

# The Influence of Moisture on the Structure and Quality of $\text{NH}_4\text{NO}_3$ -Prills

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A study has been made of high density ammonium nitrate prills with additives of 1 wt%  $\text{Al}_2(\text{SO}_4)_3$  and 2 wt%  $\text{Mg}(\text{NO}_3)_2$ . Prills with no additive have been used as reference material. The purpose has been to determine the effect of the additives on the structure of prills and the reason for resultant high-quality and good dimensional stability. The methods used were scanning-electron microscopy, optical microscopy, X-ray diffractography, electron microanalysis, and high-energy electron diffractography. The results are that the additives are not homogeneously located in the prills. The  $\text{Mg}(\text{NO}_3)_2$

additive is located in veins between the crystallites and contains 2 to 6 moles of water of crystallization. The  $\text{Al}_2(\text{SO}_4)_3$  additive is located in small aggregates, diameter 1 to 10  $\mu$ , with the formula  $\text{Al}_2(\text{SO}_4)_3(\text{NH}_4)_2(\text{OH})_2(\text{H}_2\text{O})_{8-10}$ . The better dimensional stability is principally due to the additive taking up moisture from the surrounding ammonium nitrate bulk which results in a water-content low enough ( $<0.01\%$ ) to prevent the phase transition  $\text{IV} \rightleftharpoons \text{III}$  at  $32^\circ\text{C}$ . The phase transitions were studied with X-ray diffractography.

**A**mmonium nitrate is finding increased use as a fertilizer and an explosive. One method of solving the problems of caking and storage is to manufacture prills. Additives are used to improve the quality and the dimensional stability of the product.

Many different mechanisms have been suggested for the caking of ammonium nitrate. It is known that ammonium nitrate is a very hygroscopic salt, which has sometimes been suggested as being the only reason for caking. Some authors consider that the hygroscopicity is of no importance and that the reason for caking is the phase transition  $\text{IV} \rightleftharpoons \text{III}$ . This transition takes place at  $32^\circ\text{C}$  and involves a change in volume of 4%. The effect of this should be that the crystals fall to pieces and then cake together.

Empirically good results have been obtained with additives of 1 to 2% of inorganic salts. Very little is to be found in the literature concerning the effect an additive has on the structure and quality of prills.

Very little has been written in the technical literature about the effect of moisture on prilled ammonium nitrate, although many indications of the importance of small amounts of water have been reported by authors who have studied the phase transitions of ammonium nitrate.

The purpose of this work is to determine the effect which a certain additive has on the structure of a prill and why it gives good dimensional stability. The effect of moisture on the system will also be studied.

Hendricks *et al.* (1932), Early and Lowry (1919), Hoppert (1965), and several others have shown that ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) has seven different crystalline modifications (Table I). The transition temperatures have been determined by several methods.

Many differing results have been published concerning the different phases that would be obtained during the phase transitions. Several metastable phases have been reported. Brown and McLaren (1962) have shown that in the presence of moisture the following phase transitions take place:  $\text{I} \rightleftharpoons \text{II} \rightleftharpoons \text{III} \rightleftharpoons \text{IV} \rightleftharpoons \text{V}$ . If there is no appreciable amount of moisture present, phase III will never exist and the transition  $\text{II} \rightleftharpoons \text{IV}$  takes place directly at a temperature of about  $50^\circ\text{C}$  (Shinnaka, 1956; Alekseenko and Boldyrev, 1956; Nagatani *et al.*, 1967b).

While the change in volume is a primary cause of breakage, many experiments have been made to change or eliminate the transition at  $32^\circ\text{C}$  by adding small amounts of inorganic salts. Several examples are reported in the technical literature. It is well known that an additive of 1 to 2% of  $\text{Mg}(\text{NO}_3)_2$  gives prills of high quality (Griffith, 1963; Sharma and Roy, 1967). Some authors have suggested that the  $\text{Mg}^{2+}$ -ion (radius 0.65 Å) could replace the  $\text{NH}_4^+$ -ion (radius 1.43 Å) in the unit cell. This statement does not seem plausible when it is known that ions with a larger difference in radius than 15% cannot replace each other in the unit cell (Hägg, 1963).

Hoppert (1965), and Sharma and Roy (1967) have shown that  $\text{KNO}_3$  (radius  $\text{K}^+$  1.33 Å) changes the transition temperature. In order to obtain an appreciable effect, the amount of  $\text{KNO}_3$  should be higher than 5 to 10%. Brown *et al.* (1968) have obtained prills of high quality by adding 0.2%  $\text{H}_3\text{BO}_3$ , 0.2%  $(\text{NH}_4)_2\text{HPO}_4$ , and 0.01%  $(\text{NH}_4)_2\text{SO}_4$ . The authors have stated that they have changed the transition temperature from  $32^\circ\text{C}$  to  $43$  to  $45^\circ\text{C}$  and that the transition at  $84^\circ\text{C}$  has been eliminated. Thus they have argued that the crystals are less "stressed." A similar argument has been put forward by Russo (1968). Some additives have the disadvantage of increasing the hygroscopicity of the ammonium nitrate (Brown *et al.*, 1968).

Sharma and Roy (1967) have reported that an addition of  $\text{Mg}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  gave a better product than if  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was used. They therefore suggested that the additive can take up moisture from the ammonium nitrate and thus give a better product.

The influence of moisture on analytical reagent grade ammonium nitrate seems well-established, and this means that when the amount of water is low enough, phase III will not be formed. In the literature there are different opinions on the critical amount of water. Kazakova *et al.* (1967) states 0.3 to 0.9%  $\text{H}_2\text{O}$  while Griffith (1963) has stated 0.03%.

Wolfe and Sharre (1967) have studied the kinetics of the transition  $\text{III} \rightleftharpoons \text{IV}$ . They showed that the transition is very sluggish and that the temperature difference should be about 4 to  $5^\circ\text{C}$  in order to get a faster rate of conversion.

**The Mechanism of the Transitions.** Using nmr spectroscopy, Brown and McLaren (1962) and Hovi *et al.* (1968) have shown that the  $\text{NH}_4^+$ -ion has spherical symmetry above  $-190^\circ\text{C}$ . The different phases are derived from the different energy barriers for the  $\text{NO}_3^-$ -ion. The mechanisms of the transitions

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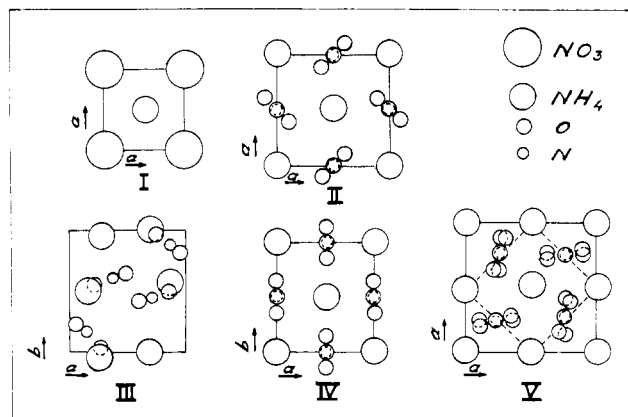


Figure 1. Projections of the structures of the different modifications of ammonium nitrate

have been discussed by Brown and McLaren (1962) and Nagatani *et al.* (1967a), and can be summarized in the following way (Figure 1).

**I → II.** The free rotation of  $\text{NO}_3^-$ -ions is hindered and hydrogen bonds form. The unit-cell-distances are transformed to the following.  $a: 4.40 \cdot \sqrt{2} = 6.20 \text{ \AA} \rightarrow 5.74 \text{ \AA}$ ;  $c: 4.40 \text{ \AA} \rightarrow 4.95 \text{ \AA}$ .

**II → IV.** At about  $50^\circ \text{C}$  the  $\text{NO}_3^-$ -ions are locked into fixed orientations. The unit-cell-distances are transformed to the following.  $a: 5.74 \text{ \AA} \rightarrow 5.75 \text{ \AA}$ ;  $b: 5.74 \text{ \AA} \rightarrow 5.45 \text{ \AA}$ ;  $c: 4.95 \text{ \AA} \rightarrow 4.96 \text{ \AA}$ .

**IV → V.** The ions are locked still more and the hydrogen bonds are stronger. The unit-cell-distances are transformed to the following.  $a: 2a = 11.5 \text{ \AA} \rightarrow 11.2 \text{ \AA}$ ;  $b: 2b = 10.9 \text{ \AA} \rightarrow 11.2 \text{ \AA}$ ;  $c: 2c = 9.92 \text{ \AA} \rightarrow 9.8 \text{ \AA}$ .

**III → IV.** Since the structure of phase III has no obvious similarities to the other phases, Brown and McLaren (1962) suggested that the phase transition takes place by the dissolution and recrystallization of the solid. The boundary between the two phases is therefore visualized as a region of almost complete disorder. This theory is supported by the fact that small amounts of water are necessary for the transition to take place, and that a very large increase in electrical conductance has been observed during the transition  $\text{III} \rightleftharpoons \text{IV}$  at  $32^\circ \text{C}$ .

#### THE OUTLINE OF THE EXPERIMENTS

In order to achieve the purposes of this work, the structure of the prills has to be studied. This means that it is necessary to find out if the additives replace any ions in the  $\text{NH}_4\text{NO}_3$ -

unit-cell, if they are uniformly spread throughout the prill, or if the additives are located to small spots.

When these facts are known, the influence of moisture can be studied by determining the transition temperature at a given water-content in the sample. If there is no water in the sample the phase transition would occur at about  $50\text{--}55^\circ \text{C}$ , and if there is water present the phase transition would occur at  $32^\circ \text{C}$ . The transition temperature might thus be determined as a function of the water-content in prills with different additives. By studying these curves it should be possible to draw conclusions concerning the effects of an additive.

#### EXPERIMENTAL

The additives which have been used in this work are  $\text{Mg}(\text{NO}_3)_2$  and  $\text{Al}_2(\text{SO}_4)_3$ . Prills without any additives have been used as a reference.  $\text{Mg}(\text{NO}_3)_2$  has been chosen since this is the most common example in the literature of an additive which gives prills of high dimensional stability. The additive is commonly in the form of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  or  $\text{MgO}$  equivalent to an amount of 1 to 2% of  $\text{Mg}(\text{NO}_3)_2$ . The second additive,  $\text{Al}_2(\text{SO}_4)_3$ , has been used, since Fosfatbolaget (Möllerstedt and Sulcs, 1968) have obtained prills of high dimensional stability by adding  $\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$  equivalent to 1% of  $\text{Al}_2(\text{SO}_4)_3$ . Finally, prills with 1% of  $\text{SiO}_2$ -particles have been used to test a hypothesis. This type is not used commercially.

This work is almost entirely concerned with high-density (HD)-prills. For the study of the structure of prills with aluminum additive, however, low-density (LD)-prills were also used. In all cases no surface-active agent has been applied to the prills. (Manufactured prills are sometimes treated with surface-active agent in order to protect the prills from the surrounding atmosphere.)

The following prills have been used: no additive, O-HD-prills; with 2%  $\text{Mg}(\text{NO}_3)_2$ , Mg-HD-prills; with 1%  $\text{Al}_2(\text{SO}_4)_3$ , Al-HD-prills; with 1%  $\text{Al}_2(\text{SO}_4)_3$ , Al-LD-prills; and with 1%  $\text{SiO}_2$ ,  $\text{SiO}_2$ -HD-prills.

**Structure Determination.** For the structure determination of the different types of prills, the most commonly used techniques were optical microscopy, scanning-electron microscopy, electron microanalysis, X-ray diffractography, and chemical analysis.

For the optical microscopic investigations, a metallurgical microscope was used. Since the  $\text{NH}_4\text{NO}_3$ -crystallites are translucent and the depth of focus of the optical microscope is small, it was not possible to obtain any detailed information with this technique. To avoid these disadvantages, prill cross-sections were made as plane as possible. By using different spectrophotometric reagents, which give a specific color for a specific type of ions, it was possible, however, to

Table I. The Different Crystalline Modifications of  $\text{NH}_4\text{NO}_3$

Phase	Temp. interval $^\circ \text{C}$	Crystal system	Density $\text{g/cm}^3$	Atomic distances, $\text{\AA}$
I (melt)	169			
I	169–125	Cubic	1.595	4.40
II	125–84	Tetragonal	1.666	5.47, 4.95
III	84–32	Orthorhombic	1.661	7.06, 7.66, 5.80
IV	32–18	Orthorhombic	1.725	5.75, 5.45, 4.96
V	–18 to –170	Tetragonal	1.725	11.20, 9.86
VI	169 (pressure 10 bar)	...	...	...
VII	–170	...	...	...

get valuable information. The plane cross-section was coated with the indicator just before the sample was put under the microscope, and thus it was possible to detect if there was any local concentration of color. Great difficulties were encountered because of the lack of depth of focus.

With the scanning-electron microscope, it was possible to get pictures with much greater depth of focus, which makes this instrument very suitable for the investigation of prills. In this case prills were prepared by breaking the prill and then studying the section. Normally, the "secondary electron image" was registered, giving information on the topography of the sample. In some cases the "back scattered electron image" was registered which can give information on the different components in the section. It was possible to get good photographs at a magnification of  $10,000\times$ . The most commonly used magnifications were  $100\times$  to  $3000\times$ . (Scanning-electron microscopes used were Cambridge Stereo Scan II and Jeol JSM-2.)

As a compliment to the microscopic investigations, an electron microanalyzer with an electron-beam diameter of  $1\ \mu\text{m}$  was used. Here it was necessary to have very plane specimens which were prepared by polishing the sections with diamond paste in absolute ethanol. This was very difficult because of the polycrystalline nature of the prills. The specimen holder allows liberal movement of the sample and thus it was possible to determine if the additives were located to spots or along veins.

Using X-ray diffractography it was possible to determine the size of the crystallites in the prills. On the other hand, this technique cannot be used to detect traces of other phases in the prill. X-ray diffractography has been used for studying the additive after isolation from the ammonium nitrate matrix.

As a compliment to X-ray diffraction, high-energy electron diffraction was used. With this method it is possible to get patterns from small areas of the section. This method was used to obtain a spectrum of an additive before it was isolated (the isolation of an additive can change the composition). With this method it was not possible to determine the identity of the additive because experimental difficulties made it impossible to get sufficient lines on the spectra.

**Determination of the Phase Transition Temperature.** The phase transition between  $\text{IV} \rightleftharpoons \text{III}$  or  $\text{II}$ , as a function of the water-content in prills, has been studied with X-ray-diffraction. This is a most accurate way of deciding when one phase disappears and a new phase appears.

The X-ray specimen holder was made of copper. The spectrum from the copper metal does not interfere with the ammonium nitrate phase-determination. The temperature of the sample was controlled by pumping water from a thermostated bath through small channels (loops) in the holder. Since ammonium nitrate is a bad thermal conductor, there will always be a temperature gradient in the sample. In order to obtain a correct value of the transition temperature, a thermocouple (Cu-constantan) was placed in the middle of the ammonium nitrate. The phase transition temperatures reported are those given by this thermocouple.

The determination of the water-content in the ammonium nitrate was made with a Karl Fischer automatic titrator (Metrohm E 452). Some difficulties were encountered with very dry samples because of the small amounts of Karl Fischer solution required. Otherwise, Karl Fischer titration is a very exact method and the water-content of prills could be determined with an accuracy of  $\pm 0.005\%$  by weight.

Ammonium nitrate samples of defined water-content were

prepared by grinding prills down to a suitable particle size for the X-ray investigation and subsequently exposing this material to an atmosphere of controlled humidity. The required levels of humidity were obtained in desiccators containing different saturated salt solutions (Young, 1967). The small particle size of the ammonium nitrate guarantees good mass transfer of water and thus homogeneously distributed water-content.

The determination of the transition temperature was made in the following ways. A weighed sample of ammonium nitrate was transferred to the Karl Fischer titrator for the determination of water-content. A second portion of the sample was placed at the same time in the X-ray specimen holder. In order to prevent any mass transfer of water to the surrounding atmosphere, the ammonium nitrate was sealed off with adhesive tape. A diffractogram was taken (for  $\text{Cu K}\alpha$  angle  $2\theta = 35\text{--}28^\circ\text{C}$ ) in order to determine the initial phase. In all cases this was phase IV. When this was verified the temperature was increased at a rate of  $0.5\text{--}1^\circ\text{C}$  per min. At the same time the goniometer was cycled over the phase IV-peak with the highest intensity (at the angle  $2\theta = 28.5\text{--}29.5^\circ\text{C}$ ). When the phase transition commences, this peak will decrease in intensity. As mentioned by Wolfe and Scharre (1967) the phase transition at  $32^\circ\text{C}$  will be detected first at about  $36\text{--}37^\circ\text{C}$  because of the sluggishness of the transition. The phase transition temperature was noted when the intensity was halved. After a few minutes, when the ammonium nitrate phase IV was no longer observable, a diffractogram was registered (angle  $2\theta = 41\text{--}15^\circ\text{C}$ ) in order to identify the new phase. Subsequently the procedure was reversed; that is to say, the ammonium nitrate was cooled until phase IV was again obtained. A diffractogram was taken (angle  $2\theta = 35\text{--}28^\circ\text{C}$ ) to verify the identity of this final phase.

The error in transition temperature determination is principally dependent on the accuracy of the potentiometer and the thermocouple, together with the temperature gradient in the sample. In order to examine the accuracy of the method, experiments were carried out on different samples with well-established transition points ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  dec. at  $32.4^\circ\text{C}$ , and piperazine melting point at  $42^\circ\text{C}$ ).

A further minor error is introduced due to the rate of temperature rise being different from one experiment to another. The advantage of using a rather high rate of temperature rise is that the loss of water is minimized.

Using this method, the accuracy of determination of the phase transition temperature was estimated to  $\pm 1^\circ\text{C}$  (estimated confidence 95%). Higher accuracy is difficult to attain, since the cycling over one peak took about 1 min and, as shown by Wolfe and Scharre (1967), the transition rate constant increases rapidly near the transition temperature.

Difficulties were encountered in determining whether it was phase III or phase II which had been obtained after the transition. This is due to the fact that the X-ray patterns are so alike. Differences are to be found in the intensities of certain peaks. The mechanism of the phase transition  $\text{IV} \rightleftharpoons \text{III}$  involves dissolution and recrystallization of the ammonium nitrate, which means that the sample, after passing the transition point, shows resultant orientation effects (*i.e.*, a statistical representation of the different crystal planes is no longer present). Thus the measured intensities are less reliable. For the purpose of this work it is not essential to determine which of these two phases has been obtained, and this issue has therefore not been subject to closer study. Utilizing some peaks of the patterns, however, it has been possible to determine very roughly the amount of the different phases.

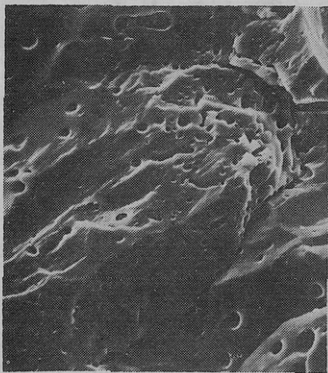


Figure 2. Cross-section from O-HD-prills (65 ×)

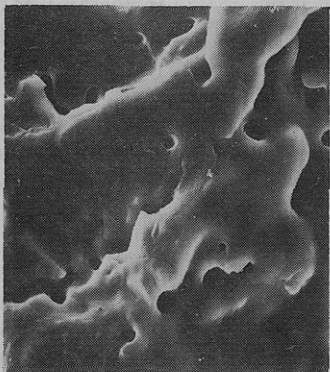


Figure 3. Detail of cross-section from O-HD-prills (300 ×)



Figure 4. Cavity from O-HD-prills (100 ×)



Figure 5. Surface from Mg-HD-prills (65 ×)



Figure 6. Cross-section with cavity from Mg-HD-prills (50 ×)

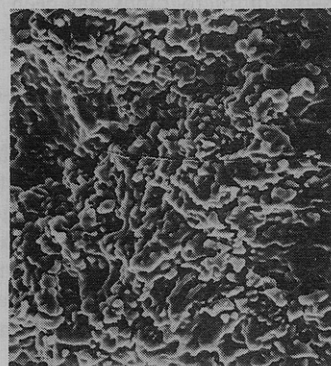


Figure 7. Cross-section from Mg-HD-prills (125 ×)

#### RESULTS—THE STRUCTURE OF THE DIFFERENT TYPES OF PRILLS

The specifications for the different types of prills which have been used are given in Table II. The test methods mentioned are commonly used by producers of ammonium nitrate prills.

**O-HD-Prills.** This type of prills has chiefly been studied with scanning-electron microscopy. Photographs of O-HD-prills are shown in Figures 2, 3, and 4, and here is seen that the crystallites were about 100  $\mu\text{m}$  in diameter or larger.

As shown in the photograph in Figure 4, prills contain a cavity. This is valid for all types of prills. This phenomenon has been explained as an effect dependent on pH and water-content. When drying prills, dehydration is said to cause this cavity formation. The present experiments have shown that these cavities are due to volume contraction during solidification. The edges of the cavity also show that an "implosion" has occurred. The volume contraction from  $\text{NH}_4\text{NO}_3$  (melt) at 180° C to  $\text{NH}_4\text{NO}_3$ (s) at 25° C was found to be approximately 12 to 15%. By measuring the volume of

the cavities, it can be shown that the cavity is about 10% of the total volume of a prill—in other words, a somewhat lower value. This is to be expected because the "first" volume contraction takes place prior to the solidification of the prill surface. When the surface has solidified, the remaining volume contraction must be taken up by an "implosion." Other facts that support this theory are that small cavities are to be seen in the cross-sections (Figures 2 and 3), and that a cavity is always seen in large prills but can be missing in small prills.

Another phenomenon, which is caused by the scanning-electron microscope on all types of prills, results in the cracks evident on the photographs from the scanning-electron microscope. This cracking is caused by the phase transition  $\text{IV} \rightleftharpoons \text{III}$ , which causes a volume expansion of 4%. The transition temperature is passed because of the local heating which occurs when the scanning electron beam is concentrated to a smaller spot at higher magnifications. This phenomenon is marked at magnifications greater than 3000 ×.

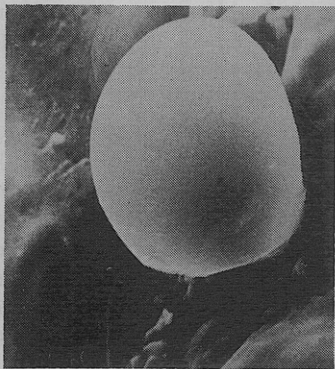


Figure 8. "Bubble" formation from Mg-HD-prills (500 ×)



Figure 9. Detail from a vein from Mg-HD-prills (1000 ×)

Photographs of the surface of a prill are shown in Figure 5. Here small scratches and veins are seen. The surface of different types of HD-prills are alike.

**Mg-HD-Prills.** This type of prills has chiefly been studied with scanning-electron microscope and optical microscope.

Photographs of Mg-HD-prills are shown in Figures 6, 7, 8, and 9. On the photographs it may be seen that the crystallites are separated by lower-situated veins. Comparison with the photographs of O-HD-prills shows that there is reason to suspect that the veins contain another compound. The back-scattered electron image also indicates that the material in the veins and in the  $\text{NH}_4\text{NO}_3$ -bulk are different in composition.

With the microanalyzer it was possible to locate magnesium to different spots on the polished section. The magnesium was located along veins and sometimes in small aggregates. It is not correct to say that  $\text{Mg}(\text{NO}_3)_2$  is regularly distributed around the crystallites. More correctly, the  $\text{Mg}(\text{NO}_3)_2$  is located in the gaps between the crystallites.

When the photographs were taken with the scanning-electron microscope at high magnifications, the veins behaved quite differently from the  $\text{NH}_4\text{NO}_3$ -bulk. The  $\text{NH}_4\text{NO}_3$ -bulk cracked (due to reasons mentioned earlier), while "bubble"-formation was observed in the vein-material (Figure 8). In the microscope it was easy to see how water left the veins. The material in the veins was of an amorphous character, and it was easy to follow the "bubble-gum"-like process of inflation and collapse of the bubbles. It was quite clear that there are two different compounds, one in the veins and the

other in the bulk. In another experiment, when a sample of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was examined in the microscope, exactly the same type of bubbles appeared. Thus, there is a reason to believe that these veins contain  $\text{Mg}(\text{NO}_3)_2$ .

With the optical microscope, the cross-section of a prill was studied by rapidly smearing the section with quinalizarin solution (alkaline aqueous solution). This indicator gives a red-orange color in the presence of  $\text{Mg}^{2+}$  ions. In the microscope it was seen that parts of the section were more or less colored. Great difficulties were met with in these experiments because of the solubility of ammonium nitrate in water, but for about 1 min effects could clearly be detected.

At first sight it seems remarkable that magnesium nitrate, which is completely soluble in the ammonium nitrate melt, is not homogeneously distributed throughout the solid prill. The following two facts show that the above results are plausible.

Melting points for the different compounds are:  $\text{NH}_4\text{NO}_3 \approx 169^\circ \text{C}$ ;  $\text{Mg}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O} \approx 124^\circ \text{C}$ ; and  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} \approx 90^\circ \text{C}$ . When  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  passes from the molten to the solid state, an amorphous phase is formed. First, after about 1 hr a crystalline solid state is formed. If  $\text{Mg}(\text{NO}_3)_2 \cdot 2-4\text{H}_2\text{O}$  solidifies from the melt, an amorphous phase is formed which needed several weeks to crystallize. With X-ray diffractography it was proven that these intermediate phases were amorphous.

Bearing these facts in mind, the mechanism of location of the magnesium additive to veins and gaps in the prill can be

Table II. Specifications for the Used Ammonium Nitrate Prills

	% Free water <sup>a</sup>	% Total water <sup>b</sup>	pH <sup>c</sup>	% Water un-soluble	% Mg	Size %				Density g/cm <sup>3d</sup>				Prill breakage <sup>e</sup>			
						>2 mm	>1.5 mm	>1.0 mm	>0.5 mm	0 c <sup>f</sup>	5 c	10 c	20 c	0 c	5 c	10 c	20 c
HD-prills without additive	0.11	0.14	4.0			0	5	60	35	1.03	0.84	0.74	...	4	36	52	...
HD-prills with 1% $\text{Al}_2(\text{SO}_4)_3$	0.09	0.14	4.8	0.51		1	10	67	22	1.00	1.00	0.99	0.99	1	...	2	1
HD-prills with 2% $\text{Mg}(\text{NO}_3)_2$	0.55	1.12	4.5		0.34	0	19	67	14	1.05	1.05	1.06	1.02	6	...	6	6
HD-prills with 1% $\text{SiO}_2$	0.24	0.40	6.0	1.0		1	10	73	16	1.00	0.83	0.65	...	10	...	64	...

<sup>a</sup> Free water = water-content by gravimetric methods. <sup>b</sup> Total water = water-content by Karl Fischer. <sup>c</sup> pH = pH of a 10% solution of the product. <sup>d</sup> Density = weight of a certain volume prills. <sup>e</sup> Prill breakage = % of total amount prills which have been crushed. <sup>f</sup> For one cycle prills have been treated to 40° C and then cooled to 15° C; time per cycle 2.5-3 hr. The density and the prill breakage have been determined before the first heating and then after different numbers of cycles.

explained as follows. When a droplet of melt is formed in the prilling tower, the ammonium nitrate on the surface begins to solidify. From the phase-diagram  $Mg(NO_3)_2-NH_4NO_3$  (Griffith, 1963) it is seen that this may be possible. The growing crystallite of ammonium nitrate excludes the amorphous or melted magnesium nitrate until all ammonium nitrate is solidified. After this the point of solidification for magnesium nitrate is reached. This solidification is also connected with a volume contraction (measured to 8–10%) which can explain why the veins are slightly lower than the level of ammonium nitrate bulk surface.

**Determination of the Composition of the Mg-Additive.** Since no method of isolating the additive was found, experiments were made using high-energy electron diffraction to determine the composition of the magnesium additive. As mentioned above, magnesium nitrate will lose water under high vacuum and be transformed to an amorphous phase (the bubbling-phenomenon in the scanning-electron microscope). Many experiments were carried out in the electron diffractograph without any patterns of the additive. The only compound that was identified was  $NH_4NO_3$  (IV). Even when pure magnesium nitrate was used, it was impossible to get any patterns.

Although it has been impossible to determine the formula of the Mg-additive in prills with the available instruments, it has consequently been indirectly shown that the additive is in fact magnesium nitrate, with a content of water between 2 and 6 moles per mole of magnesium.

**Al-HD-Prills.** This type of prill has been studied mainly with the scanning-electron microscope, optical microscope, microanalyzer, and high-energy electron diffractograph. The composition of the aluminum additive (Al-additive) has been determined with X-ray, ir-spectroscopic, and several analytical methods.



Figure 10. Cross-section from Al-LD-prills (optical microscope) (50 X)

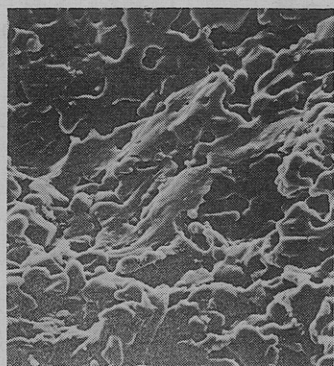


Figure 11. Cross-section from Al-LD-prills (100 X)



Figure 12. Detail of cross-section from Al-LD-prills (500 X)

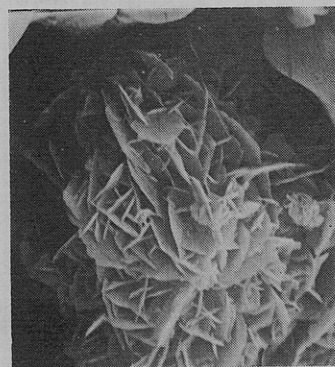


Figure 13. The Al-additive from Al-LD-prills (5500 X)

Using the optical microscope, cross-sections of prills were studied which had been smeared with an alcoholic solution of chromazurol. This indicator gives a violet color in the presence of aluminum. In the microscope a large number of small violet spots were observed on the section, which consequently indicated the Al-additive (Figure 10). It was rather difficult to get good photographs with the optical microscope due to reasons mentioned previously, but it was obvious that the aluminum was located in small spots and not homogeneously spread over the cross-section. The diameters of these spots were estimated to be smaller than 10  $\mu m$ .

With the microanalyzer it was shown that aluminum was situated in small spots in the section and that sulfur was located at these same spots. The diameter of these spots was estimated to be a few  $\mu m$  or less.

The scanning-electron microscope gave a better result (Figures 11–17). From the photographs it is obvious that the aluminum is located in small aggregates in the section. These Al-additive aggregates have a very characteristic structure. The diameters of the aggregates were determined to 1 to 10  $\mu m$  for Al-LD-prills and to about 1  $\mu m$  for Al-HD-prills.

**Determination of the Composition of the Al-Additive.** The addition of aluminum is made by adding  $Al_2(SO_4)_3 \cdot 17H_2O$  to a melt of  $NH_4NO_3$ . After about 10 sec a white colloidal precipitate is obtained and the pH is lowered to about 1. This decrease in pH is regulated to about 5 by adding  $NH_3$ -gas. The white precipitate is insoluble in water, ethanol, and methanol.

With series of experiments in which the  $NH_4NO_3$ -melt is held for different times at different pH, it was shown that no growth of the Al-additive could be detected. On the other hand, an agglomeration of the particles takes place if pH is greater than 6.

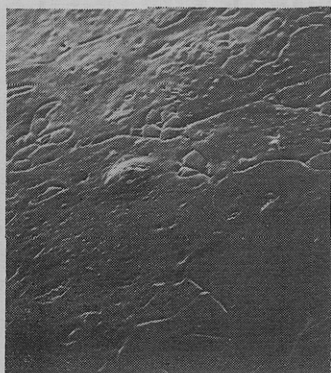


Figure 14. Surface from Al-HD-prills (350 X)

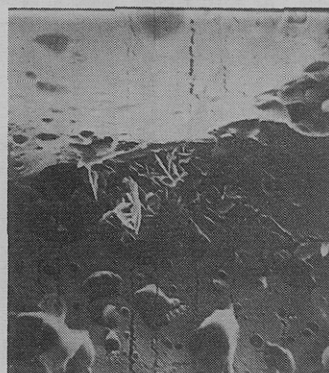


Figure 16. Detail of cross-section from Al-HD-prills (3150 X)

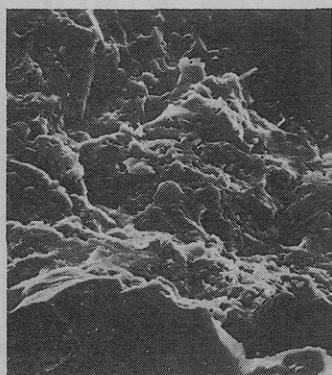


Figure 15. Cross-section from Al-HD-prills (100 X)

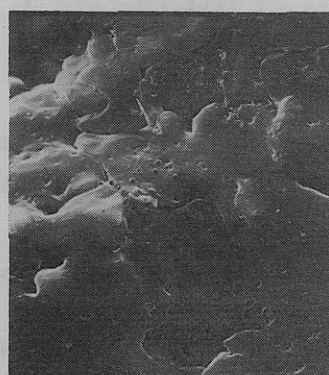


Figure 17. Detail of cross-section from Al-HD-prills (650 X)

In order to determine the composition of the Al-additive, it was isolated by dissolving the  $\text{NH}_4\text{NO}_3$  in absolute ethanol. Absolute ethanol was chosen because the Al-additive should not be exposed to water. In this way the Al-additive was obtained as a white powder. With high-energy electron diffraction it was shown that the Al-additive isolated in this way has the same structure as in the prill cross-section.

By evaporating the absolute ethanol, the rest of the  $\text{NH}_4\text{NO}_3$  could be analyzed with respect to  $\text{Al}^{3+}$  and  $\text{SO}_4^{2-}$ . In a concentrated aqueous solution of this  $\text{NH}_4\text{NO}_3$ , no traces of  $\text{Al}^{3+}$  (<10 ppm) or  $\text{SO}_4^{2-}$  (<50 ppm) could be detected with common chemical methods [chromazurol for  $\text{Al}^{3+}$  and  $\text{Ba}(\text{NO}_3)_2$  for  $\text{SO}_4^{2-}$ ]. By ir- and chemical analysis it was shown that isolated Al-additive contained about 1% of  $\text{NH}_4\text{NO}_3$ .

With X-ray diffraction several experiments were carried out to determine the structure of the isolated Al-additive. Because of the small crystallites' size (shown with the scanning-electron microscope) a broadening of the peaks was obtained in the diffractograms. The patterns were derived from a compound, which was not registered in ASTM index.

Since the X-ray diffractograms gave no conclusive information, ir-analysis was carried out on the following compounds (by standard KBr-pellet technique): Al-additive; ammonium sulfate  $(\text{NH}_4)_2\text{SO}_4$  (*pro analysi*); ammonium nitrate  $\text{NH}_4\text{NO}_3$  (*pro analysi*); aluminum sulfate  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  dried for 15 min at  $90^\circ\text{C}$ ; aluminum sulfate  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  dried for 20 hr at  $180^\circ\text{C}$ ; and aluminum oxide  $\text{Al}_2\text{O}_3$ . By comparing the diagrams from the Al-additive and from the above compounds, certain similarities were established. The peaks for  $\text{Al}_2(\text{SO}_4)_3$  were not identical with the Al-additive, and furthermore the amount of water seems to be of importance. The different functional groups in the dif-

ferent diagrams were not identical, but it is obvious that the Al-additive contained  $\text{NH}_4\text{-Al-SO}_4$ .

In order to determine the ratio of the different chemical constituents in the Al-additive it was subjected to chemical analysis. Because of the small amounts of Al-additive available, the analysis was less accurate in certain respects.

The analysis gave the following results.

$\text{Al}^{3+}$	9.14%
$\text{SO}_4^{2-}$	about 60% (uncertain value)
$\text{NH}_4$ -nitrogen	7.05%
$\text{NO}_3$ -nitrogen	0.88%
Nitrogen (total)	7.93%

From these data the probable composition of the Al-additive was calculated. It was assumed that remaining — % is  $\text{H}_2\text{O}$  or  $\text{OH}^-$ , and that the analysis of Al is the most secure. In the added compound,  $\text{Al}_2(\text{SO}_4)_3$ , the mole ratio is 1/1.5 and, as shown earlier, all Al and  $\text{SO}_4$  is located to the Al-additive. Considering this fact, and the fact that every  $\text{NH}_4^+$  needs one  $\text{OH}^-$  in order to retain electroneutrality, the following formula was obtained:  $\text{Al}_2(\text{SO}_4)_3(\text{NH}_4)_2(\text{OH})_2(\text{H}_2\text{O})_{10}$ .

In order to verify the calculated formula, the Al-additive was heated for 20 hr at  $550^\circ\text{C}$ . At this temperature water-free  $\text{Al}_2(\text{SO}_4)_3$  should be the product, because  $\text{Al}_2(\text{SO}_4)_3$  begins to decompose first at about  $600^\circ\text{C}$  and ammonium sulfate decomposes at about  $300^\circ\text{C}$ . It was shown with X-ray diffractography that the product formed was water-free  $\text{Al}_2(\text{SO}_4)_3$  (ASTM-index 1-0566). In the same way another sample, which had been heated for 20 hr at about  $1200^\circ\text{C}$ , was shown to be  $\alpha\text{-Al}_2\text{O}_3$  (ASTM-index 10-173).

Pilot-plant experiments have shown that the mole ratio between the added aluminum and the  $\text{NH}_3$  gas added for neutralization purposes was about  $2/3$ . This result supports

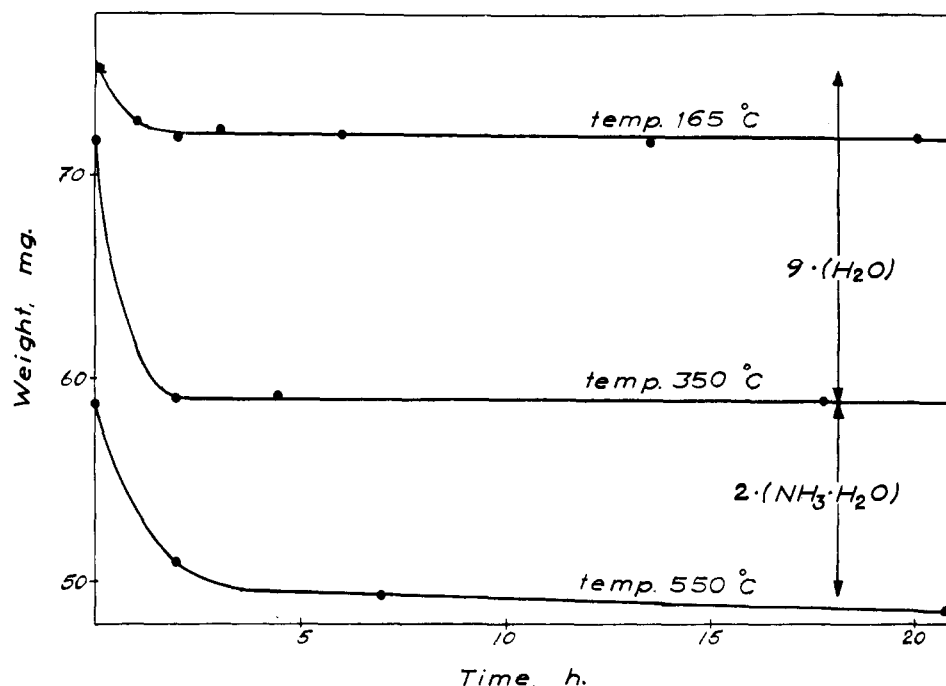


Figure 18. Decrease in weight of the Al-additive as a function of time (parameter, temperature)

the above formula, since a certain amount of  $\text{NH}_3$  should neutralize the decomposed  $\text{NH}_4\text{NO}_3$ . At the temperature of the melt ( $\approx 180^\circ\text{C}$ ) the rate of the decomposition  $\text{NH}_4\text{NO}_3$  ( $1 \rightarrow \text{NH}_3(\text{g}) + \text{HNO}_3$ ) is rather high (pH decreases from 5 to 3 in 2 hr). Calculations on these data support the fact that the mole ratio  $\text{Al}/\text{NH}_3$  should be 1/1.

The conclusion from these experiments is that the calculated formula should be correct. Some doubt exists, however, about the amount of water. The amount of  $\text{OH}^-$  could also be different because  $\text{HSO}_4^-$ -ions can be present.

Since the isolated Al-additive is an insoluble salt, Karl Fischer's method cannot be used for determining the water-content. For this reason, gravimetric experiments were carried out in order to verify the proposed formula.

The experiments were made by heating a certain amount of Al-additive at different constant temperatures and calculating the weight differences as a function of time. Results from an experiment with 58.7 mg Al-additive are shown in Figure 18. The following conclusions can be made. If the sample is completely dehydrated at  $350^\circ\text{C}$  and no  $\text{NH}_4\text{OH}$  has decomposed (loss 28.45%), the amount of water should be 9 moles. As the additive is water-free  $\text{Al}_2(\text{SO}_4)_3$  at  $550^\circ\text{C}$  and the loss in weight is 41.7%, this indicates water amounting to 10 moles. Another experiment where the final product was  $\alpha\text{-Al}_2\text{O}_3$  indicates an amount of water equivalent to 6 moles. There are some difficulties connected with the above experiments because one compound can start to decompose before the other is completely decomposed (e.g., temp.  $550^\circ\text{C}$  in Figure 18).

From the above results it is obvious that the water of crystallization amounts to between 6 and 10 moles. The validity of the proposed formula  $[\text{Al}_2(\text{SO}_4)_3(\text{NH}_4)_2(\text{OH})_2(\text{H}_2\text{O})_{6-10}]$  is further supported by the established identity of the intermediate products of thermal decomposition. The deviation of results for the water-content is not unexpected, because it is very possible that the water-content can vary. Probably there are two different types of water, one bonded harder to the Al-additive and the other of a physically adsorbed (zeolite) nature. Alternatively, the Al-additive may contain

a varying amount of material with the formula  $\text{Al}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2(\text{OH})_2(\text{H}_2\text{O})_{6-9}$  or similar plausible compounds.

#### THE PHASE TRANSITION $\text{IV} \rightleftharpoons \text{III}$ OR $\text{II}$ AS A FUNCTION OF THE MOISTURE-CONTENT

**O-HD-Prills.** The experiments were performed as previously described. The results from these investigations are presented in Figures 19 and 20. If the water-content is more than 0.1%, the phase transition  $\text{IV} \rightarrow \text{III}$  or  $\text{II}$  (Figure 19) takes place at a constant temperature of  $37^\circ\text{C}$ . On the other hand, as the water-content is decreased below this value, the phase-transition temperature rises rapidly and takes place at  $50\text{--}55^\circ\text{C}$  for a completely water-free sample. These results agree well with those of Griffith (1963) (Figure 19).

At very low water-content ( $<0.01\%$ ) the X-ray patterns showed that phase  $\text{II}$  is predominant and at higher water-content ( $>0.5\%$ ) that phase  $\text{III}$  is predominant. In the interval between these two extremes a mixture of both phase  $\text{III}$  and  $\text{II}$  was observed, but in all cases it was difficult, for reasons discussed earlier, to quantitatively determine the relative amounts of the two phases.

In Figure 20 the transition temperature for  $\text{II}$  or  $\text{III} \rightarrow \text{IV}$  is plotted as a function of water-content. The curve is a mirror-image of that for the phase transition in the opposite direction. Here it is always phase  $\text{IV}$  that was obtained. After an appreciable period of time (5 min) after the appearance of phase  $\text{IV}$ , traces of phase  $\text{II}$  and  $\text{III}$  could still be detected. This phenomenon was only detected on samples with lower water-content, and depends on water being involved in the kinetics of this phase transition. Probably this is the phenomenon called "aging" sometimes mentioned in literature (Alekseenko and Boldyrev, 1956).

Another phenomenon, which was noted and has also been reported earlier by Brown and McLaren (1962), is that a sample which has first been heated and subsequently vacuum-treated for a time behaved quite differently from other samples. These samples had a phase transition temperature which was lower than normal but the phase transition to  $\text{IV}$  was extremely slow. One such sample was held at  $0^\circ\text{C}$  for



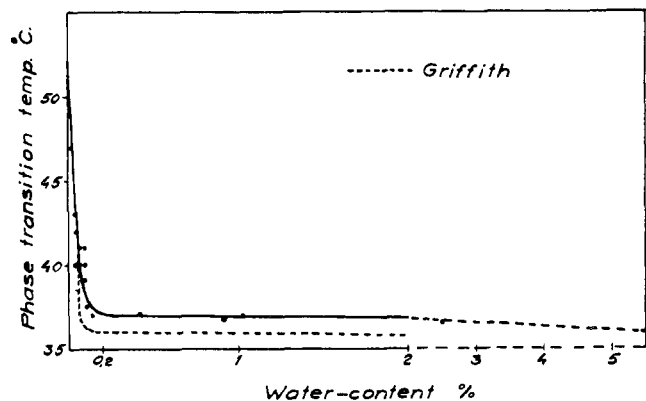


Figure 19. The phase transition temperature IV  $\rightarrow$  III; II as a function of the water-content for O-HD-prills

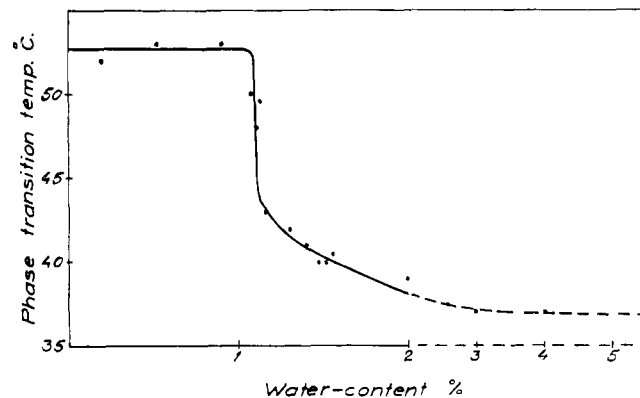


Figure 21. The phase transition temperature IV  $\rightarrow$  III; II as a function of the water-content for Mg-HD-prills

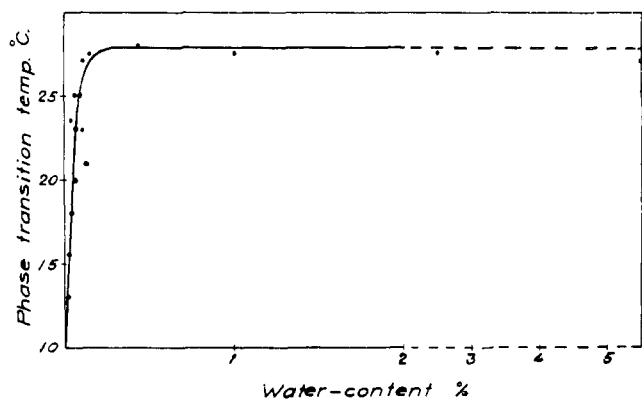


Figure 20. The phase transition temperature III; II  $\rightarrow$  IV as a function of the water-content for O-HD-prills

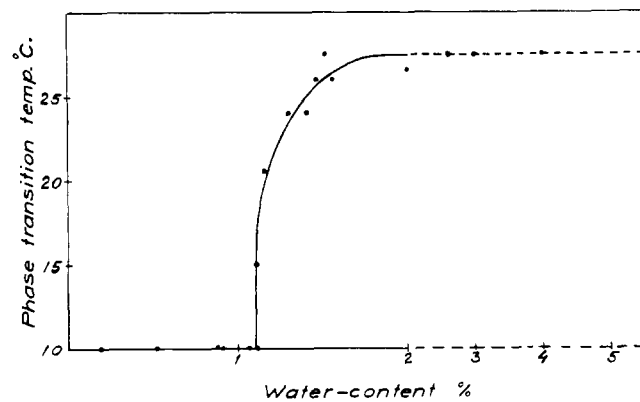


Figure 22. The phase transition temperature III; II  $\rightarrow$  IV as a function of the water-content for Mg-HD-prills

2 months without completely transferring to phase IV. No explanation of this phenomenon has been described in the literature.

**Mg-HD-Prills.** The experiments were performed as previously described. One difficulty with this type of prills was that samples with a water-content lower than about 1.5% were very hygroscopic, which could result in somewhat larger error in the determination of the water-content. The results from these investigations are given in Figures 21 and 22.

If the water-content is more than about 2.5%, the phase transition IV  $\rightarrow$  III takes place at a constant temperature of 37° C (Figure 21). With a water-content of less than 1.09%, the phase transition is received at a constant temperature of 52 to 53° C. In the range 1.09 to 2.5% the transition temperature decreases rather rapidly. Another difference between the curves for Mg-HD-prills and O-HD-prills is to be found in the slope in the intermediate region, which is not so steep in the case of Mg-HD-prills.

The same phases were formed as for O-HD-prills, with the difference that phase II was predominant as soon as the water-content was lower than 1.09%. The intermediate region, where both phase II and III are formed, was much broader (1.0 to 3.0%) in Mg-HD-prills.

The curve (Figure 22), which shows the phase transition from II or III  $\rightarrow$  IV, is a mirror-image of that for the phase transition in the opposite direction. Due to experimental difficulties, it has not been possible to determine the exact transition temperature for the samples with the lowest water-content.

The anomalous behavior of heat- and vacuum-treated samples was also noted here.

**Al-HD-Prills.** The experiments were performed as previously described. The water-content which has been given in this case is not entirely correct. This is due to the insolubility of the Al-additive. The amount of water which is determined by Karl Fischer titration consists of the water in the  $\text{NH}_4\text{NO}_3$ -bulk and weakly-bonded water on the surface of the Al-additive only.

For this reason the water-content has been determined also by gravimetric methods. The sources of error are, however, very large because of the small weight loss of water and because of the decomposition of  $\text{NH}_4\text{NO}_3$ . A correction for the decomposed  $\text{NH}_4\text{NO}_3$  was made. The reproducibility of the gravimetric analysis results was rather low but as an average value the water-content determined with Karl Fischer was shown to be about 0.15% too low.

The results from these investigations are shown in Figures 23 and 24 and in all cases the given value of the water-content is as determined by Karl Fischer. If the water-content is more than 1.0% the phase transition IV  $\rightarrow$  III or II (Figure 23) is obtained at a constant temperature of 37° C. With a water-content less than 0.05% the phase transition temperature is constant at 52° C. When the water-content is more than 0.05% the transition temperature decreases rather rapidly up to a water-content of 1%. In this case the slope of the intermediate region lies between the values for O-HD-prills and Mg-HD-prills. The appearance of the different slopes is seen in Figure 25. If consideration is taken to the gravi-

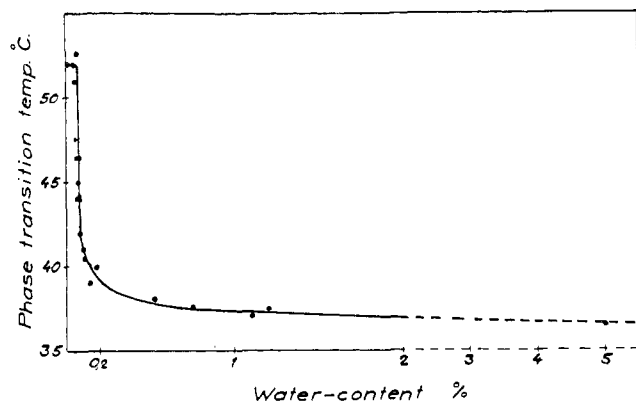


Figure 23. The phase transition temperature IV  $\rightarrow$  III; II as a function of the water-content for Al-HD-prills

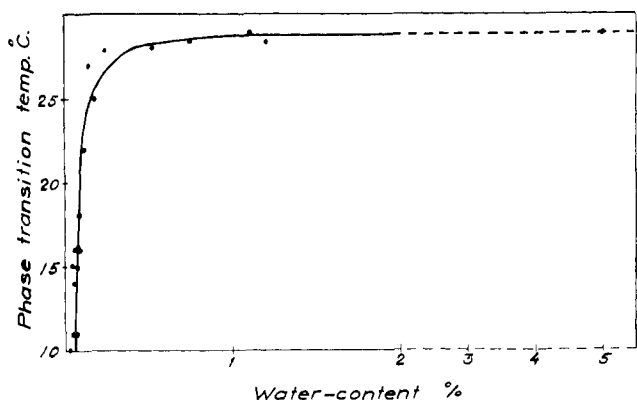


Figure 24. The phase transition temperature III; II  $\rightarrow$  IV as a function of the water-content for Al-HD-prills

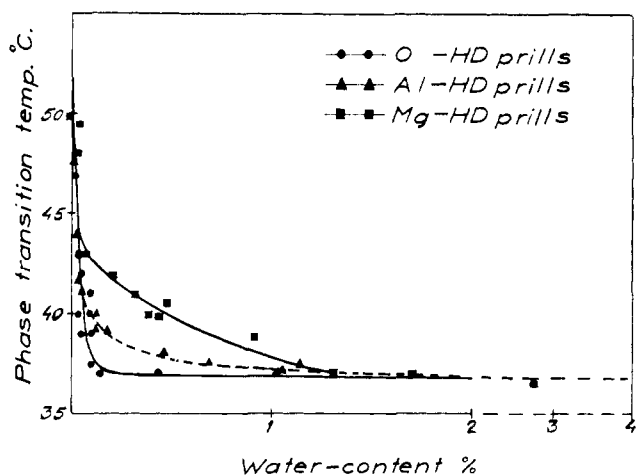


Figure 25. The appearance of the different slopes for O-HD-, Mg-HD-, Al-HD-prills. (Zero points: O-HD-prills = 0.00%; Mg-HD-prills = 1.09%; Al-HD-prills = 0.05%)

metric results the "plateau" for Al-HD-prills should be at 0.20% water-content instead of 0.05%.

Also, here the same phases were obtained as for O-HD-prills, with the difference that phase II was formed when the water-content was lower than about 0.05%, and the intermediate region with both phases II and III was between 0.05 to 1.0%.

The curve (Figure 24) which shows the phase transition from II or III  $\rightarrow$  IV has also, in this case, an appearance

which is a mirror-image of that for the phase transition in the opposite direction. Here it has also been difficult for experimental reasons to determine the exact temperature for the samples with the lowest water-content.

The previously mentioned phenomenon with samples treated in heat and under vacuum was also noted here.

#### THE EFFECT OF THE ADDITIVES

From the curves which show the phase transition temperatures as a function of the moisture, it is seen that the curves for both Mg-HD-prills and Al-HD-prills are, in principle, very similar. The differences are to be found in the length of the "plateau" and the slope of the intermediate region. There are, consequently, reasons to suggest that the effect of the additives on ammonium nitrate prills should be the same.

The effect of the additives is that it takes up the water from the  $\text{NH}_4\text{NO}_3$ -bulk and thus dehydrates the ammonium nitrate. The water-content of the  $\text{NH}_4\text{NO}_3$ -bulk is so low that the phase transition IV  $\rightleftharpoons$  III cannot take place, and instead the phase transition IV  $\rightleftharpoons$  II is predominant. This is the reason why a "plateau" is formed, because when the  $\text{NH}_4\text{NO}_3$ -bulk has a water-content lower than 0.01%, the phase transition IV  $\rightarrow$  II is the only one possible. This must be the most probable explanation, since the  $\text{NH}_4\text{NO}_3$ -bulk can pass through the phase transition IV  $\rightarrow$  II, although the prills contain quite large amounts of water, which consequently must be located solely in the additives.

In the scanning-electron microscope it was shown that Mg-HD-prills with a water-content less than 1% did not show any sign of cracking. This means that the increase in temperature was not high enough to get a phase transition IV  $\rightarrow$  II. Only in the boundary to the magnesium nitrate veins could cracking be seen. A similar effect was also shown to be valid for Al-HD-prills.

A further possible effect of an additive is that it may act as an initiator for the cracking. The additive, which is embedded in the  $\text{NH}_4\text{NO}_3$ -bulk as small aggregates and veins, makes it possible for many small cracks to be formed instead of fewer larger cracks, the latter being more detrimental to the dimensional stability of the prills.

**The Additive as a Hygroscopic Material.** The course of events during manufacture of  $\text{NH}_4\text{NO}_3$ -prills with different additives and high quality should consequently be as follows.

**Mg-HD-prills.** When  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is added into the melt of ammonium nitrate, a homogeneous melt is obtained. This means that the water should also be homogeneously distributed in the melt. The melt then passes an evaporator which lowers the water-content to about 1%. At this stage the temperature is about 180°C and the magnesium ions should be in the anhydrous form. When the prilling takes place, rapid crystallization ensures that water will still be located in the  $\text{NH}_4\text{NO}_3$  bulk. After prilling, the product is cooled, treated with hydrofobic surface-active agent, and then stored. During these stages the remaining water in the  $\text{NH}_4\text{NO}_3$  bulk will be taken up by the magnesium nitrate veins, which immediately after prilling contains less than 6 moles of water of crystallization. This is possible because magnesium nitrate with less than 6 moles of water of crystallization is much more hygroscopic than ammonium nitrate, and the mass transfer of water will take place until a "hydrostatic equilibrium" is reached. Thus the  $\text{NH}_4\text{NO}_3$ -bulk will be almost free from water, so that the phase transition IV  $\rightleftharpoons$  III will be prevented.

In prills with 2%  $\text{Mg}(\text{NO}_3)_2$ , this means that a decrease in the water-content of the  $\text{NH}_4\text{NO}_3$ -bulk of 0.24% corresponds

Table III. The Mass Transfer of Water Between O-HD-Prills and  $Mg(NO_3)_2$

Sample	Weight	Water-content before %	Time days	Water-content reference sample	Water-content sample	Decrease in water-content %
Whole prills	2.5539	0.068	9	...	0.060	12
Whole prills	2.6108	0.073	17	0.071	0.066	10
Whole prills [ground $Mg(NO_3)_2 \cdot 3H_2O$ ]	2.7833	0.070	20	0.076	0.060	14
Crushed prills [ground $Mg(NO_3)_2 \cdot 3H_2O$ ]	1.3745	0.075	4	0.079	0.041	45
Crushed prills [ground $Mg(NO_3)_2 \cdot 3H_2O$ ]	1.6660	0.079	16	0.080	0.0073	91

to an increase of 1 mole of water of crystallization in the magnesium nitrate additive.

Calculating on position of the "plateau" of the curve in Figure 21 shows that this "plateau" should correspond to 4.5 moles of water in the magnesium nitrate. The reason that the "plateau" does not correspond to 6 moles of water of crystallization may be explained by the fact that a mixture of  $Mg(NO_3)_2 \cdot 2H_2O$  and  $Mg(NO_3)_2 \cdot 6H_2O$  with an average water amount of 4.5 moles of water is in "hydrostatic equilibrium" with almost water-free ammonium nitrate. A similar discussion is also valid in the intermediate region, and this explains why the slope is less steep than for O-HD-prills.

In order to verify this discussion, whole and crushed O-HD-prills were placed in a hermetically sealed space together with  $Mg(NO_3)_2$ , with an average amount of water of about 3 moles. The results from these experiments are presented in Table III. Here it is seen that whole prills did not change very much due to the bad mass transfer. On the other hand, crushed prills attained a water-content low enough to prevent the phase transition  $IV \rightleftharpoons III$ .

Sieverts' and Petzold's (1932) data concerning the hygroscopicity of  $Mg(NO_3)_2$  and  $NH_4NO_3$  (at 25° C  $P_{H_2O}$ : for  $Mg(NO_3)_2 \cdot 6H_2O = 11.4$  mm Hg; for  $Mg(NO_3)_2 \cdot 2H_2O = 0.5$  mm Hg; for anhydrous  $NH_4NO_3 = 14.7$  mm Hg) support these results very well, and confirm the proposed mechanism.

**Al-HD-prills.** For Al-HD-prills, the same conclusions are reached, *i.e.*, the effect of the additive is to "draw" the water from the  $NH_4NO_3$ -bulk, thus preventing phase transition  $IV \rightleftharpoons III$ .

When the aluminum sulfate is put into the  $NH_4NO_3$ -melt, the Al-additive is rapidly formed, as mentioned earlier. At the high temperature of the  $NH_4NO_3$ -melt (180° C), the additive will not have the same amount of loosely-bonded zeolitic water as it would have at lower temperatures. From Figure 18 it is apparent that the loss of water is about 2 to 3 moles at 165° C. Here the mechanism should be the same as for Mg-HD-prills, which means that the water is first homogeneously distributed in a prill, and that the water in the  $NH_4NO_3$ -bulk is gradually transferred to the Al-additive. The discussion, valid for Mg-HD-prills, is consequently the same for Al-HD-prills.

With "wide line nmr for protons" it was shown that the Al-additive contained zeolitic water. This zeolitic water disappeared when the Al-additive has been heated to 180° C (the temperature of the melt) for 8 hr, and was taken up again at room temperature. These experiments confirm the proposed mechanism.

In prills with 1%  $Al_2(SO_4)_3$ , this means that a decrease in the water-content of the  $NH_4NO_3$ -bulk of 0.20% corresponds to an increase of 4 moles of water in the Al-additive.

**The Additive as a Crack Initiator.** From the results it is obvious that the primary cause of the improved dimensional stability of Mg-HD-prills and Al-HD-prills is that the additive can take up water from the  $NH_4NO_3$ -bulk and thus prevent the phase transition  $IV \rightleftharpoons III$ .

As mentioned earlier, a subsidiary cause may be that the additive can initiate the cracking. In order to determine how important this effect was, prills were made containing 1% of  $SiO_2$  particles ( $SiO_2$ -HD-prills).  $SiO_2$  particles were chosen because they are only able to bind a few molecular layers of water to the surface (Gregg and Sing, 1967). Analysis with Karl Fischer showed this statement to be valid. With this type of prills it should consequently be possible to separate the two effects.

**$SiO_2$ -HD-Prills.** The  $SiO_2$ -particles used were of the same size as the Al-additive aggregates and the concentration of the particles was about the same. The scanning-electron microscope photographs of this type of prills are shown in Figures 26, 27, and 28.



Figure 26. The  $SiO_2$ -particles used (5000 ×)

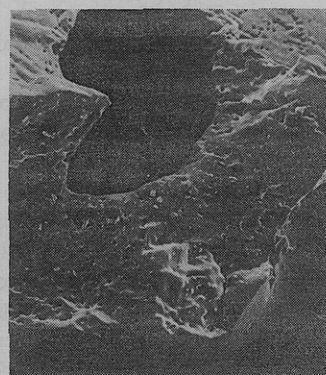


Figure 27. Cross-section from  $SiO_2$ -HD-prills (50 ×)

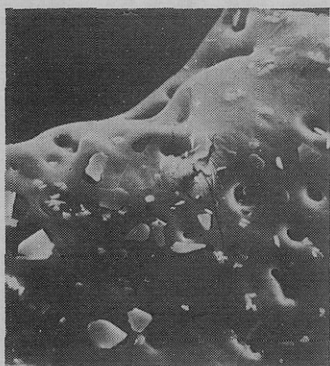


Figure 28. Detail of cross-section from  $\text{SiO}_2$ -HD-prills (250  $\times$ )

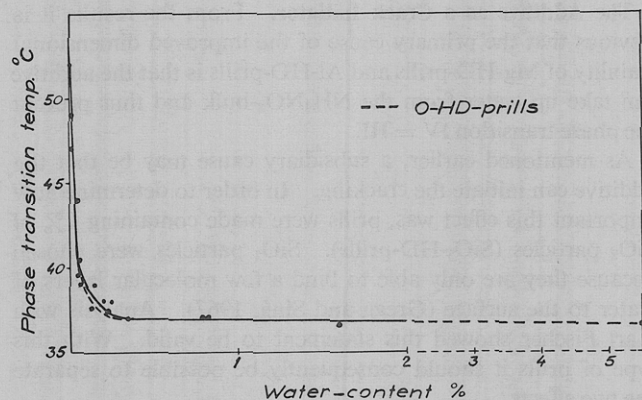


Figure 29. The phase transition temperature IV  $\rightarrow$  III; II as a function of the water-content for  $\text{SiO}_2$ -HD-prills

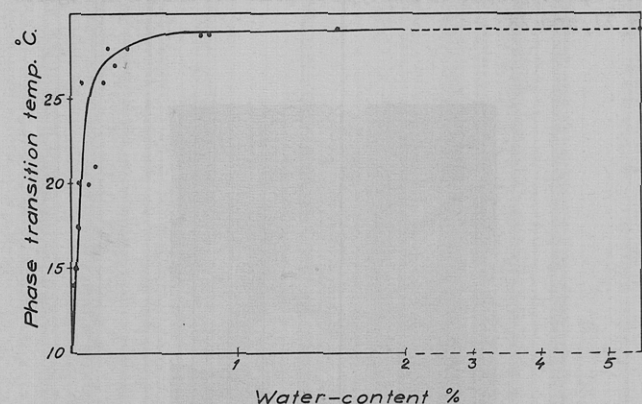


Figure 30. The phase transition temperature III; II  $\rightarrow$  IV as a function of the water-content for  $\text{SiO}_2$ -HD-prills

$\text{SiO}_2$ -HD-prills did not show any improved dimensional stability compared with O-HD-prills (Table II).

The phase transition temperature as a function of the moisture is shown in Figures 29 and 30. The experiments were performed as described previously. In Figure 29 it may be seen that the curve is almost identical with that valid for O-HD-prills. There is only a small difference in the slope. This difference may depend on the small amounts of ammonia which this type of prills happened to contain. Figure 30 shows that the curve for the phase transition II or III  $\rightarrow$  IV is also the same as for O-HD-prills.

From these experiments it is evident that the effect of the additive as an initiator for the cracking cannot be of any

greater importance. On the other hand, the possibility of this effect cannot be completely excluded because the  $\text{SiO}_2$  particles do not have the same appearance as the Al-additive aggregates.

**The Dependence of pH.** In pilot-plant experiments it has been noted that the pH has an influence on the dimensional stability. The effect of pH on prills is of an indirect nature and can be explained as follows: Low pH (less than about 3) is caused in the melt by the decomposition of  $\text{NH}_4\text{NO}_3$ , as described earlier, and by the addition of  $\text{Al}_2(\text{SO}_4)_3$ . Some  $\text{NH}_3$  leaves the melt in gaseous form and some  $\text{NH}_3$  is chemically bonded to the Al-additive, thus making the melt rich of free  $\text{HNO}_3$ . This free nitric acid is hygroscopic and the  $\text{NH}_4\text{NO}_3$ -prills are therefore very difficult to dry; thus, the resultant prills have a higher water-content. On the other hand, if pH is too high (more than about 6) large amounts of free  $\text{NH}_3$  will be present which can hold some water. High pH also causes the Al-additive to agglomerate. This product is, however, easier to dry than that containing free nitric acid. The problem of pH is of great technical importance because it is very difficult to regulate this system since the desired pH (about 4 to 5) is at the point of inflection of the titration curve.

From the above, the influence of pH is clear and the effect on prills depends on the water-content and perhaps also on any free ammonia which may be present.

#### CONCLUSIONS AND RECOMMENDATIONS

From the results obtained it is obvious that the most important factor governing the dimensional stability of  $\text{NH}_4\text{NO}_3$ -prills is the water-content. It is also obvious that the two different additives have a similar effect and can take up water from the  $\text{NH}_4\text{NO}_3$ -bulk. The obtained phase transition temperatures cannot be explained by the replacement of ions in the unit cell.

At first sight the results of this work would appear to indicate that the best additive would be  $\text{Mg}(\text{NO}_3)_2$ , since this additive exhibits a very large "plateau." As reported in the literature, an addition of  $\text{Mg}(\text{NO}_3)_2$  makes the prills much more hygroscopic than O-HD-prills. Consequently the prills can take up moisture from the air already at rather low relative humidity, and although the "plateau is 1.09%," the prills will take up water very fast. This disadvantage can in practice be limited by treating the prills with hydrofobic surface-active agents, thus preventing the prills from taking up moisture from the surrounding atmosphere.

Al-HD-prills have a much smaller "plateau" than Mg-HD-prills, but despite this the Al-additive is more suitable since it does not increase the hygroscopicity of the prills. On the other hand, this type of prills is sensitive to high pH, because of the agglomeration of the Al-additive which takes place at a pH higher than about 6. These Al-additive agglomerates will fasten in the spray nozzle and make the prilling impossible.

The results of this work have made it possible to explain some previously uncertain factors in prill-testing.

The conclusions of this present work are that, in order to obtain prills of high quality, it is necessary to use a suitable additive which can take up moisture from the  $\text{NH}_4\text{NO}_3$  bulk without changing the hygroscopicity of the prills. The melt must have a suitable pH in order to give an easily dried product, and finally the prills must be uniform in size and should be treated with a surface-active agent before storing.

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