrast, use of H₃BO₃, (NH₄)₂HPO₄, and (NH₄)₂SO₄ lowers the index to 265.

The improved resistance to caking greatly reduces bag set after storage and caking in bulk shipment.

Determination of Transition Temperatures. Table V shows the effects of some chemical additives on the occurrence of crystal transition points when heating the samples from 0° to 320° F. Transition points occur near the expected temperatures (90°, 183°, and 257° F.) for high and low density prills containing no additives. For example, transition temperatures occur at 89°, 176°, and 253° F. Prills containing phosphoric acid show the expected transition points plus a new transition at 304° F. Magnesium nitrate causes additional transition points to occur at 74° and 102° F. while showing the expected transitions of 86°, 181°, and 256° F. Of these three lowest transition temperatures, the 74° F. transition is the most pronounced.

For low density prills containing H₃BO₃, (NH₄)₂HPO₄, and (NH₄)₂SO₄, the 90° F. transition is shifted to 110° F. and no other transition occurs until 254° F. For high density prills containing these same additives, the 90° F. transition is shifted to 111° F. and no other transition occurs until 252° F. These data show that the 183° F. transition is eliminated by using a mixture of H₃BO₃, (NH₄)₂HPO₄, and (NH₄)₂SO₄.

Because of the elimination of the 183° F. transition, prills are not subjected to the normal stresses encountered at 183° F. in production facilities. This alone results in greatly improving prill hardness and stability. Shifting of the 90° F. transition to 110° F. results in prills passing through the transition fewer times in storage. The shape of this curve at 110° F. for the samples containing H₃BO₃, (NH₄)₂HPO₄, and (NH₄)₂SO₄ is flatter, indicating it takes longer to pass through the transition than it does for the

Table IV. Accelerating Caking Tests

Type	Additive		Prill Density	Crushing Strength of Cake, P.S.I.G.
	Type	%		
None		0	Low	375
H ₃ BO ₃ , (NH ₄) ₂ HPO ₄ , (NH ₄) ₂ SO ₄		0.2, 0.2, 0.01	Low	315
None		0	High	360
Nucleating agent		2.2	High	385
Mg(NO ₃) ₂		1.2	High	325
H ₃ BO ₃ , (NH ₄) ₂ HPO ₄ , (NH ₄) ₂ SO ₄		0.2, 0.2, 0.01	High	265
H ₃ PO ₄		1.2	High	375

Table V. Effect of Additives on Crystal Transitions

Type	Additive		Prill Density	Transition Temperatures, °F.	
	Type	%			
None		0	Low	89	174 255
None		0	High	89	176 253
H ₃ PO ₄		1.0	High	89	177 253 304
Mg(NO ₃) ₂		1.2	High	74 86 102	181 256
Nucleating agent		2.2	High	89	175 255
H ₃ BO ₃ , (NH ₄) ₂ HPO ₄ , (NH ₄) ₂ SO ₄		0.2, 0.2, 0.01	Low	110	254
H ₃ BO ₃ , (NH ₄) ₂ HPO ₄ , (NH ₄) ₂ SO ₄		0.2, 0.2, 0.01	High	111	252

All samples contained from 0.2 to 0.4% moisture, except the last two which were studied over the range 0.13 to 0.92% moisture. Moisture in this range showed no effect on transitions for the last two samples.

samples containing the other additives or no additives. This results in much less thermal shock to the prills as they pass through the transition and greatly stabilizes the prills.

A study of the effects of moisture on transition temperatures of ammonium nitrate (Nagatani, 1964, 1965) shows transition temperatures change as moisture content changes. A complete study of this phenomenon was outside the scope of this research because the authors' warehouse storage tests show that prills containing H_3BO_3 , $(NH_4)_2HPO_4$, and $(NH_4)_2SO_4$ do not exhibit physical breakdown within the moisture range studied (0.1 to 2.0%). On the other hand, prills containing magnesium nitrate show rapid physical breakdown of prills as the moisture content exceeds 0.5%. This indicates some additives cause moisture to have marked effects on transitions while a mixture of H_3BO_3 , $(NH_4)_2HPO_4$, and $(NH_4)_2SO_4$ eliminates the effect of moisture on the transitions. Determination of transition temperatures for the samples containing H_3BO_3 , $(NH_4)_2HPO_4$, and $(NH_4)_2SO_4$ were made over a moisture content range of 0.13 to 0.92%. The data indicate the moisture content has no effect on the transition temperatures within this range.

PLANT EXPERIENCE

The mixture of H_3BO_3 , $(NH_4)_2HPO_4$, and $(NH_4)_2SO_4$ is prepared as a solution. The solution can be fed into ammonium nitrate melt ahead of the prilling tower by a proportioning pump. Because the additive solution has a low viscosity and dissolves in ammonium nitrate, pumping is no problem and spray heads do not plug.

After 9 months of continuous use in a low density plant and test runs in a high density plant, an evaluation of the process indicates the following advantages:

Prior to using this additive mixture in the low density plant, the prill temperature at the bottom of the prilling tower had to be maintained between 165° and 178° F. to prevent excessive formation of dust and cracked prills. Use of this additive mixture permits temperatures from 160° to 200° F. and formation of fines is greatly reduced. In addition, air velocity can be reduced through the tower, thus reducing dust emission from the tower.

A marked reduction occurs in the amount of dust formed in the dryer and cooler drums. A reduction in weak liquor occurs in the dryer and cooler dust collectors. This means less water to evaporate, giving an impressive steam saving.

Less equipment cleaning is required.

After 2 years of storage, low density product is in excellent condition after more than 300 transitions. Although some of the product now contains 0.6 to 0.8% moisture, no caking has occurred.

Plant capacity is increased 10%.

Resistance to caking of both high and low density prills is greatly improved.

In the high density plant, the amount of fines leaving the prilling tower and the cooler is reduced to about 30% of that present without additives.

Prills of unprecedented thermal and mechanical stability are produced. High density prills with a hardness index of 80 and higher resulted, representing the hardest prills tested. More important, these prills retain their hardness with aging.

Moisture absorption and moisture migration is reduced considerably.

Clay and diatomaceous earth adherence is improved. In fact, 2.5% can be uniformly applied to high density prills. Previous industrial experience without H_3BO_3 , $(NH_4)_2HPO_4$, and $(NH_4)_2SO_4$ showed a maximum of about 1.0% can be applied.

Production costs can be decreased \$0.30 to \$2.00 per ton, depending upon the particular plant. In addition, savings resulting from reduced buyer complaints and reduced re-processing of returned or stored product have resulted. Savings from reduced bag breakage were also realized.

Performance is equally impressive with mixed fertilizers containing ammonium nitrate. For example, a 10-fold improvement in storage stability is observed in an ammonium nitrate-ammonium phosphate mixed fertilizer. Fertilizer containing the H_3BO_3 , $(NH_4)_2HPO_4$, and $(NH_4)_2SO_4$ shows no caking in bulk storage after 6 weeks, whereas fertilizer containing no additive shows severe caking.

ACKNOWLEDGMENT

The authors express their appreciation to David Arnold and Milton Bradley for their assistance and contributions to this work, and to Bob Sherling and the Operating Department for their valuable assistance and suggestions in plant operations.

LITERATURE CITED

- Brown, M. L., Green, A. W., Blanton, E. L. (to Mississippi Chemical Corp.), U. S. Patent **3,317,276** (May 2, 1967).
Campbell, A. N., Campbell, A. J. R., *Can. J. Research* **24**, 93-108 (1946).
Dieckmann, H., Opp, K., Roos, H., Schulz, H. (to Badische Anilin- and Soda-Fabrik), U. S. Patent **3,171,716** (March 2, 1965).
Griffith, E. J., Stites, J. G. (to Monsanto Chemical Co.), U. S. Patent **3,148,945** (Sept. 15, 1964).
Guth, E. D. (to Phillips Petroleum Co.), U. S. Patent **3,018,164** (Jan. 23, 1962).
Harvey, R. J., Proc. 15th Annual Meeting Fertilizer Round Table, November 1965.
Hendricks, S. B., Posnjak, E., Kracek, F. C., *J. Am. Chem. Soc.* **54**, 2766-86 (1932).
Janecke, E., Hamacher, H., Rahlfs, E., *Z. Anorg. Allgem. Chem.* **206**, 357-68 (1932).
McFarlin, R. F., Stites, J. G. (to Monsanto Chemical Co.), U. S. Patent **3,030,179** (April 17, 1962).
Nagatani, M., *Kogyo Kagaku Zasshi* **68**, 1842-45 (1965).
Nagatani, M., Seiyama, T., *Kogyo Kagaku Zasshi* **67**, 2010-14 (1964).
Russo, V. J., Division of Fertilizer & Soil Chemistry, 152nd Meeting, ACS, New York, N. Y., September 1966.
Stengel, L. A., Brodhacker, J. W. (to Commercial Solvents Corp.), U. S. Patent **2,657,977** (Nov. 3, 1953).
Whetstone, J., *Can. J. Research* **26**, 499-502 (1948).
Received for review September 8, 1967. Accepted March 6, 1968. Division of Fertilizer and Soil Chemistry, 154th Meeting, ACS, Chicago, Ill., September 1967.