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STRAIGHT AMMONIUM NITRATE FERTILIZER GRANULE-PRILL STABILIZATION: THEORETICAL POSSIBILITIES (a)

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1. Physicochemical Properties of Pure Ammonium Nitrate

The behaviour of ammonium nitrate (AN) against thermo-cycling is affected by its peculiar physicochemical properties. The three main influencing properties are: water affinity, heat transfer and polymorphism. They are detailed underneath so that the following chapters with regard to fertilizers could be better understood.

1.1 Solubility-Critical relative humidity

Ammonium nitrate is strongly hygroscopic at the ambient temperature and has a lower critical relative humidity (CRH) than other common salts. It also has exceptionally high water solubility with the water held as a solution rather than combined as water of crystallization.
The temperature coefficient of solubility of the salt in water is also exceptionally high.
The solubility of ammonium nitrate decreases with the pressure. This particular behaviour promotes the caking of AN fertilizers during piling in the storage: Indeed, the liquid phase in the contact region between two granules starts to be in supersaturation ; new crystals appear promoting some caking tendency between granules.

Table1. Comparison of temperature, coefficient. of solubility, water solubility, and critical relative humidity of some common salts.

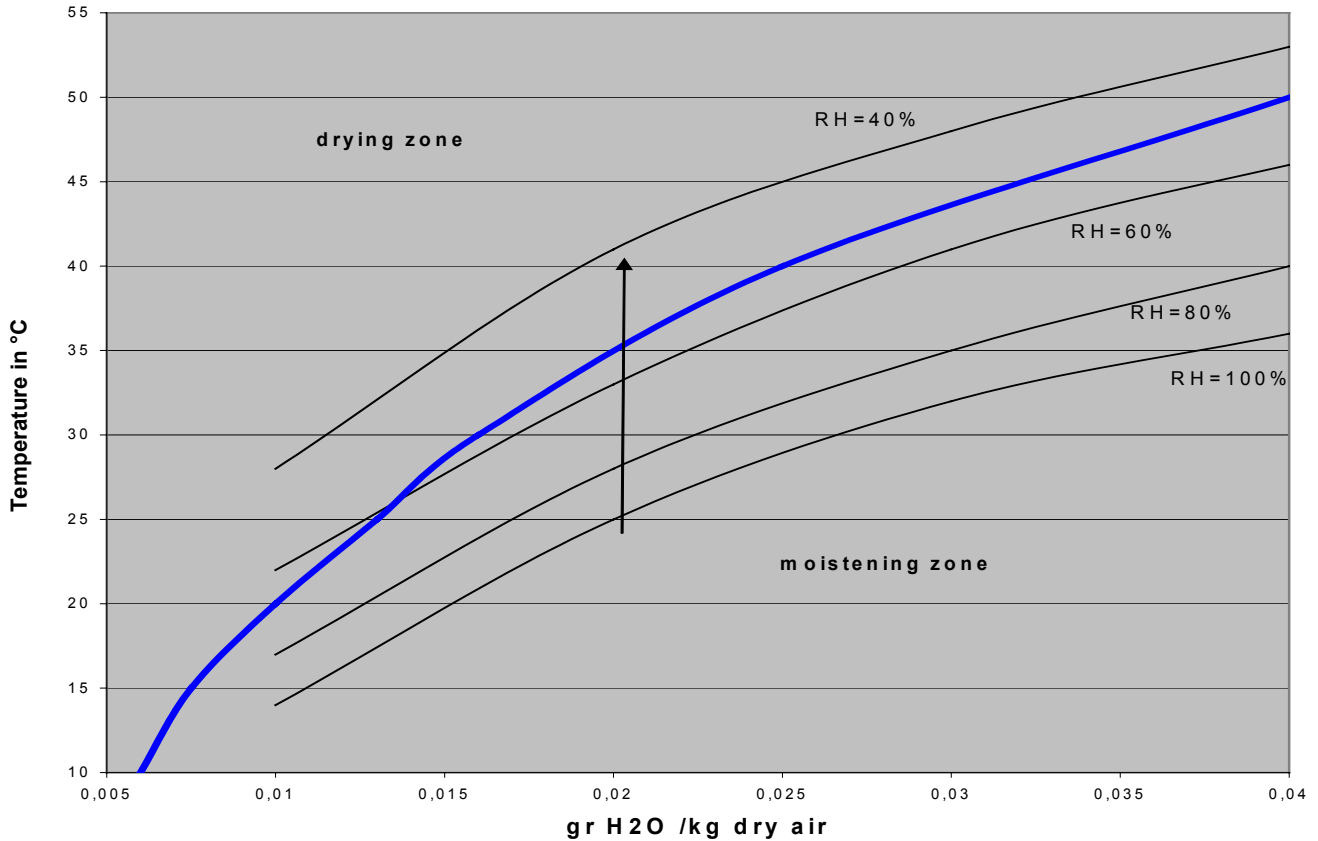| Salt	$\Delta S/\Delta T$ (20-30°C)	Solubility (20°C)	Critical relative humidity (20°C)
	Gr./ 100gr water	Gr. / 100 ml solution	%
NH_4NO_3	4.94	66.0	66.9
$NaNO_3$	0.79	46.7	77.1
NH_4Cl	0.42	27.1	79.3
$(NH_4)_2SO_4$	0.26	42.85	81.0
KNO_3	1.42	24.0	92.3
NaCl	0.025	26.37	77.6

Depending on the temperature and relative humidity of the air, ammonium nitrate can either absorb or desorb moisture to the atmosphere. Table 2 gives the hygroscopic point, or the relative humidity of air at which the vapour pressure of water in the air is equal to the vapour pressure of water over saturated ammonium nitrate solutions, at different temperatures. For instance, at 30°C if the relative humidity of the air is higher than 60%, AN absorbs moisture in the form of a saturated solution.

Table 2.Influence of temperature on the CRH of ammonium nitrate

Temperature °C	10	15	20	25	30	40	50
Critical relative humidity of AN%	75.3	69.8	66.9	62.7	59.4	52.5	48.4
Gr H2O/kg dry air that air handle at the above temperature and relative humidity	6	7	10	13	16	25	41

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Changes in temperature of the AN or the atmosphere cause moistening or drying leading to recrystallisation of AN and, consequently, to the caking between the crystals.

Mollier diagram including moistening and drying zone of AN

drying zone

RH=40%

RH=60%

RH=80%

RH=100%

moistening zone

Temperature in °C

55

50

45

40

35

30

25

20

15

10

0,005   0,01   0,015   0,02   0,025   0,03   0,035   0,04

gr H2O /kg dry air

In various ways explained in the following chapters, the hygroscopic nature of ammonium nitrate together with thermo-cycling will affect the caking of fertilizers.

1.2 Thermal conductivity

The thermal conductivity of dry, granular AN fertilizer compared to other material is low (Table 3). During the cooling of a fertilizer, the low thermic transfer affects the gradient of temperature inside the granules.

This difference of temperature linked with change of volume during thermo-cycling can promote cracks and affects the storage behaviour of the product.

Table 3. Comparison of thermal conductivity of AN with other materials at 18°C

Material	Rate of travel of heat through material Cal/(sec).(cm2.).(°C/cm)
Iron	0.161
Soft glass	0.0025
Dry sand	0.00093
Paraffin	0.0006
Dry, granular ammonium nitrate (density 0.7g./cc.)	0.00057
AN33.5 Kemira Tertre (0.35%H2O-density 0.965)	0.000208
CAN 27% Kemira Tertre (0.10% H2O-density 1.020)	0.000344
Fire brick	0.00028

1.3 Polymorphism

1.3.1 Stable crystal forms-density-specific heat-heat of transition

Ammonium nitrate, NH4NO3 containing 35% nitrogen has the following properties: density at 20°C, 1.725 gr/cm3; specific heat at 20°C, 0.422Kcal./kg°C ; heat of fusion 16.75-18.3Kcal/kg and a melting point of 169.6°C.

Ammonium nitrate is polymorphic and can assume at least at ordinary pressure five crystalline forms with different densities and enthalpies.
Every form, designed by a roman number, is stable over a certain temperature range. The stable form at ambient temperature is the form IV.
During normal cooling at atmospheric pressure, ammonium nitrate passes successively through the crystalline forms I to V. The change in crystal state occurs with a change of volume and heat of transition.
The crystal changes, associated specific volume, energy changes and solubility in water are shown in Table 4 and Graphics 1-2-3.

Table 4. Phase transitions during normal cooling

Crystalline form	Temperature range in which crystalline form is stable	Specific volume	Specific heat	Solubility	Transition temperature	Transition	Heat of transition
	°C	cm3/gr	Kcal/kg°K	% by weight	°C		Kcal/kg
Liquid	169.6	0.697					
I Cubic	169.6-125.2	0.642-0.627	-0.477	100-96.1	169.6	Melt→I	16.75-18.3
II Tetragonal	125.2-84.2	0.612-0.603	0.454-0.441	96.1-87.4	125.2	I→II	13.25
III Orthorhombic	84.2-32.2	0.613-0.605	0.386-0.356	87.4-70.9	84.2	II→III	4.03
IV Orthorombic	32.3- -16.9	0.582-0.572	0.423-0.374	70.9-42.3	32.3	III→IV	5.08
V Tetragonal	<-16.9-	0.589-			- 16.9	IV→V	1.41

1.3.2 Metastable transitions

Forms III and IV transform themselves quickly each one another and present rarely a delay to transformation.

In another way, form II shows a considerable delay during cooling to form III. It can happen that form II transforms immediately to form IV, by-passing the form III.

So, in addition to the four stable transitions V→IV, IV→III, III→II and II→I, ammonium nitrate shows also a metastable transition IV→II. This transition occurs at 51°C and can be easily explained: the II and IV phases have close structures, differing only by the orientation of the NO3 plans; form III being very different from the others. The direct transition II-IV happens by simple rotation of the NO3 plans.

One can even realise the direct stable transition from II to IV without passing trough III form if we prevent, under very high pressure, the volume dilatation requested to pass from II to III.

The impact of this transition on the specific volume, specific heat and variation of enthalpy is shown in Graphs 1,2 and 3.

The direct transition II to IV is accompanied with 5.56 Kcal/kg of heat of transition compared to 9.11 needed for the successive transitions II→III→IV.

Accordingly, to respect the thermodynamic low, the specific heat in the metastable zone is higher than the one of phase III (Table 5 and Graph 2).

Table 5. Direct transition II →IV

Crystalline form	Temperature range in which crystalline form is stable	Specific volume	Heat of transition	Specific heat
	°C	cm3/gr	Kcal/kg	Kcal/kg°K
II	84.2-51	0.603-0.598		0.441-0.431
II→IV	51		5.56	
IV	51- -16.9	0.585-0.572		0.442-0.374

Metastable form II which subsists during cooling of pure AN can transform to phase III just below the transition point of II to IV at 51°C. The transition heat can be estimated to 1.41 Kcal/kg (table 6).

Table 6. Transition II→III at 51°C and III→IV at 32.2°C

| Crystalline form	Temperature range in which crystalline form is stable	Specific volume	Heat of transition	Specific heat
	°C	cm3/gr	Kcal/kg	Kcal/kg°K
II	84.2-51	0.603-0.598		0.441-0.431
II→III	51		1.41	
III	51-32.2	0.608-0.605		0.367-0.356
III-→IV			5.08	
IV	32.2- -16.9	0.582-0.572		0.423-0.374

Graph1: Variation of specific volume for different crystalline forms of ammonium nitrate according to:
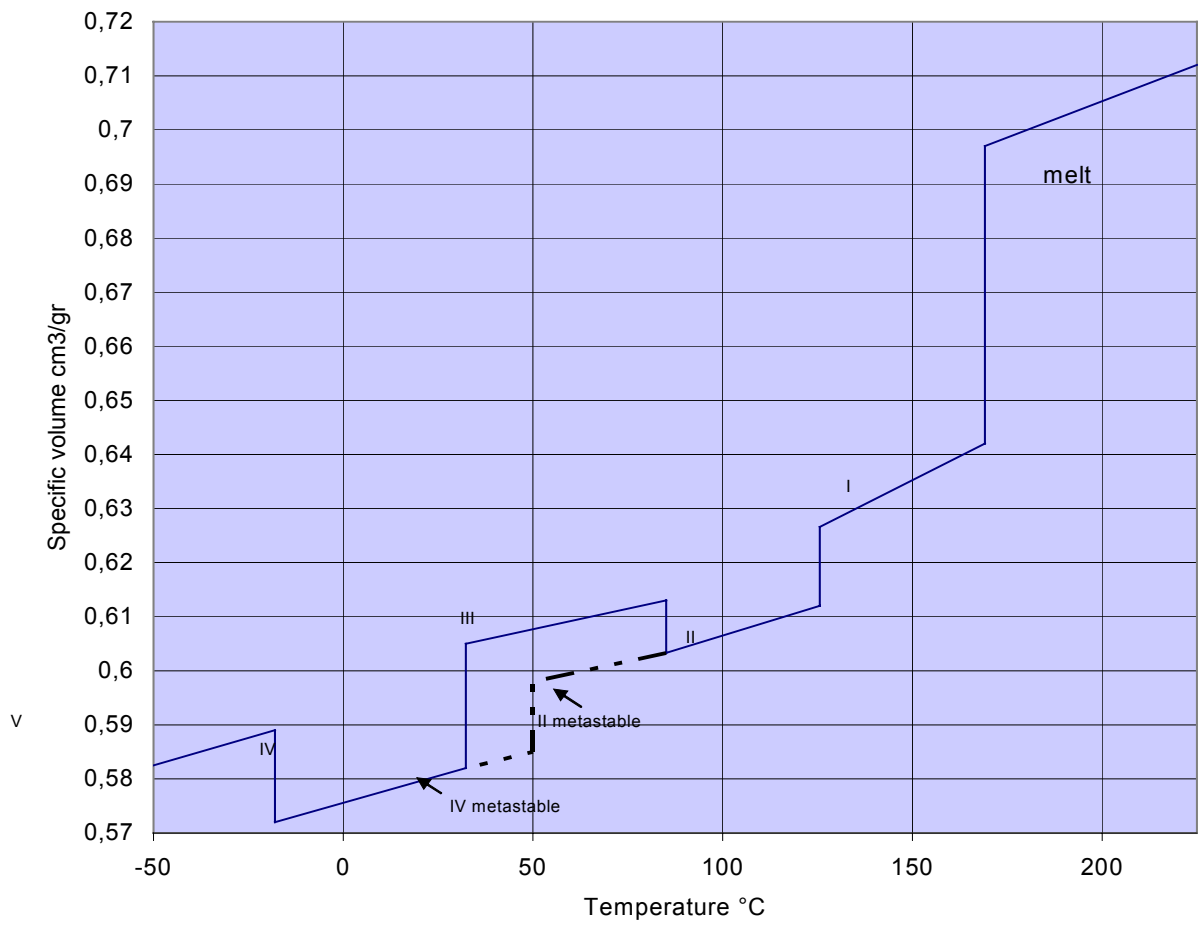
Graph 2: Specific heat of ammonium nitrate
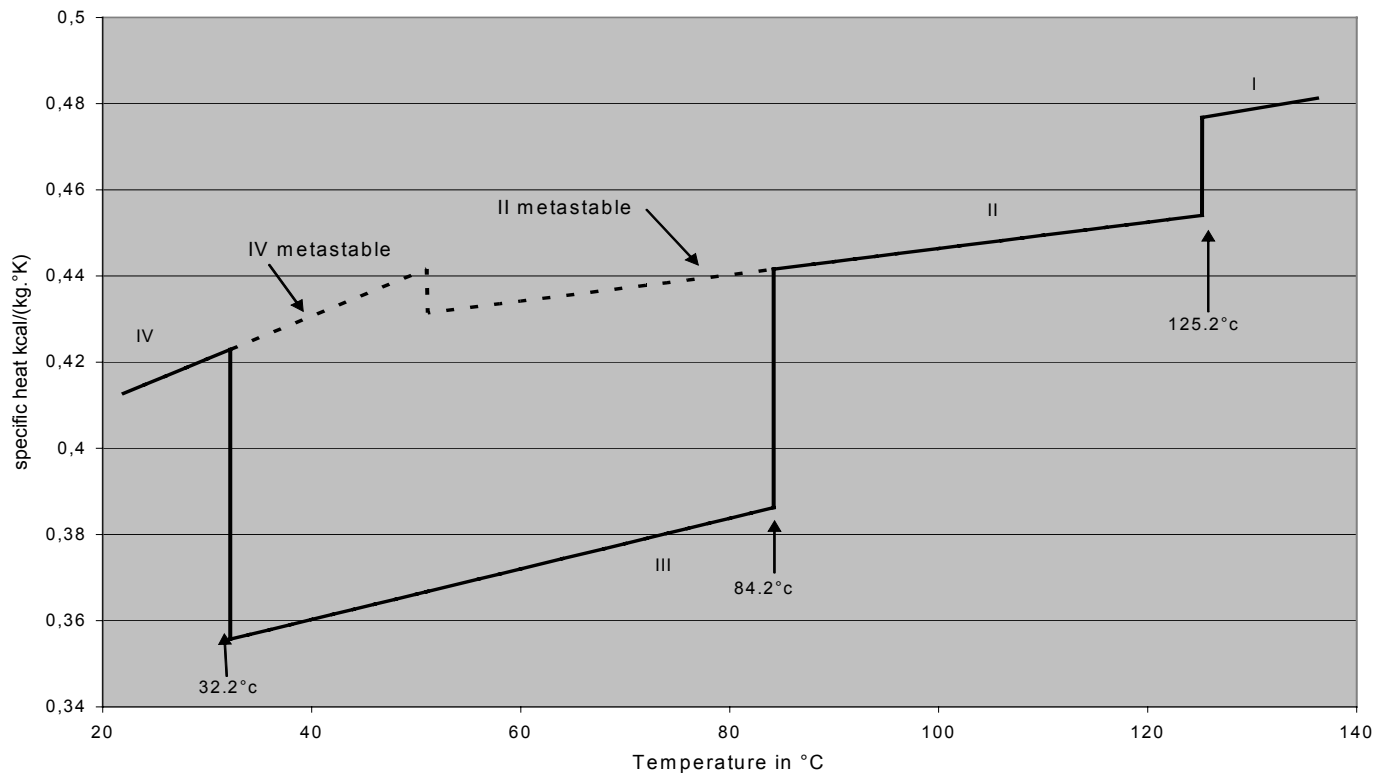
Graph 3: Influence of type of transition:stable (IV-->III-->II) and metastable (IV-->II) on the enthalpy variation of ammonium nitrate with temperature form IV)
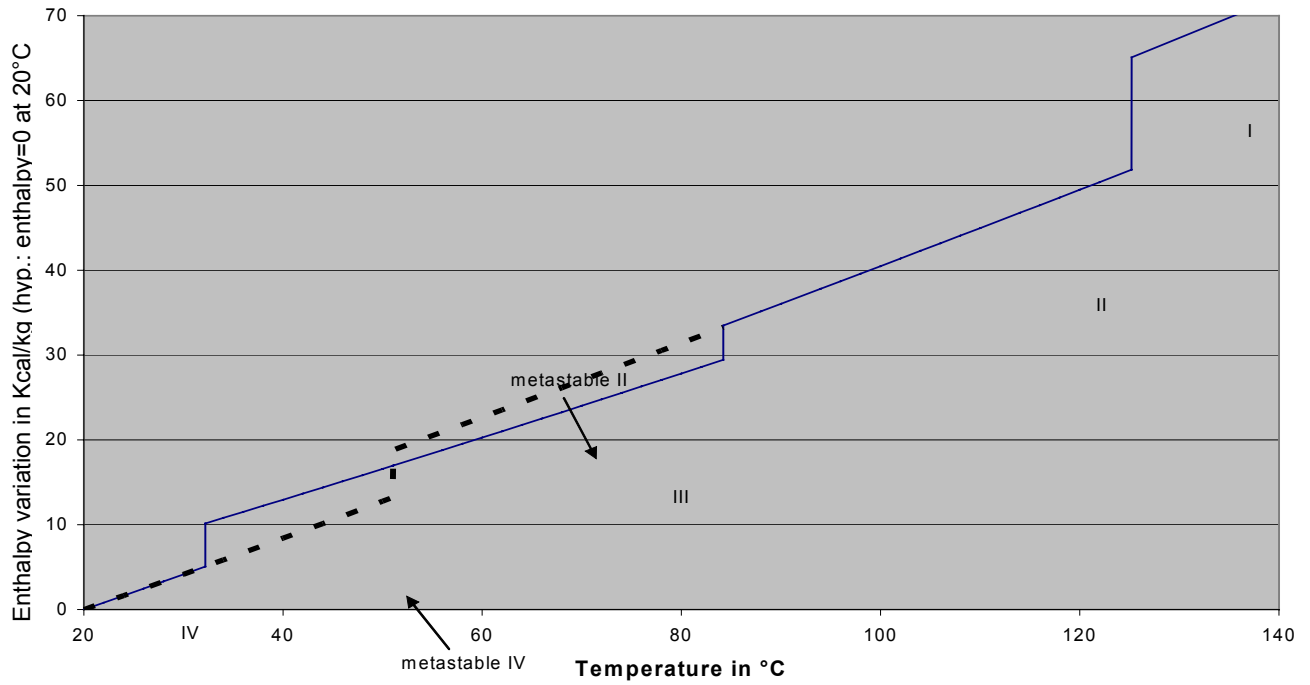
1.3.3 Transition delay – hysteresis

Most of the transformations show considerable delays. One can obtain metastable forms by undercooling or superheating AN far away from its transition point. This is done by entering more or less in the stability field of a neighboured crystalline form.

The delay is bigger when the change of temperature is fast and the temperature low.
The greatest gap is observed with the IV→III inversion, which, as an example, can start at 36-40°C with rising temperature and 28-25°C with falling temperature. When both phases are initially present, the delay is very much less.

This delay and the fact that the transitions are slow close to the transition temperature have complicated the determination of the transitions points and heat transitions from V to IV and IV to III .

If the temperature rises above the II→I transition at 125°C, then, on subsequent cooling, the form II does not invert directly back to III as above , but it persists down to 48 or 45°C, when it changes to form IV.

1.3.4 Kinetic of transition

The kinetic of transition between forms III and IV is influenced by:

> ➢ the number of seeds of the form where the transition goes or in other words the previous thermic treatment of the crystal

> ➢ the humidity of the salt

> ➢ the speed of change of temperature and the temperature

Depending probably upon these factors, it is practically observed that the transition point is shifted in the way of a reduction of temperature after a certain number of transitions.

1.3.4.1. Number of seeds

The transition does not occur homogeneously in the mass.
It pre-exists points where this transition is generated which then diffuse further in the mass.

These points are made of crystals that for any reason have not change during the previous transition in the opposite direction. The number of points depends upon the temperature and duration at which the crystal was kept during the previous transitions.

As an example, analytical AN containing 0.5% H_2O heated at 5°C/min. will make a IV →II transition while the same AN melted and cooled down at room temperature a few days before will make at the same heating speed the IV→III→II transitions.

The analytical AN heated at a slower rate of 1°C/min. will also show the IV→III→II transitions.

1.3.4.2. Humidity

The III →IV transition of moist ammonium nitrate is progressing faster than a dry one.

The kinetic at 31.1°C presented in Graph 4 is obtained by the dilatometric method: one sample is poured in a glass vessel equipped with a capillary tube.

The dilatometer is filled with xylene and immerged in a bath kept at constant temperature. One measures during the time the volume variation and expresses the transformation by recording the graduation of the dilatometer.

The percentage of transformation at the time t_1 is the ratio of volume variation at t_1 divided by total volume variation when transition is finished.

Graph 4: Kinetic of transition III-->IV at 31.1°C
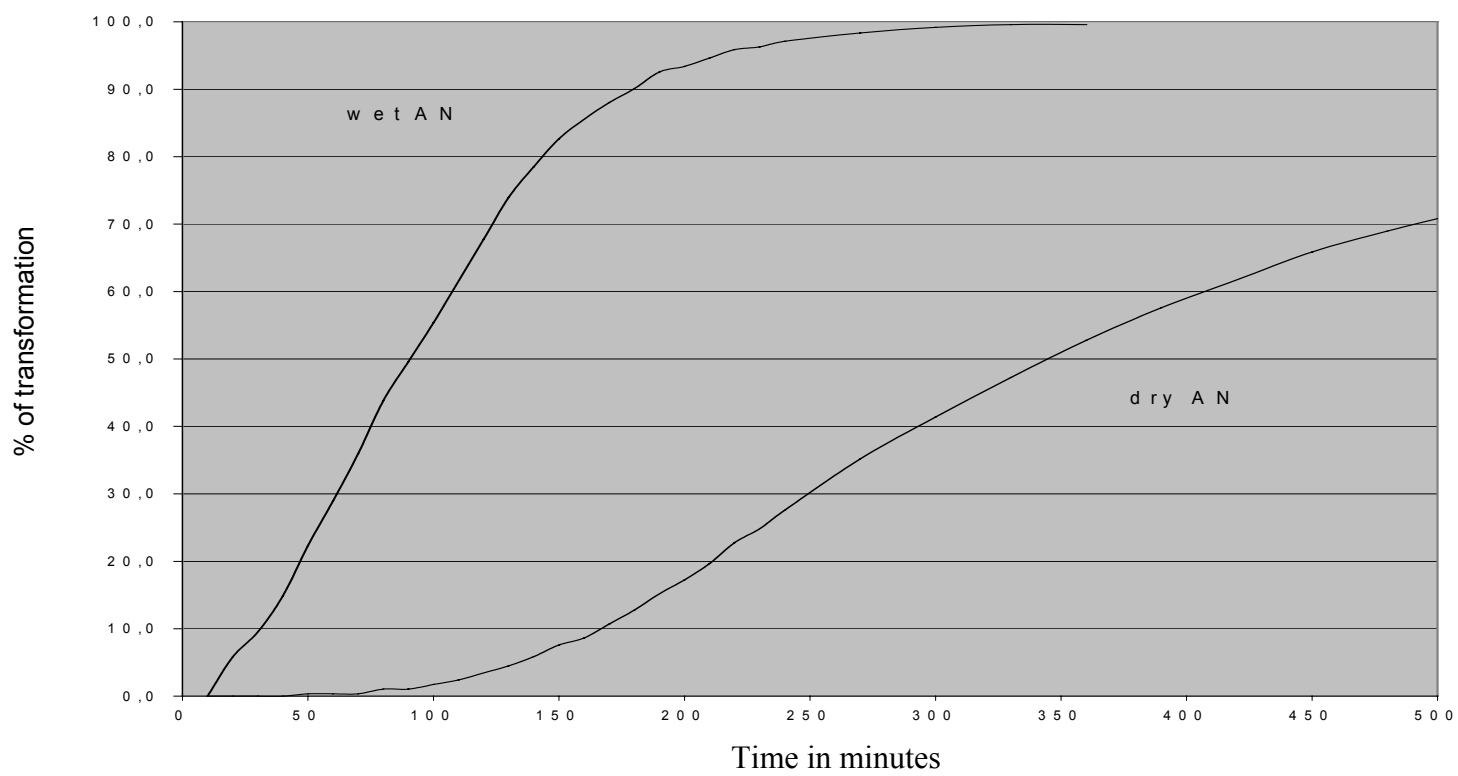
Moisture is contained in the form of a saturated solution: the higher the temperature, the greater the amount of salt dissolved in the water contained in ammonium nitrate. Ammonium nitrate which is very hygroscopic absorbs easily air humidity (Table 1).

The saturated solution enhances greatly the transition of one form to another because it can be realised through the intermediate of the solution. It is suggested even that the IV-III transition can only be made through the dissolution-recrystallisation route.

Practically, one observes that cooling a dry AN compared to a wet one lowers the transition temperature especially when the cooling speed is bigger.

In that case, the salt has the opportunity to cool down before the kinetic of transition has got the opportunity to be in a measurable magnitude.

This is shown in Graph 5 for 3 samples more or less dried in a dessicator where the cooling curve temperature-time is plotted for AN more or less dried.

The III→IV transition temperature is easely observed by the prolonged arrest in the neighbourhood of 32-28-26°C.
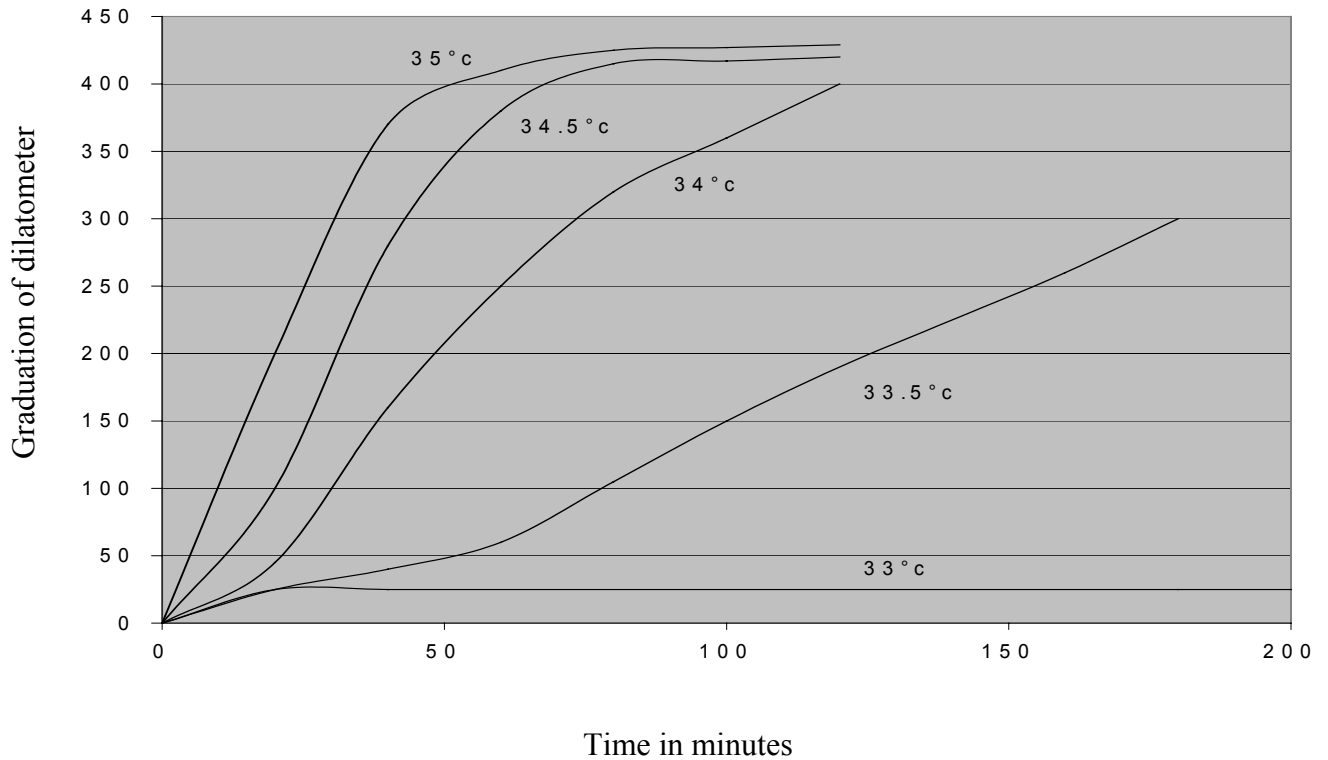

1.3.4.3. Temperature

The kinetic of transition increases when passing the transition temperature if we impose a broader difference of temperature between the surrounding media and the crystal (Graphs 6-7 obtained also by the dilatometric method).

The kinetic increases indefinitively when increasing the temperature while with a decrease of temperature, it increases up to a certain temperature under which the speed of transition reduces again. Undercooling and overheating may occur.

Graph 5: Influence of humidity on undercooling of ammonium nitrate transition III
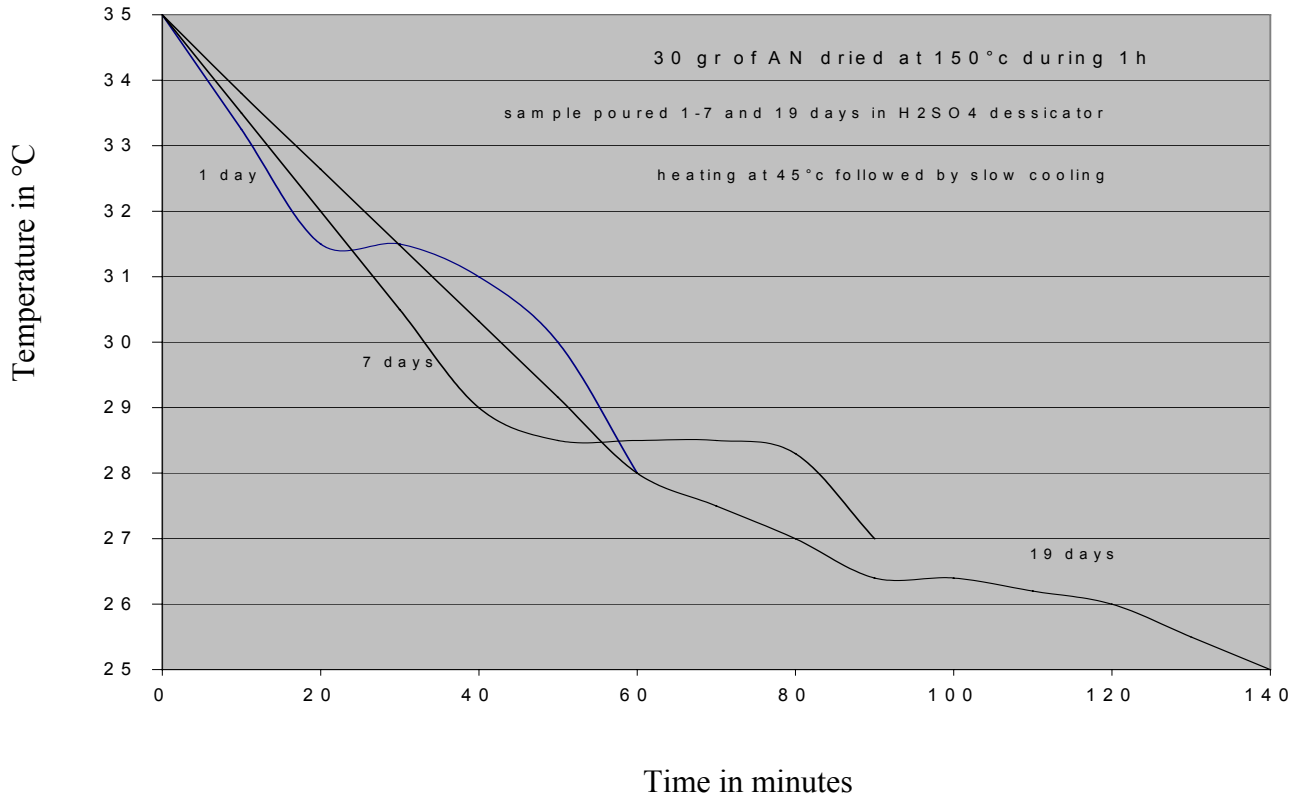
Graph 6: Influence of temperature on IV III transition kinetic on standard AN

The minimum and maximum transformation speed obtained by the dilatometric method with dry and wet AN-CAN fertilizers in function of the temperature around 32.2 and 84.2°C are presented in Graphs 8 and 9.

The curves have been obtained by the dilatometric method on granules and therefore represent a combination of the kinetic of transition but also of the thermic transfer from the granule to the external media.
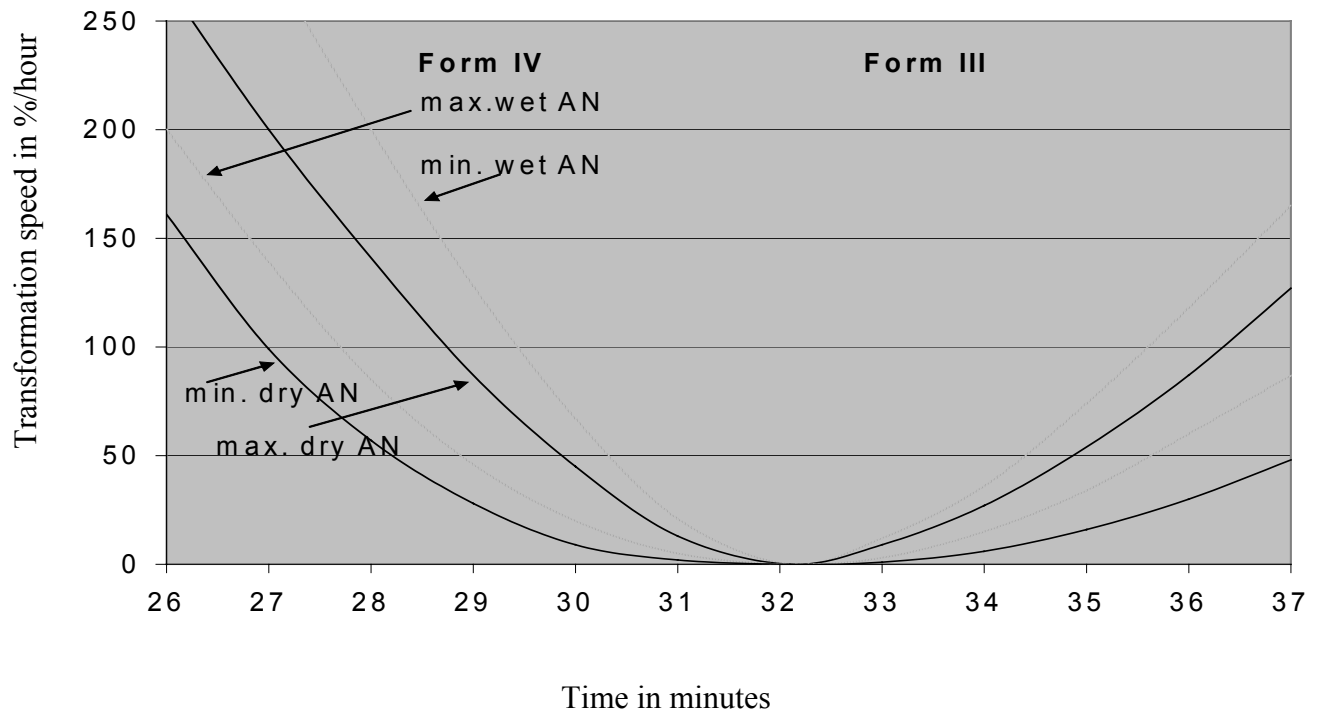
Graph 7: Influence of temperature on IV-->III transition kinetic on dry AN
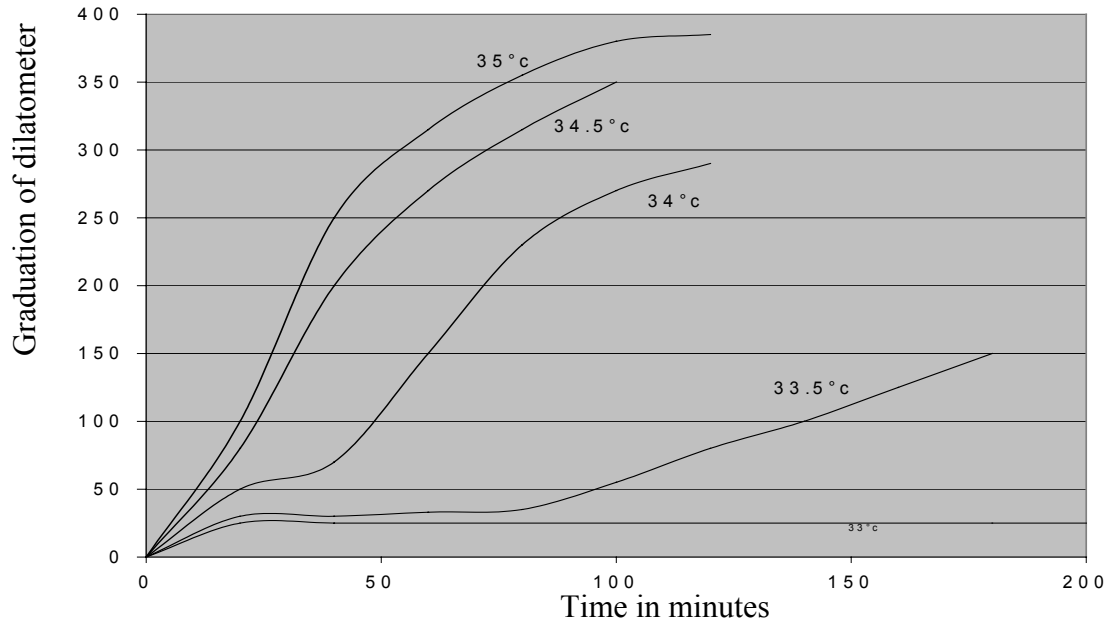

They show that:

- ➢ the transformations are fastened by humidity.

- ➢ the transformation speed increases as much as one is far from 32 or 84°C. The kinetic is bigger at 84°C compared to 32°C.

- ➢ the transformation from III→II and III→IV are quicker than the inverse transitions. This means that the transformations with contraction of volume are faster.

Graph 8: Influence of temperature-humidity on the transformation speed at 32.1°C

Graph 9: Influence of temperature-humidity on the transformation speed at 84.2°C
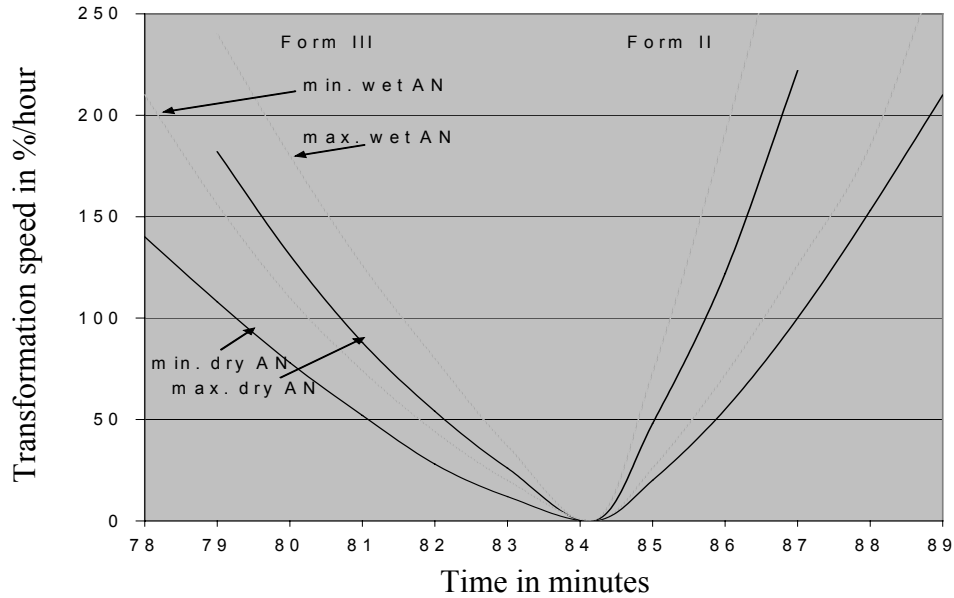
2. Definition of Thermocycling and Thermal Stability

Thermo-cycling is applied on discrete particles of ammonium nitrate fertilizers by raising and lowering their temperature through the phase transition temperatures, of which the 32°C transition point is the most significant in practice related to conservation properties.

The thermal stability is preventing or alleviating the well known phenomenon of thermal shock and cracking of the particles due to deformation at phase transition temperature such as 32°C, in order to modify its properties so that the product may be safely stored for extended periods of time without the development of dust, caking or low density which increases the susceptibility to detonation.

The following equipment is needed to apply the thermo-cycles and to measure the thermal stability.

2.1 Equipment

A climate chamber equipped with the following devices: cooling and heating coils thermostatically controlled, a fan, a heating-cooling timer and a multi-point temperature recorder.

A sample sealed in a container can be thermo-cycled around 32°C or 84 °C several times in a certain period of time. The example in Graph 10 shows a 15-50°C cycle made in 6 hours.
During heating and cooling, one observes stops in product temperature regularly distributed but hardly observed without hysteresis.

Experience shows that rapid thermo-cycle enhance the transition temperature elevation by a superheating effect, which breaks the corralation with field performance.

Thermo-cycles can also be done in a humidified atmosphere.

Graph 10: Example of one thermocycling in a climate chamber: 15-50°c during 6 hours
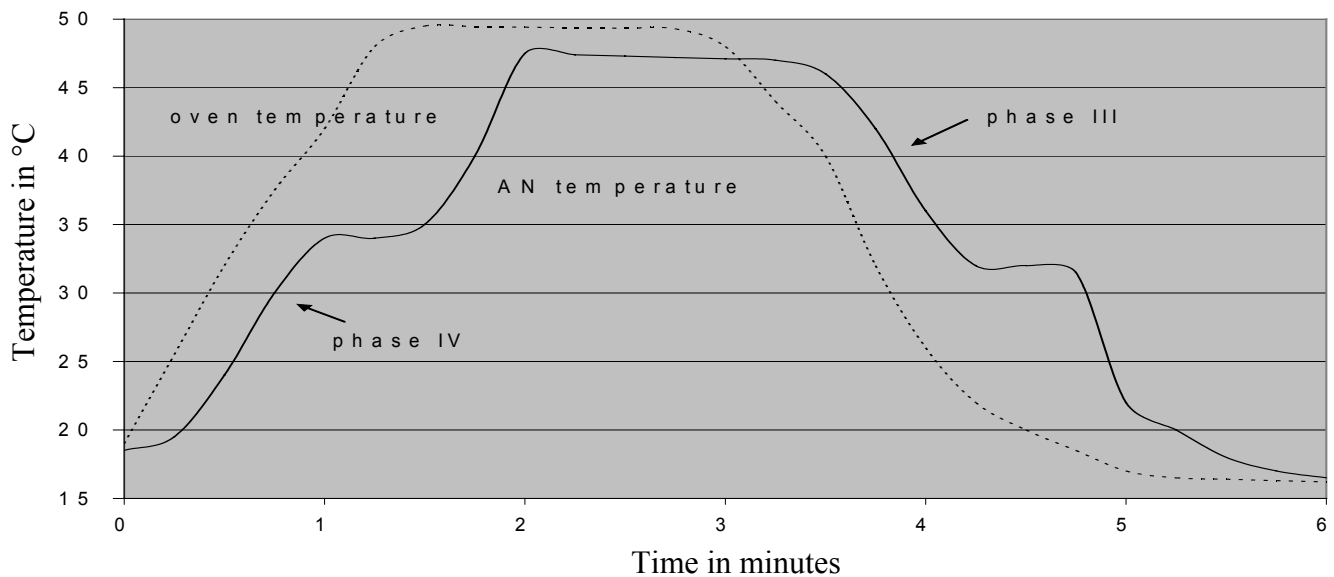
2.2 Measures

The sample can then be further checked for caking, friability, hardness, porosity, swelling, density,etc.
One can measure the percentage of unbroken granules/prills after each cycle.

2.3　Related tests and index

One can tackle stability by the following parameters related to safety and quality:

- ➢ Stability limit for safety: Maximum number of cycles supported by the product before the density is reduced in such a way that the aptitude to detonation becomes apparent.

- ➢ Stability limit for quality: maximum number of cycles supported by the granules without destruction. In practice, one can consider as a stability limit the number of cycles which reduces the initial hardness of granules at a hardness too low for handling.

- ➢ Inertia: number of cycles supported by the granules without any modification of hardness.

- ➢ Hardness angle :mean modification of the initial hardness after one cycle, as per following formule tg $\& = (P°-P)/(P(N-1))$ where $P°$=initial hardness, P =hardness after N cycles, N=number of cycles

3.　**Legal Requirements in Europe**

Several accidents have ensured a poor reputation for ammonium nitrate.
AN has some aptitude to detonation which becomes apparent when it is mixed with some form of organic material. One kg of AN is susceptible to decompose in 0.98 Nm3 releasing 360 Kcal.

Another problem arising from the chemical properties of ammonium nitrate is the risk of decomposition. The onset-temperature is about 200°C, but this may be lowered by certain sensitizing agents, such as chloride ions, copper salts or low pH.

The aptitude to detonation is favoured by the porosity of ammonium nitrate. The porosity can be significantly increased by cracking of the crystals during the crystal transitions. This may lead to the detonation of material which would not have detonated before cycling. The EEC considers that it is necessary, especially when dealing hazardous aspects, to make a judgement on the behaviour of ammonium nitrate under the conditions in which it is being handled.

Therefore, straight ammonium nitrate fertilizers with more than 80% of ammonium nitrate is regarded as a special case on account of potential hazard on which detonation test is done not on the product as such but after 5 thermo-cycles.

However, it is not only the risk of explosion or the possibility of decomposition that are widely discussed nowadays but also the problems of degradation and caking. These are commented in Chapter 4.

Regulations have been set fixing limits for porosity, pH, carbon, chloride and heavy metals.
The legislation of European Economic Community for Europe is resumed underneath.

The EEC directive 80/876/EEC updated successively by the 87/94/EEC and 88126/EEC directives require the straight ammonium nitrate based fertilizer containing more than 28% N to fulfill limits and characteristics of Annex I-II in order to have the EEC label.
These characteristics including thermal stability guarantee the safety of the fertilizer.

Annex 1:
1.The porosity (oil retention) of a sample submitted to 2 TC from 25 to 50°C can not exceed 4% in weight
2.The percentage of combustible material, measured in a carbon form, cannot exceed 0.2% for fertilizer >=31.5% N and 0.4% for fertilizers < 31.5% and >=28%.
3.The pH of 10gr of fertilizer in 100ml H2O must be equal or above 4.5
4.The fraction below 0.5 and 1mm cannot exceed respectively 3 and 5% by weight
5.The maximum chloride level is 0.02% by weight
6.The copper content cannot exceed 10ppm

Annex 2: The detonability of a sample submitted to 5 thermocycles is conclusive when the deformation of one or more Pb supports is less than 5%

Method 1: Method to apply thermocycles

A 70gr sample poured into a 150 ml Erlenmeyer flask is brought through a thermostatic bath to 50°C and maintained at that temperature for 2 hours. The sample is then cooled at 25°C and maintained at that temperature for 2 hours.

These 2 successive phases at 50°C and 25°C defines a thermocycle.
After submitted to 2 or 5 thermocycles, the sample is maintained at 20°C before performing the porosity or detonability tests.

Remarks: some additional requirements are made by some countries. France for instance requests a detonation test every 6 months.

4. The Impact of Thermocycling on AN Based Straight N Fertilisers Quality

Ammonium nitrate, as seen in the previous chapters, possesses a big affinity for moisture, a low thermal conductivity and different crystal forms. All these properties affect the quality of the fertilizers. Therefore, the influencing parameters promoting particles softening, dust and setting are likely to be more complicated than with other inorganic salts. It is easier to consider these parameters as being due to fundamental processes which can be treated individually.

In this chapter, one emphasises particularly more on the impact of change of volume during transitions on the quality and safety of AN-CAN fertilizers.
The impact of transitions during the cooling process at plant site and during the storage is reviewed.

The nitrogen content of AN and CAN is respectively 33.0-34.5% and 20-27%.
NH4NO3 comprises 57-98.5% of the total weight. Water content is less than 0.5%. The rest (limestone, dolomite…) is mostly inorganic additive applied to reduce hygroscopicity and caking of the fertilizer and provide a pH buffer.

4.1 Impact of change of volume on behavior of AN cristals during successive transitions

The forms of practical interest in the production and storage of AN are form IV, which is stable between –16.9 and 32.3°C , and form III, which is stable between 32.3 and 84.2°C.

4.1.1 The cooling process

The cooling of AN-CAN granules which is part of the post-granulation treatment will affect the storage properties of the final product by inducing mechanical stresses.

A granule submitted to cooling, by heat removal from its external surface, develops a thermal gradient, the slope of which determined by the thermal conductivity of the product and the cooling rate.

As a result of this gradient, the colder outside layers shrink more rapidly than the core of the granule resulting in a tension of the crust; the external layer being pulled inwards. As further cooling of the core proceeds, the tension is gradually relieved. When the heat removal is stopped, temperature equalisation starts, which results in a slight increase of the temperature of the outside layers.

The polymorphous transitions during the cooling process around 84 and 32°C, occurring respectively with a 1.3% volume increase and a 3.6% volume decrease, complicate the above scenario.(Table 7).

Table 7. Impact of transition on specific volume

Transition temperature °C	Volume variation %
I to II	2.1 decrease
II to III	1.3 increase
III to IV	3.6 decrease
IV to V	2.9 increase

The II→III transition (84°C)
This transition produces a volume expansion of 1.3%.

After going through the transition at 84°C, the outer layer continues to cool down and starts to contract more rapidly than the underlaying layers.On a further step, the shrinking outer layer encounters an opposite force as the core of the granule starts to expands by going also through the II→III transition. The tension resulting from the contraction of the crust and the expansion of the core will be relieved by the formation of micro-cracks and porosity generating fines.

The III→IV transition (32°C)
This transition produces a volume contraction. The tension created in the crust by cooling is relieved when the core goes through the transition and contracts. Consequently, less porosity is normally created during the III→IV transition.

The various cooling processes take account of this particular behaviour:

1. The cooling procedure can be adjusted to take into account the crystal transformations of ammonium nitrate.
As an example, the back-mixing of granules up and down in a fluidised bed cooler will expose their outlet layer to varying temperatures. This temperature cycling has no damaging effect as long as the outer layer does not cycle through the 32°C transition point.

2. The drum cooler has the advantage that the product progress countercurrently to the cooling air in such a way that it makes the transition only once.

3. In a drum granulator, severe degradation can occur if product leaving the granulator is below 84°C and is reheated above in the drier in order to assist the drying. This will increase the porosity and prolongs the cooling time as does the heat released during the crystal transition at 32°C. The recycling of granules below 84°C in the granulator will also increase the porosity.

4.1.2 The storage of straight AN fertilizers

One can distinguish the caking coming immediately after production and the one appearing after a prolonged storage. Both are influenced partly by the crystal transitions according the following scenarios:

Fresh product leaving the plant
Caking is not only due to polymorphous transitions since dry ammonium nitrate does not cake.
It is a speculation whether the freedom from setting of perfectly dry ammonium nitrate on passage through 32°C is due to complete absence of moisture or to the non-occurrence of transition : the latter being replaced by a II→IV transition at about 50°C.

The caking due to the presence of water is explained as follow :

➢ -During cooling, the saturated solution recrystallizes on the surface of the crystals. This cements them together by a solid bonding of considerable strength.
For instance, 1 tonne of ammonium nitrate with 0.5% moisture at a temperature of 40°C holds in solution about 14 kg ammonium nitrate of which 3.5 kg recrystallizes on cooling to 25°C.

➢ -The effect of the pressure is to lower the solubility of ammonium nitrate. The sudden application of pressure to moist ammonium nitrate during piling in the storage might bring some crystallisation at the points of contact of granules.

➢ The caking of product entering in the storage above 32°C can also be explained by allotropic transformations during the storage:

➢ -As it is suggested that the III →IV transition can only be made through a dissolution-recrystallisation process which as explained above cements the particles.

➢ -The fact that the AN-CAN granules enter in the storage at a temperature below the II→III or III→IV transitions does not guarantee that the transformation is complete.
As an example, based on the graph 7-8, one can say that AN requires at least 30 min. to be completely converted when it is cooled down 5°C under 32.2°C.
The transition can therefore progress in the storage. Due to poor thermic transfer, the release of heat is mainly used to increase the temperature of the mass.
For AN leaving the plant above the transition temperature, one calculates that in the worst case, the release of 5.08 Kcal/kg during transition II →III can increase the temperature by 12°C. The subsequent dissolution-recrystallisation will promote caking.

➢ -A study of the solubility curves of ammonium nitrate in water gives the most plausible explanation of the rapid setting following a transition III-IV. Normally there is a considerable delay in this transition, in the upward direction it may not take place until 45°C, and on cooling until 20°C, so that transition is likely to take place well outside the normal temperature stability range of the salt present. There is a marked difference in the solubilities of the metastable and stable forms of ammonium nitrate

around 32°C. Therefore, in a slightly moist sample, a delayed transition will result in the rapid crystallisation of part of the dissolved solid of the salt. Thus coalescence of continuous granules may occur exactly in the same manner as with temperature variation of moist ammonium nitrate, but in a very sudden and accentuated degree.

Prolonged storage
-Poor thermic exchanges with the external media will cool down the product slowly to the transition temperature of 32.2°C. At that stage, the transition heat will maintain almost indefinitively the temperature to 32°C before it goes down. This passage can cause some cracked granules and dust formation.

On storage, the cycling of ammonium nitrate through the 32°C transition zone induced by diurnal temperature variations is accompanied with a 3.6% expansion in volume. After several cycles, AN prills or granules may soften, fracture, expand and finally convert to a fine powder with an increased detonability properties (bagged products can even burst the bags). Even if dust is absent from the product when packed, it will subsequently be formed on handling and storage rendering the product more difficult to handle and the spreading pattern uneven.
Another consequence of that physical weakness is that the product turn to a solid, hard cake during storage.

The dissolution-recrystallization of the saturated solution on the surface of the crystals during thermo-cycles even milder than those needed to cause transitions destroy the granules:
Indeed, the water migrates also across granule boundaries when the temperature cycles are milder then those needed to cause transitions.
The disintegration of the external surface during thermocycles may serve to release included saturated solution, and thereby give rise to caking, on further temperature variation of the salt. These inclusions present as a mother liquor are located in elongated cavities included between the long, needlike and often tabular ammonium nitrate crystals.

Ammonium nitrate is a very hygroscopic salt. The formation of a wet skin of saturated solution on the surface of the crystal exposed to air during storage will therefore participate to the destruction by increasing the kinetic of transition and recrystallisation phenomenon.
Coating oils that are used to suppress the immediate caking can increase the degradation caused by temperature changes through the crystal transitions, especially when they contain secondary amines and short length amines.

In conclusion, it is probable that the setting of ammonium nitrate on passage through the 32°C transition must be explained by a cumulative effect of all the phenomenon described above.
A good resistance to thermocycle will improve the quality by reducing degradation during transport and storage. The transition at 32.1°C is particularly harmful in climates where ambient temperature is often close to that number or when bags are exposed to sunshine.

For this purpose, various cycling tests using laboratory oven were developed by the industry. The stability against thermocycles can be characterised by several parameters based on physical properties of granules and by establishing criteria for quality after each or several thermocycles.
These measurements can be the density, granulometry, swelling, hardness, porosity, friability, dust, etc.

The minimum values of physical properties that are needed to overcome quality problems and assure product safety are settled in order to be in accordance with a standard.
These tests are used to select additives in order to improve the thermal stability.
The additives that are proposed are presented in chapter 5.

5. <u>Ways to Improve the Thermal Stability</u>

As the change in volume is a primary cause of breakage, many experiments have been centered on the elimination of transition III-IV, on the extension of the temperature range over which the ammonium nitrate exists in the forms IV or on the shift of the transition point of the crystal form to a temperature range never occurring during storage, handling and use of the product.

It is done by deep drying or by inclusion of a small amount of conditioning agent to the ammonium nitrate preferably in the melt prior to the particle forming.
It was also developed where insufficient cooling of the product has been carried out prior to storage or bagging.

Many materials have been tested alone or in combinations like natural phosphates, potassium metaphosphate, mono and diammonium phosphate, sulfates (ammonium, calcium, potasssium), potassium chloride, magnesium salts, calcium salts, sodium silicate, clays, sodium-calcium and potassium nitrates, iron cyanides and copper oxides.

Numerous salts equilibrium with AN have been studied in order to prepare double salts which could be easier to use to prepare fertilizers.

The practical advantage is to increase discrete particles's resistance to degradation by temperature cycling and often also the quality of prills or granules.

There are several ways to overcome the cycling problems and many patents have been granted for additives with varying effectiveness:

5.1 Increasing the transition temperature

5.1.1 <u>Minimizing the free water content</u>

5.1.1.1.By deep drying

Since the structure of phase III has no obvious similarities with the other ones, it is suggested that the transition III –IV must take place by the dissolution and recrystallisation of the solid.

This theory is supported by the fact that the transition at 32°C disappears when AN is exhaustively dried and is replaced by a transition at about 50-55°C. It is generally conceded that this transition is a metastable transition between forms IV and II and therefore eliminates form III from the phase diagram together with the transition at 84°C.

As shown in Graph 11, the transition temperature from form IV to III is a continuous function of the percentage of water contained in the nitrate between 32 and 55°C. So, depending of the water in the sample, the transition from form IV to III may occur anywhere in the temperature range between 32 and 55°C. The transition temperature form III →IV plotted also as a function of water content is the mirror-image of that for the phase transition in the opposite direction. Drying the AN fertilizer below 0.03% H2O can therefore be a method of stabilizing against thermo-cycles. Some salts like sodium nitrate (0.1%) overcome the influence of dehydrating the ammonium nitrate.

Graph 11: Influence of water on the IV-->III transition temperature of pure ammonium nitrate
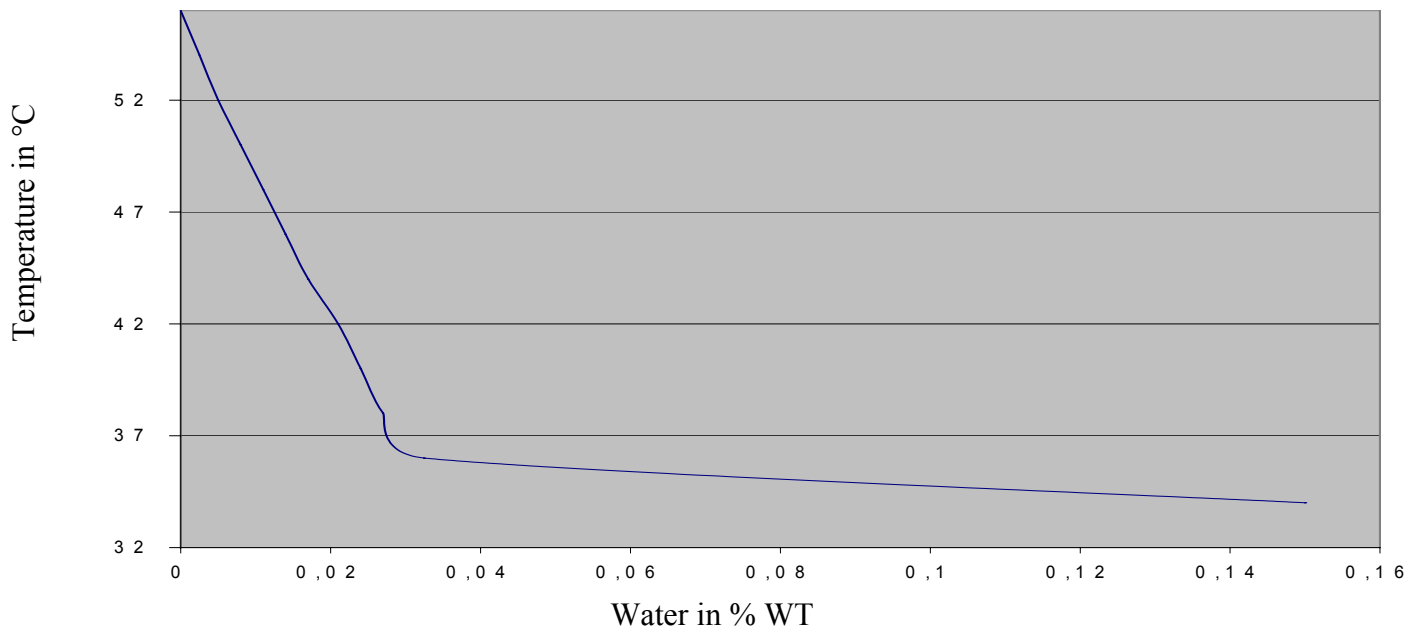
5.1.1.2. By addition of internal dessicants

Stability can be obtained by adding additives taking up moisture from the surrounding ammonium nitrate bulk.
This results in a water content low enough to prevent the phase transition IV—III at 32°C.

5.1.1.2.1. Additives binding crystal water
Some inorganic additives bind reversivly crystal water. As an example, one can follow the dehydratation of aluminium sulfate in function of the temperature in Graph 12. It shows hydrates containing 18, 16, 10 and 6 moles of H2O.
During the granulation process, these salts can lose partly their crystal water in the AN melt and pick it up again during the storage.

Graph 12: Al2(SO4)3.18H2O dehydratation
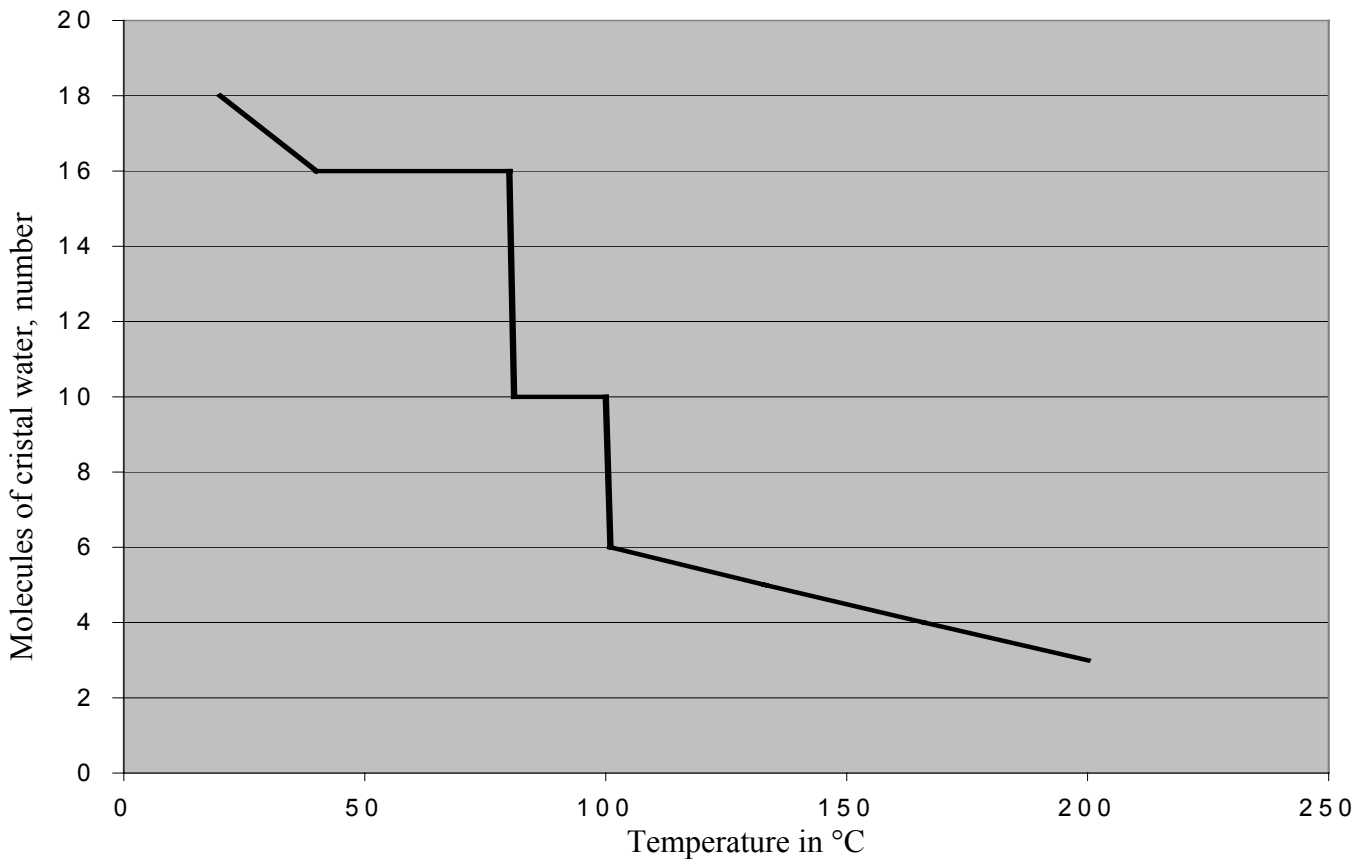
Al2(SO4)3.17H2O at a rate equivalent to 2% Al2(SO4)3

The addition of aluminium is made by adding Al2(SO4)3.17H2O to a melt of NH4NO3.

A white colloidal precipitate of additive is obtained rapidly and the pH is lowered to about 1.

The decrease in pH is regulated to about 5 by adding NH3.

No growth of aluminium additive can be detected if pH is maintained below 6. Above 6, the aluminium additive starts to agglomerate.

Aluminium is located in small aggregates of 1-10μ diameter in the prills; the following formula being probable : Al2(SO4)3(NH4)2(OH)2(H2O)6-10 where NH3 is chemically bound.

The amount of loosely bound zeolitic water of the additive in the AN melt depends of the temperature. 2 to 3 moles of water could be bound with AN at 165°C while all the zeolitic water disappears at 180°C after 8 hours.

In prills with 2% Al2(SO4)3, this means that a consumption of 0.40% H2O corresponds to an increase of 4 moles of water in the Al-additive. This material has a lower buffer capacity in the case of moisture uptake than Mg(NO3)2

<u>MgO or Mg(NO3)2.xH2O (X=4-6) equivalent to 1-2% Mg(NO3)2</u>

Magnesium nitrate is probably the most popular inorganic salt used to prevent caking. Magnesium nitrate increases the IV to III transition continuously from 32 to 55°C and the III to II transition from 84 to 90°C (Graph 13)

Graph 13: Phase diagram for the anhydrous system NH4NO3-Mg(NO3)2
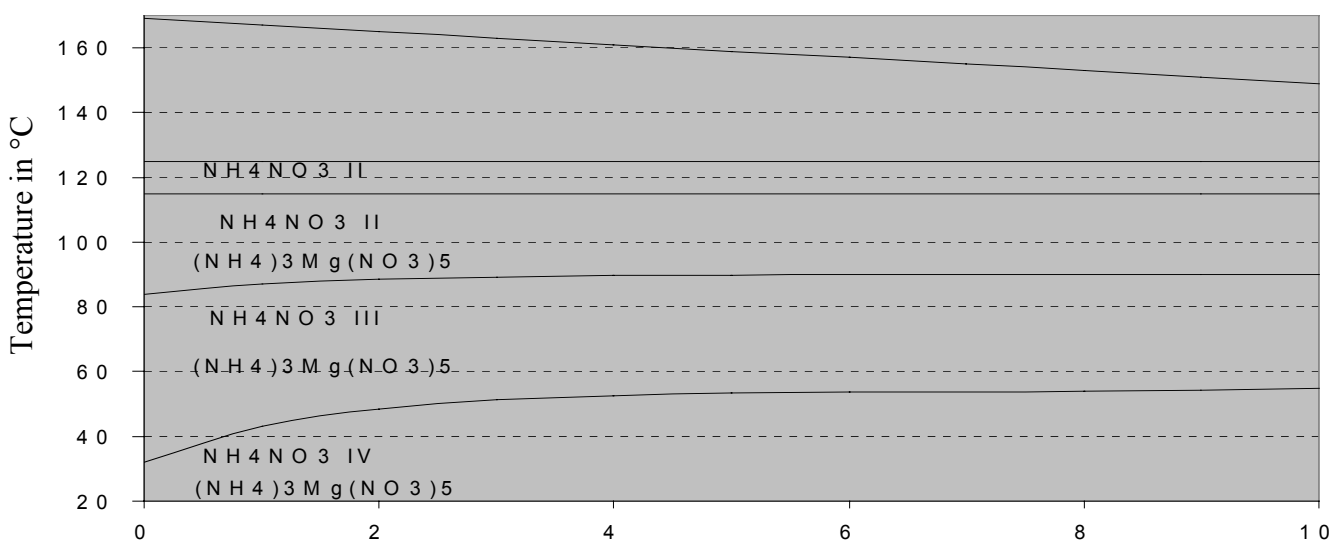
Mg(NO3)2.2H2O is recognised to give better stabilisation than if Mg(NO3)2.6H2O is used. It is therefore suggested that the additive can take up moisture from the ammonium nitrate.

Magnesium nitrate is added in the AN melt. At this stage, the high temperature and low amount of water brings magnesium in a soluble and anhydrous form.

One observes that the additive does not distribute homogeneously throughout the solid prill but in veins in the (NH4)3Mg(NO3)5 form.

This vein distribution is due to the different melting points of the salts : the AN that crystallizes first excludes magnesium nitrate until it is all solidified.

After the granulation, magnesium nitrate pumps the remaining water in the NH4NO3 bulk until it reaches an hydrostatic equilibrium. This is possible because magnesium nitrate with less than 6 molecules of H2O is much more hygroscopic than AN. Thus the AN bulk will be almost free from water, so that the transition IV→III will be prevented.

As an example, AN prills containing 2% Mg(NO3)2 and more than 2.5% H2O will show a

$$Mg(NO3)2 \text{ %WT}$$
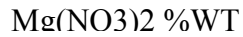
phase transition IV→III taking place at a constant temperature of 37°C. With a water content of less than 1.09%, the phase transition is received at a constant temperature of 52-53°C. In the range 1.09 to 2.5%, the transition temperature decreases rather rapidly (Graph 14).

Graph 14: Phase transition temperature IV-->III;II as a function of the water content for magnesium-ammonium nitrate (2%) prills
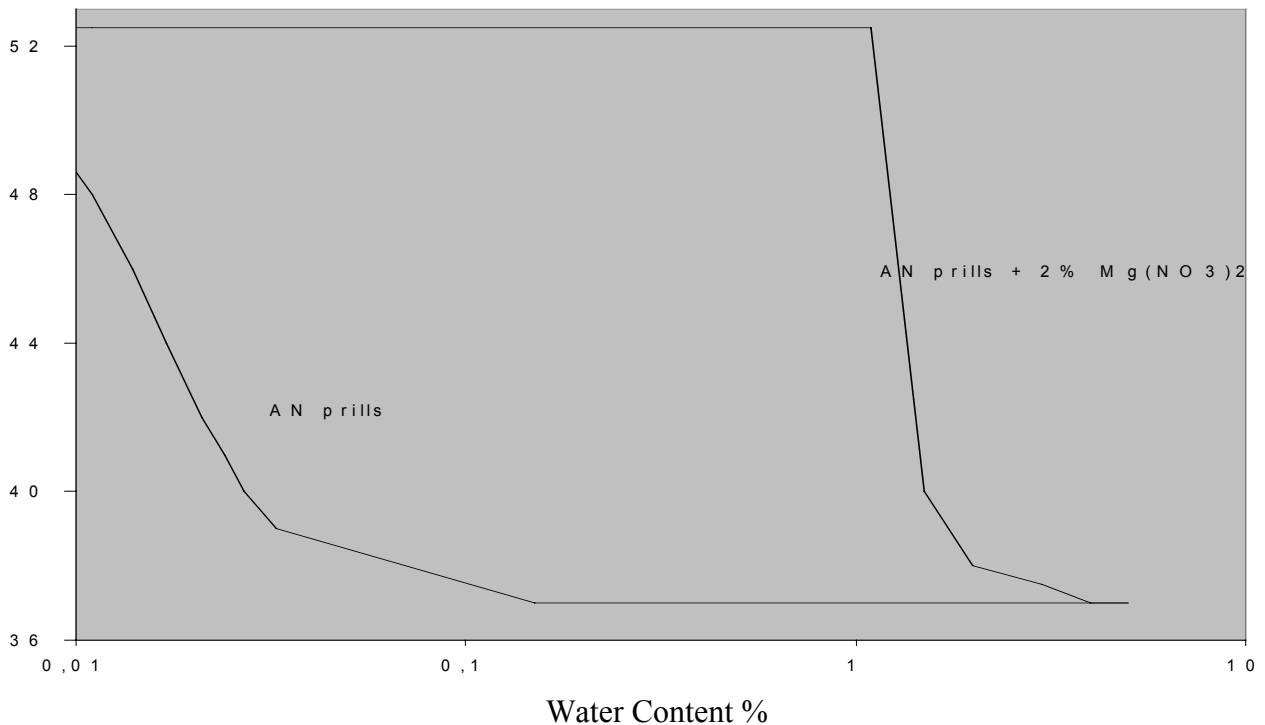
Water Content %

This means that a consumption of the water-content of the AN bulk of 0.24% corresponds to an increase of 1 mole of water of crystallization in the magnesium nitrate additive.

The position of the plateau in the curve in Graph 11 should correspond to 4.5 moles of water in the magnesium nitrate.This may mean that a mixture of Mg(NO3)2.2H2O and Mg(NO3)2.6H2O with an average water amount of 4.5 moles of water is the hydrostatic equilibrium with almost water-free AN.

Normally, producers use an excess of Mg(NO3)2 so that their product contains a internal drying capacity against moisture uptake, and any water picked up during storage and transport is bound as water of crystallisation.

Magnesium nitrate can be formed by adding MgO or MgCO3 to the nitric acid flow before the neutralizer.

Adding as little as 0.1% MgO to the melted ammonium nitrate will move the transition temperature between form IV to III to 40°C. Increasing the MgO to 1% raises the transition to 55°C. In that case, a sample cycled hundred of times in the temperature range between 20-45°C will not show any transition, swelling or caking. This is due to a slow reaction that occurs between AN and MgO to produce ammonia, water and magnesium nitrate.

A potential disadvantage to use soluble salt is their contribution to hygroscopicity.
As compared to standard prills, Mg(NO3)2 containing prills have a critical relative humidity below 10%.

Since hygroscopicity is almost as important as particle stability, other methods of stabilisation have been investigated for bulk storage as the initial fast water pick-up rate could be a factor in serious caking if product is not quickly bagged.

Some companies have developed a hydrophobic coating which allows them to use the powerful Mg(NO3)2 stabilisation without getting into troubles with hyroscopicity by bulk handling.

Ca(NO3)2.4H2O
Calcium nitrate also extends the stability of form IV → III up to a maximum of 50°C.
It has little influence on the temperature of the III →II transition.
Under low pressure, the transition II to IV occur; after release of the pressure occurs an immediate retransformation to form II.

A content of Ca(NO3)2 also leads to a very hygroscopic product.

Clays.
0.5 to 3% of porous inorganic substance with a particle size <100μ like alumina gel, silica gel, bentonite, attapulgite, zeolites, montmorillonite are often used to increase the strength of the particles and improve the resistance to transition.
Montmorillonite is also a nucleating agent (see chap.5.4.2.)
As an example, one can see in table 8 the effect of 15kg/T of various clays on CAN 27% dolomite based.
It shows that the quarry from which the clay is originated has a dramatic effect on its efficiency.

Table8: Influence of clays on thermal stability of CAN 27% dolomite based.

			Blanco	Attapulgite			Montmorillonite
				Min-U-Gel	African	Tolsa	
AN		Kg/t	771	771	771	771	771
Dolomite		Kg/t	229	214	214	214	214
Clay		Kg/t		15	15	15	15
Hardness		N	52	100	62	67	81
	After 10TC	N	12	72	36	48	68
	After 20TC	N	4	50	9	17	49
	After 30TC	N	2	44	4	10	49

5.1.2 Double salt formation

5.1.2.1. Ammonium sulfate (AS)

Small amount of sulfates improves the stability of AN only at moisture contents <0.3%.
As an example, K2SO4 is known to stabilize AN but not to improve the strength of the particles.
In addition, ammonium sulfate (AS) increases also the strength even at 0.6% moisture by favoring a more compact packing of the crystals.
Ammonium sulfate (AS) forms with AN 2 double salts having different molar ratios of nitrate to sulfate, containing free AN and AS : 3NH4NO3.(NH4)2SO4 and 2NH4NO3.(NH4)2SO4
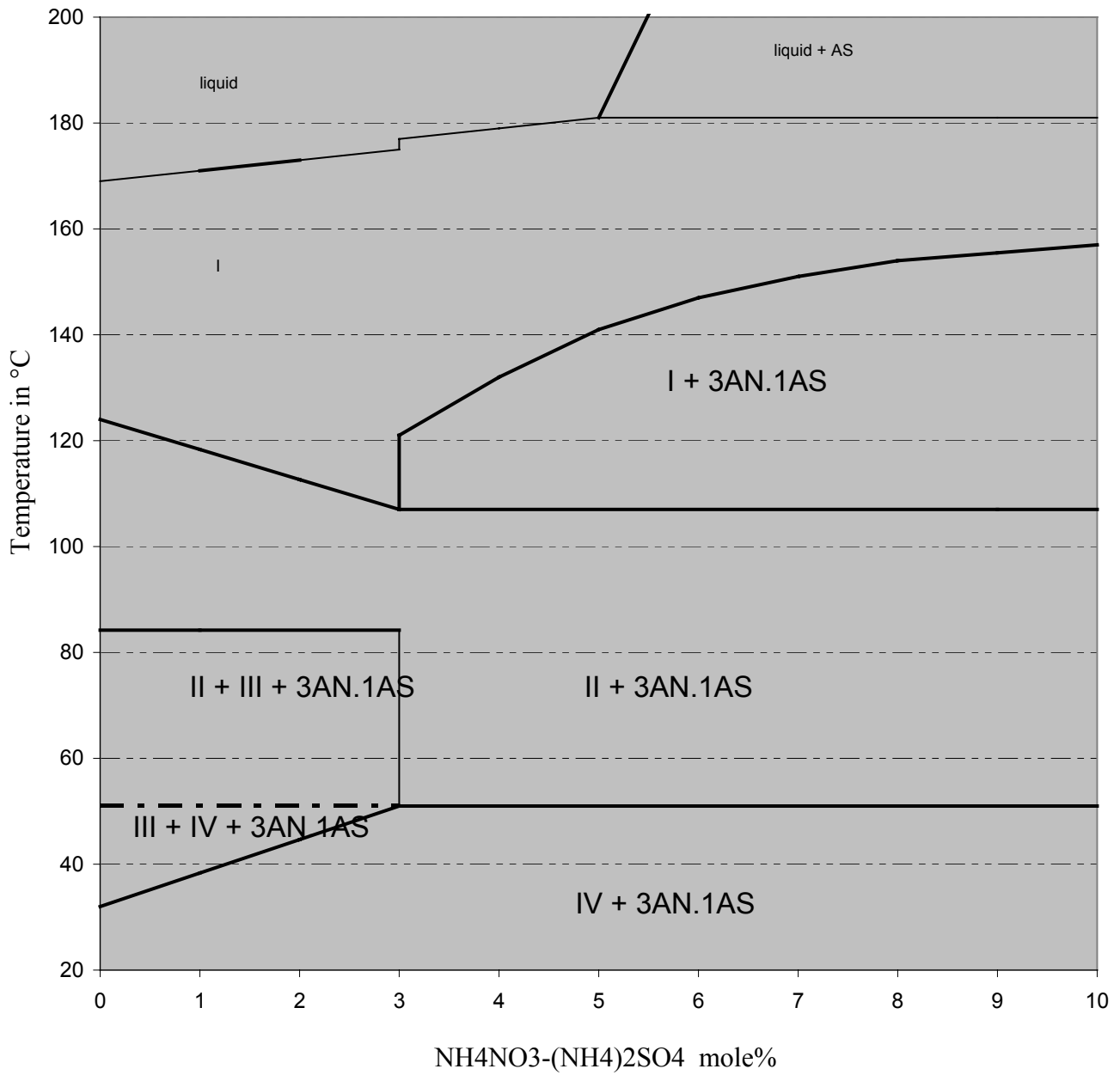The phase diagram of AN-AS is presented in Graph 15.

3 Cases can be considered:
  ➤ AS >5% molar: Above 5%, the melting point rises quickly from 181°C and AS crystallises alone from the melt under cooling.
  ➤ AN form I crystallises at 181°C and 3AN.1AS appears at 140 (5%AS) or 162°C (10%AS). By heating above 162°C, 3AN.1AS decomposes into AN form I and AS.
  ➤ The form III is suppressed: form IV transforms directly in form II at 51°C. The transition I → II is done at 107°C instead of 124°C.

3<AS<5% molar: *idem* except that all AS is dissolve in AN melt. The double salt appears at a lower temperature.

AS<3% molar: melting point increases from 169 to 176°C. The transition I→II+3AN.1AS is lowered from 124 to 107°C. Between 0 and 3% AS, the transition point IV→III gradually increases from 32 to 51°C.

Graph 15: Phase diagram pf NH4NO3-(NH4)2SO4 system

liquid

liquid + AS

I

I + 3AN.1AS

II + III + 3AN.1AS

II + 3AN.1AS

III + IV + 3AN.1AS

IV + 3AN.1AS

Temperature in °C

NH4NO3-(NH4)2SO4 mole%

5.1.3 H3BO3 0.2%-(NH4)2HPO4 0.2%-(NH4)2SO4 0.01%

Basic patents have been granted in the sixties in order to stabilize both low and high density prills through the addition of boric acid (or ammonium or an alkaline salt) + mono or di-ammonium phosphate + ammonium sulfate.

A mixture of 0.4% by weight of the 3 following ingredients is used to achieve the highest degree of stabilisation: 0.135% H3BO3, 0.01% (NH4)2SO4 and 0.2% (NH4)2HPO4.
Large amounts of ammonium phosphate are usually required to improve the stability of ammonium nitrate. However, when used in conjunction with the boric acid and diammonium sulfate, very small amounts effectively improve the stability.

These prills withstand 10 cycles between 2-60°C and 1400 transitions between 21-43°C without any breakage.

The transition temperature at 32.2 and 125.2°C are relocated to 43-45 and 124°C and the transition at 84.2°C no longer occurs. It is claimed to reduce water absorption.

5.2 Lowering the transition temperature

5.2.1 Addition of cations that replace NH4+and blocks the transition

Ammonium nitrate can give solid solution by substitution of NH4+ ion. Attempts to substitute NO3- have been unsuccessful.

The ionic radius of NH4 being 1.43A°, it can be substitute by ions having same radius: K, Rb, Tl, Ca

The influence of these ions is linked to their radius value.
The IV$\rightarrow$III and III$\rightarrow$II transitions are facilitated, and their temperature lower when the ion is smaller than ammonium (like K) and more difficult, and their temperature higher when the ion is bigger than ammonium (Ca,Tl)

KNO3:

Potassium has a radius of 1.33A° which is lower than NH4+ radius: 1.43A°.
At ambient temperature, at least 25% of NH4+ in the form III can be substituted by K. A double salt NH4NO3.2KNO3 appears when K is above 25%.

It can be added as potassium nitrate in the HNO3 before neutralisation or in the AN melt.
As shown in graph 16, potassium nitrate lowers the IV$\rightarrow$III transition about 6°C for each percentage which is added. By adding sufficient KNO3, it is possible to render form III the stable form throughout the range of normal temperature.

In order to obtain an appreciable effect, the amount of KNO3 should be higher than 5-10%.

At a rate of 2% in a 34%N prilled fertilizer, it is said that it increases the hardness, density, reduce the volume expansion at the transition temperature and hygroscopicity by increasing the CRH.

It is interesting to note that a 10% KNO3-90% AN mixture, although not specially dried, cannot be made to set hard on temperature variation through 32°C, any setting experienced being slight and easily explained by the effect of simple solubility changes with temperature. Another advantage is that it reduces the cooling needed as it is not needed to take out the transition heat III→IV.

In a dry sample, potassium nitrate is effective to cause the persistence of phase III below the transition point of IV to III.

Graph 16: Phase diagram of NH4NO3-KNO3 system
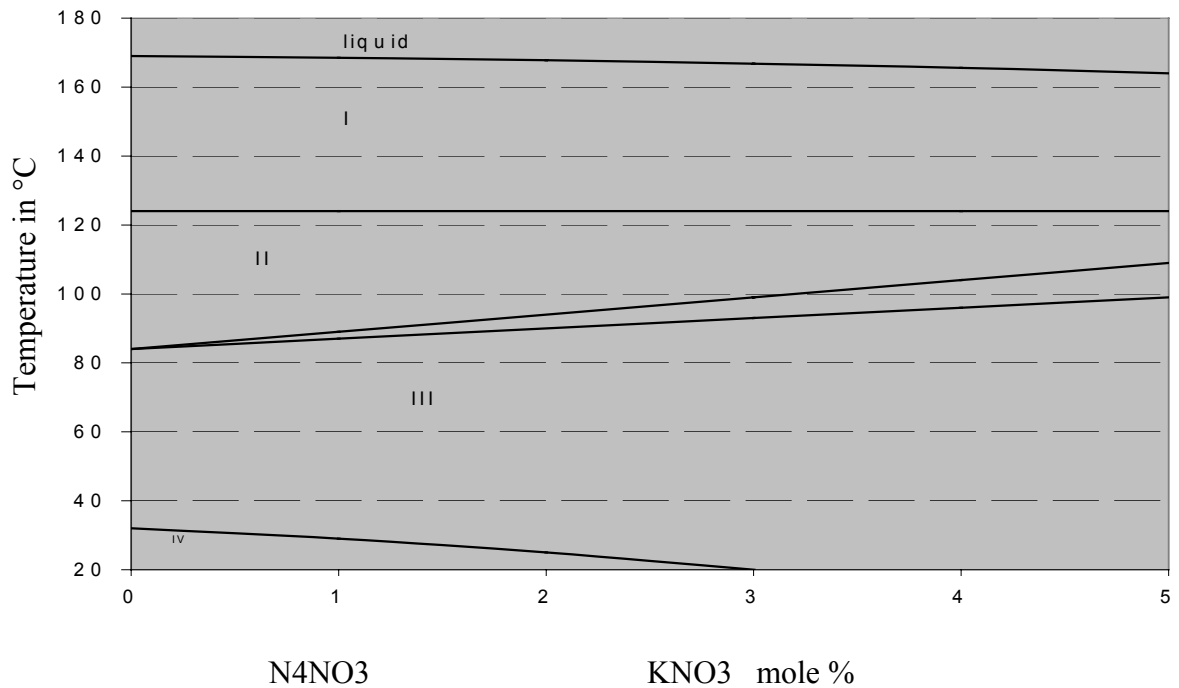
5.3 Reduction of the kinetic

It is said that acid magenta reduces the kinetic of transformation from form IV to III.

5.4 Crystal habit modifiers

5.4.1 Tensioactives

Small amounts of external materials dissolved in mother liquid can modify crystal habit.
These materials can be incorporated by adsorption, solid solution, crystallisation in the crystals when these are in formation. They modify the habit by reducing the growth speed of some particular faces.

On AN, the habit modifiers induce crystallisation in forms such as prisms, plates or scales rather than the usual, less desirable elongated prisms or needles. The surfactants reduce surface tension of the saturated solution, thereby reducing the cross-sectional area of bridges between adjacent particles.

Crystallisation of AN added with acid magenta results in the deposition of extremely soft lamellar aggregates of the modified crystals, which when isolated are very fragile, thin plates or scales. The setting tendency of the salt is very greatly reduced.

It modifies the habit of the dissolved salt during the subsequent re-crystallisation process (which normally produces the hard setting), causing the formation of thin, fragile, platy crystals instead of the usual more robust prisms and needles.

Thus the bonding between the crystals in the mass becomes of much reduced mechanical strength, readily broken by light shearing forces.

By the addition of surface-active agents to the molten AN in very small amounts, between 0.0001 and 1%, rhombic, needle-shaped or plate-shapped crystals in form IV are obtained. These are very brittle and friable, as they have a dendritic structure.

5.4.2 Nucleation agent

Recognising the influence of solid impurities on the ammonium nitrate prills, C&I/Girdler Corp. have tested nucleating agents in the range of 0.1-10%. The aim is to produce a fine-grained crystal, as compared to a large-stressed crystal, by eliminating super cooling in the prilling tower.

They have found that it is now possible to discharge the product from the cooler below 51°C without experiencing prill degradation during processing and storage.

5.5 Various other experiments have been published

- -2.5-5% ammonium polyphosphates or potassium polyphosphate shift the IV-III conversion into a higher temperature range: 42-55°C. NH4 polyphosphates can be obtained by addition of urea phosphate

- -less than .5% each of Na2SiF6, (NH4)2HPO4 and (NH4)2SO4

- -2-5% reactive dehydrated gypsum and 2-5% (NH4)2SO4

- -0.5-2% potassium fluoride (KF)

- -diammine dinitrate of Ni, Cu raises the transition above 50°C. The effect of the Zn complex is less marked.

- In nitrochalk, MgSO4 or (NH4)2SO4 stabilizes the NH4NO3

- dispersive additives (1-3%) of natural minerals like glauconite, pyrophyllite or clinoptilite increase the thermal stability and strenght of granules.

- Zn(NO3)2 0.5% stabilises AN at 51°C

6 Pro's and Con's in Selecting the Optimal Stabilizer

Only a few additives have been successful commercial.

The selection of one additive from another is possible after establishing criteria for requested product and a series of laboratory tests for measuring conformity to a standard.

The simple following tests are used: measurements of hardness, friability, bulk density, caking, hygroscopicity, porosity applied before and after thermo-cycles.

The selected additive should also fit the best with the following requirements:

- -prevent thermal shock and cracking at phase transition temperature during the process and storage ; so reducing the fines formed during the granulation and avoid dust-caking during storage

- -be efficient at low amounts. This is particularly important in concentrated AN fertilizers like 34.5%N where there is no place for a filler. The addition of several additives working in combination can reduce the total amount: AS +AlS additives containing nitrogen can be valorised: magnesium nitrate, ammonium sulfat

- -incorporated in the molten ammonium nitrate prior to solidification. Advantage is that it is better disseminated in the mass.

➢ inexpensive: clays can be inexpensive if quarrys are close to the plant; the same for AS if there is caprolactam, cokery waste available (needs to be pure enough).

➢ readily available at production sites. This is especially the case when it is part of the used materials or by-products at fertilizer complexes like silicofluorides, phosphatic shales…

➢ safe: Aluminium sulfate is suspected to promote Alzheimer's disease.

➢ simple to apply: AS has to be dissolved in the AN melt in order to form double salts; otherwise there will be no effect on thermal stability and some post-reaction during storage generating caking.

➢ improve the physical properties of the particles: like increasing the density, the hardness; acting as a binding agent during the granulation….instead of bringing disadvantages:

Indeed, some additives can bring disadvantages, despite their very good protection against thermo-cycles, that render them unusable in some particular cases.
As shown in table 9, some additives increase the hygroscopicity of AN so much that they are inappropriate in case of bulk storage in a humid atmosphere.

Table 9: Hygroscopic points of salts + ammonium nitrate mixtures
influence of soluble inorganic additives on CRH of ammonium nitrate

	CRH at 30°C expressed in % of relative humidity
NH_4NO_3	59.4
K_2SO_4	96.3
$NH_4NO_3+K_2SO_4$	69.2
$(NH_4)_2SO_4$	81.1
$NH_4NO_3+(NH_4)_2SO_4$	62.3
KNO_3	90.5
$NH_4NO_3+KNO_3$	59.9
$Ca(NO_3)_2.4H_2O$	46.7
$NH_4NO_3+Ca(NO_3)_2.4H_2O$	23.5
$Mg(NO_3)_2.6H_2O$	48
$NH_4NO_3 +Mg(NO_3)_2$	<10

One can see in table 10 a summary of the pro and con's of some additives.

Table10. Comparison of various additives: pro's and con's

	Useable amounts	Thermal stability	Physical quality	Hygroscopicity	Particular effect	Safety	Impact on N content	Cost
Al sulfate	1-2%	++	-Improve hardness, granulating agent		-bound water depending of AN melt temperature	-sensitive to high pH :agglomerate above pH 6, -lowers the pH of AN melt -Alhzeimer disease	Reduce the N content	+
Mg nitrate	2%	+++	No caking, improve hardness	inappropriate to bulk storage without special coating			NO3 valorized	Less costly if from MgO,MgCO3
Boric acid phosphates+AS	0.4%	+++	More resistant to caking, lower friability, improve hardness, reduce sensitivity to humidity	Sligtly less hygroscopic		Increased porosity	-Low amount of additives needed. -doesn't affect the N content	
KNO3	5%	+++			Reduce the cooling needed by stabilising form III instead of IV		NO3 valorized	+++ loss of K
AS	5%	++	Improve hardness	+			NH3 + S valorized	Low if waste from caprolactam, cokery...industries available
K2SO4	5%	+++	No effect on hardness					++, loss of K
Ammonium phosphates		Little practical experience					NH3 valorized	++, loss of P
Clays	0.5-3%	++ depending clay characteristic	Improve hardness, acts as granulating agent			Contains often carbonates acting as pH buffer		Variable