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PHYSICO - CHEMICAL PROPERTIES OF THE AMMONIUM NITRATE - AMMONIA SYSTEM AND THEIR RELATION TO AEROSOL AND DUST EMISSION IN AMMONIUM NITRATE PRILLING PROCESS

Z. Krawiec
Institute of Nitrogen Industry, Poland

ABSTRACT

The relationship between the physico-chemical properties of ammonium nitrate - ammonia system and ammonium nitrate aerosol and dust emission from industrial plants is been presented. It describes the properties connected with the quality of the product obtained and that the empty space inside the granules is formed as a result of turbulent solidification processes. It has been known and published in literature the causes of dust and aerosol emission from the prilling tower and we can add new data in this paper.

The last stage of solidification, that is, the transition from drops into granules can also be the source of considerable ammonium nitrate emission besides evaporation of ammonium nitrate and splitting of streams into drops in the upper part of the prilling tower with the simultaneous formation of the so called satellites.

In the literature the solidification of pure ammonium nitrate has been widely discussed. The solidification of ammonium nitrate melt containing and/or other additives has not been discussed in the available literature.

The condition of unfavorable turbulent solidification and the way to prevent it are also given in this paper.

1. INTRODUCTION

The importance of ammonium nitrate meant that many million tons are produced every year. Most of it is used as fertilizer; part of it goes for manufacture of nitrous oxide which is used in anaesthetic mixtures and some of it for the production of explosives, rocket fuels, etc.

From the physico-chemical point of view ammonium nitrate is a compound having very specific properties. They have been studied for a long time [1-5] but certain areas still remain uncovered. The most interesting forms of ammonium nitrate are: The crystal state, ammonium nitrate melt, and also ammonium nitrate solution in various solvents. Large scale production of ammonium nitrate requires modern technology which must be based on up-to-date physico-chemical basis.

Generally we can describe the present-day ammonium nitrate technologies using the following scheme:

The first stage consists of the neutralization of moderately concentrated nitric acid with ammonia. The resulting aqueous solution of ammonium nitrate is then submitted to multistage concentration which produces ammonium nitrate melt containing a small amount of water.

All these processes take place in the alkaline environment i.e. in excess of ammonia. Then ammonium nitrate melt is pumped on top of the prilling tower where it forms streams as they fall. They split into drops, cooling as they fall and then gradually solidify.

They reach to the bottom of the prilling tower in the form of solid granules having nearly spherical shape.

The present scope of ammonium nitrate technology requires the knowledge of physico-chemical properties of ammonium nitrate over a wide range of temperatures and in different physical states from molten salt to solidification process and the transition of solid phase through various crystal structures to the stage of granular product.

It is also important to know the kinetics of thermal decomposition and the factors having a restraining effect on the decomposition process. The knowledge of surface properties of pure ammonium nitrate and the dependance of these properties on different compounds added to the melt such as ammonia, ammonium sulphate, magnesium nitrate etc. are also of great importance.

Ammonium nitrate production is associated with an inherent potential for losses: through ammonium nitrate aerosol and dust emission.

Ammonium nitrate aerosol and dust are formed in various parts of the plant but mainly during the solidification of ammonium nitrate inside the prilling tower.

Removal of ammonium nitrate aerosol and dust is difficult because there are many different sources of emission and many physico-chemical reasons causing this phenomenon.

It was stated earlier [6] that the emission from several plants which were inspected reaches 33,000 tons of ammonium nitrate aerosol and dust per year.

The problem of ammonium nitrate emission was widely studied [7-12] from the point of view of possible removing or at least reducing it. It was proposed to change the way of prilling [8], to use adequate methods of removing aerosol and dust [9], to fine tune the operation of the ammonium plant or to resort to hermetisation of the process [11,12]. But still, there are no simple and efficient methods of removing ammonium nitrate emission.

The aim of this paper is to present unknown properties of the $\text{NH}_4\text{NO}_3 - \text{NH}_3$ and $\text{NH}_4\text{NO}_3 - \text{H}_2\text{O} - \text{NH}_3$ systems affecting ammonium nitrate aerosol and dust emission and influencing the quality of the product granules.

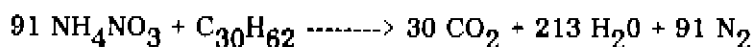
2. SOURCES OF AMMONIUM NITRATE AEROSOL AND DUST EMISSION

All the stages of the operations during the manufacture of ammonium nitrate take place in excess of ammonia. The alkaline medium delays thermal decomposition and improves the quality of the product [13-17,31].

The presence of ammonia may in some circumstances becomes the reason of greater ammonia nitrate emission but this problem has not been exhaustively treated in scientific literature. All known sources todate on ammonium nitrate emission are presented briefly in Table I.

The analysis of data given in Table I confirms the complexity of the process of ammonium nitrate aerosol and dust formation. Initially, hypotheses had been put forward that the additional causes of the ammonium nitrate emission were:

- ammonium nitrate decomposition and nitrous oxide formation,
- formation of carbon dioxide resulting from the oxidation of hydrocarbons introduced into ammonium nitrate plant together with ammonia:



These hypotheses were not confirmed. Using gas chromatography, it has been proved that there was no nitrous oxide and the study of the ammonium nitrate melt did not oxidize in the presence of ammonia.

Also the hypotheses try to explain the increased ammonium nitrate emission with the gas desorption e.g. Air did not prove right by these experiments. The solubility of all gases having contact with NH_4NO_3 melt is poor in comparison with NH_3 and they do not cause any perturbation during solidification.

3. SPECIFIC GRANULE STRUCTURE

Repeated gravimetric analysis of the product collected at the bottom of the prilling tower yielded results shown in Figure 1. Besides gravimetric analysis the general appearance of the granule and their diameter cross section was also observed. The typical appearance of granules forming separate fractions is given above the distribution curve in Figure 1. Particles forming the separate fractions underwent processes mentioned in Table I and the processes exerted an influence on their shape and structure.

We can talk about a specific configuration of a granule being formed. Numerous details have been written in proceedings.

The specific configuration consists of:

- the external shape of granules showing the peculiar character of surface tension forces, aerodynamic forces, and gravimetric forces,
- the crystal structure of granules shaped by the speed of drops cooling, the influence of the additives contained in the melt and occluded gas bubbles captured during the solidification. This in turn is related by the degree of ammonization of ammonium nitrate melt before the prilling process,
- the internal structure of granules i.e. walls enclosing the empty space inside the granules which above all depends on ammonia concentration in the melt, the melt temperature and the drop diameter.

The ability to read the details written in this specific configuration would help avoid any irregularities in the process.

It turns out that if we know the behaviour of the ammonium nitrate - ammonia system as a function of ammonia concentration, temperature, pressure etc. we can read some of the details and understand the reasons of occurrence of a certain granule structure formed in particular circumstances.

4. PHYSICOCHEMICAL PROPERTIES OF THE AMMONIUM NITRATE - AMMONIA SYSTEM

The investigation of behaviour of the ammonium nitrate - ammonia system as a function of temperature makes the reading of the specific configuration easier. It is important to consider the system between 193 K and 475 K.

The behaviour of the system is presented in Figure 2.

The most important question concerns the interaction forces between ammonia molecules and ammonium and nitrate ions in liquid ammonium nitrate or in solid state.

Figure 2 shows the known facts on nature of these forces available from literature and in the light of the results obtained in the present experiments.

In the temperature range 193 - 233 K, the interaction forces are strong enough for a well-defined crystal $\text{NH}_4\text{NO}_3 \cdot 3 \text{NH}_3$ to be formed. Such a compound was obtained many times as a result of cooling of ammonium nitrate solution in liquid ammonia to temperature lower than 233 K. There is also information in the literature about this compound [35]. Chemical analysis of the ammoniate proved that its composition is expressed by the formula $\text{NH}_4\text{NO}_3 \cdot 3 \text{NH}_3$ [27]. This ammoniate is unstable. It melts at temperatures above 233 K decomposing into ammonia, ammonium nitrate and liquid in which the ratio ammonia to ammonium nitrate is not constant. Such solutions called Divers' liquids [1-5], are unstable at room temperature because ammonia pressure is higher than atmospheric pressure [2, 36, 37]. Equilibrium pressure of ammonia above such solutions as a function of temperature is defined by an empirical dependance deduced from literature and by own experiments [2, 36, 37]:

$$\ln P_A = - \frac{2986.1}{T} + 21.71 \quad (1)$$

where: P_A is ammonia equilibrium pressure of the Divers' liquid in P_A at the given temperature T.

Interaction forces between NH_4NO_3 and NH_3 become weaker as the temperature increases but can be detected using infrared spectroscopy [38] and gas chromatography [37].

At the ammonium nitrate melting point 442.7 K, the interaction forces between ammonia and ammonium nitrate are much more weaker than the forces which made the formation of ammoniate at 233 K possible but still they allow ammonia solution in the molten ammonia solution to be formed. In the literature there are no quantitative data concerning the solubility so we measured it and defined it by an empirical formula [28]:

$$\ln S_A = \frac{3222.52}{T} - 12.74 \quad (2)$$

where: S_A is ammonia solubility in liquid ammonium nitrate in kg NH_3 per kg NH_4NO_3 at a given temperature T.

5. SOLIDIFICATION IN THE AMMONIUM NITRATE - AMMONIA SYSTEM

The behaviour of the ammonium nitrate - ammonia system in the temperature range 373 - 453 K is interesting from the practical point of view as the changes inside the prilling tower proceed in this temperature range.

Phase transition liquid \rightleftharpoons solid for this system proceeds under atmospheric pressure and practically at the same temperature as for pure ammonium nitrate at 442.7 K and it is especially interesting because of some peculiarities it has.

Investigating the solidification of ammonia solutions in the molten ammonium nitrate we discovered that this process is turbulent in the last stage when the temperature inside the solidifying drop falls to about 442 K. The solidification of drops of ammonia solution in ammonium nitrate hung on a stainless steel loop is shown in Figure 3A.

Irrespective of drop size (the diameters of the hung drops were various: 1.5, 2.0, 2.5, 3.0 mm etc.) the process of solidification was the same, only the time after which the interior of the drop reached temperature 442 K was different.

Violent eruption of gaseous emulsion, contained inside each drop, on last stage of solidification formed characteristic efflorescence on every drop. The efflorescence mass form 7 to 12% of the mass of drops collected for investigation. It is interesting to note that analogous results were obtained in experiments where the drops or rather their most internal part solidifies in static condition after 20 m of free falling.

The interpretation of the observed process of solidification is as follows: as the drop temperature falls ammonia desorbs only from their surface because of low ammonia pressure in the environment. In the internal parts of drops ammonia is still in the solution because its solubility increases when the temperature of melt falls (see Figure 2 Ammonia solubility curve in liquid ammonium nitrate). Such dependance of gas solubility in liquids is observed for numerous gas - liquid systems.

The critical moment occurs when the ammonia solution in liquid ammonium nitrate reaches the solidification point and the solid phase being formed at temperature 443 K and under atmospheric pressure, cannot bind mass of ammonia which dissolves in the liquid phase (Figure 2.)

Cross-section of solidified drops shows their characteristic structure: The inside is empty and spherical in bigger granules. The volume of the empty space is two or three times larger than that which should be caused by contraction of volume during the solidification of pure ammonium nitrate it constitutes about 8%. This phenomenon is clearly seen if we compare the shape of granules in separate fractions (see Figure 1).

Vermede [7] and Kozakova [22] have made interesting hypotheses connecting the empty space inside granules to high temperature [7] and with leakage of not quite solid ammonium nitrate from inside the granules through cracks under pressure of shrinking solidifying external coat and under capillary tension [22].

In industry the whole process of drops cooling and solidification proceeds in dynamic condition: the drops fall and are cooled by countercurrent air stream.

The mechanism of process is a little bit different than in static condition - first of all in dynamic conditions there are no efflorescence because they fall off when they are formed. This mechanism is shown schematically in Figure 3B. This is an intensive process of aerosol and dust formation. It causes also considerable increase of ammonium nitrate surface. In consequence, the amount of evaporated ammonium nitrate increases in a plant of capacity 1000 - 1500 tpd when the number of drops reaches value of about 10^6 - 10^{10} and their surface tens of square metres.

Everything indicates that the smallest fractions shown in Figure 1 come not only from splitting of liquid ammonium nitrate streams but they are also formed in the latter part of the solidification of individual drops.

The results of our own experiment suggest the following mechanism of the prilling process. As the outer layer of the drop cools it solidifies forming a shell. As the thickness of the shell increases the forming solid liberates ammonia bubbles. The rate of ammonia liberation is directly proportional to the rate of cooling. The liberation ammonia accumulates in the interior of a sphere which is not quite solid, forming there gaseous emulsion composed of ammonia and ammonium nitrate melt. Solidifying layers occlude only smallest bubbles which have not penetrated to the inside of a granule. Such a mechanism is confirmed by a series of picture made with a scanning electron microscope (Figure 4). Finally pressure in the inside of a granule becomes higher than the atmospheric which causes cracking of the solid coat of a granule being formed and in this way rapid leakage of gaseous emulsion $\text{NH}_4\text{NO}_3 \cdot \text{NH}_3$. This threshold pressure at given temperature is expressed by the relationship (1).

6. INVESTIGATION TEST FOR SOLIDIFICATION PROCESS OF THE AMMONIUM NITRATE - AMMONIA SYSTEM

The above consideration has led a simple test for the investigation of the solidification process of various systems with ammonium nitrate as the main component. The possibility to define quickly the properties of such systems has practical value because one can draw conclusion concerning the industrial scale of process. The test is carried out in test-tube and we can observe its course. Certain amount of ammonium nitrate is added into a test tube and melted in required temperature. Then additives are added e.g. gaseous ammonia. The test tube is then cooled until the melt solidifies. Figure 5 shows pictures of the result of such a test. Applying the test we can quickly estimate the influence of additives in ammonium nitrate on the solidification process and we can eliminate negative phenomena in an industrial plant on the basis of the results. Test shown in Figure 5 represents the influence of ammonia concentration on the ammonium nitrate solidification.

7. SURFACE PROPERTIES OF AMMONIUM NITRATE MELT AND AMMONIA AND WATER SOLUTIONS IN THE MELT

In Table I, Item 3 the possibility of certain specific interaction of ammonia and water molecules at the interface liquid ammonium nitrate / air is mentioned. According to the known physico-chemical rule concerning the surface phenomena we should observe drop of the surface tension if ammonia and water were surface active compounds.

Measurements taken with the method of maximum bubble pressure do not show ammonia and water influence on the value of the surface tension of liquid ammonium nitrate at the temperature range 443 - 473 and under the atmospheric pressure.

The surface tension of the above mentioned system in the given temperature range and under atmospheric pressure was similar and can be defined practically with the same relationship which we obtained in our laboratory and which is very close to the Addison and Coldrey's relationship [27,39]:

$$\sigma_{AN} = -0.1036 T + 147.77 \quad (3)$$

where: σ_{AN} is the surface tension [mN/m] of ammonium nitrate melt at a given temperature T.

Only under higher ammonia and water pressure we can observe decrease of ammonium nitrate surface tension.

8. CONCLUSIONS

1. Ammonia concentration in ammonium nitrate melt influences substantially the ammonium nitrate solidification and that is why in an industrial process the concentration of ammonia should be kept within strictly defined limits (about 1/3 of these calculated for 470.2 K from equation (2)).
2. Various additives in melt may reduce any irregularities of solidification process of ammonium nitrate melt but only to a small extent.
3. A simple solidification test is available to check the behaviour of ammonium nitrate and its mixtures in an industrial process.
4. Surface phenomena at the interface liquid ammonium nitrate / gas in the presence of ammonia and water have rather small influence on dust and aerosol emission because of their low surface activity.

5. In the specific configuration of granules, we have already known many details concerning the mechanism of prilling but we must, first of all, obtain information about the ammonia concentration in drops and granules cooling inside the prilling tower, etc.

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TABLE I
SOURCE OF AMMONIUM NITRATE AEROSOL AND DUST EMISSION
IN COMMERCIAL FERTILIZER PLANTS

No.	Source of emission in commercial fertilizer plants	Physical chemistry of the source of emission [literature]	Comments on concentration and possibilities of removing aerosol and dust
1	2	3	4
1	Concentration of ammonium nitrate aqueous solutions containing ammonia	Boiling of solutions containing volatile compounds	2.7-3.0 g NH ₄ NO ₃ /m ³ in waste gases Evaporators must work in closed system
2	Splitting of ammonium nitrate melt streams into drops during free fall	Surface phenomena at the interface molten salt/air [19 - 22]	It is difficult to fix the concentration of aerosol and dust formed during this process. Splitting of streams in monodispersives, e.g. application of vibrators
3	Process of intensive evaporation and the boiling at the interface molten salt/air in the low pressure evaporator	Phenomenon of interfacial concentration of compounds lowering free surface energy of NH ₄ NO ₃ - H ₂ O - NH ₃ system: Langmuir - Hardy - Harkins' rule [23 - 34]	The known concentration from the prilling towers is estimated at about 0.05-0.3 g/m ³ . Reduction of ammonia concentration in ammonium nitrate melt also in its aqueous solutions before concentration
4	Process of evaporation and dissociation of ammonium nitrate from 378 K to 453 K	Kinetics of appropriate processes [28 - 34]	Components of ammonium nitrate concentration mentioned in items 2 and 3
5	Splitting of too large drops into smaller ones during their free fall	Interaction of surface surface tension forces and hydro-dynamic and aerodynamic forces [34]	This factor has a weak influence because it can be easily eliminated
6	Process of solidification of ammonium nitrate melt drops and formation of granules	Physical chemistry of solidification of solution of gases in liquids [23 - 27]	Component of concentration at the outlet from prilling tower. If the concentration of NH ₃ in the melt is closed to saturation state it can cause considerable dispersion of ammonium nitrate

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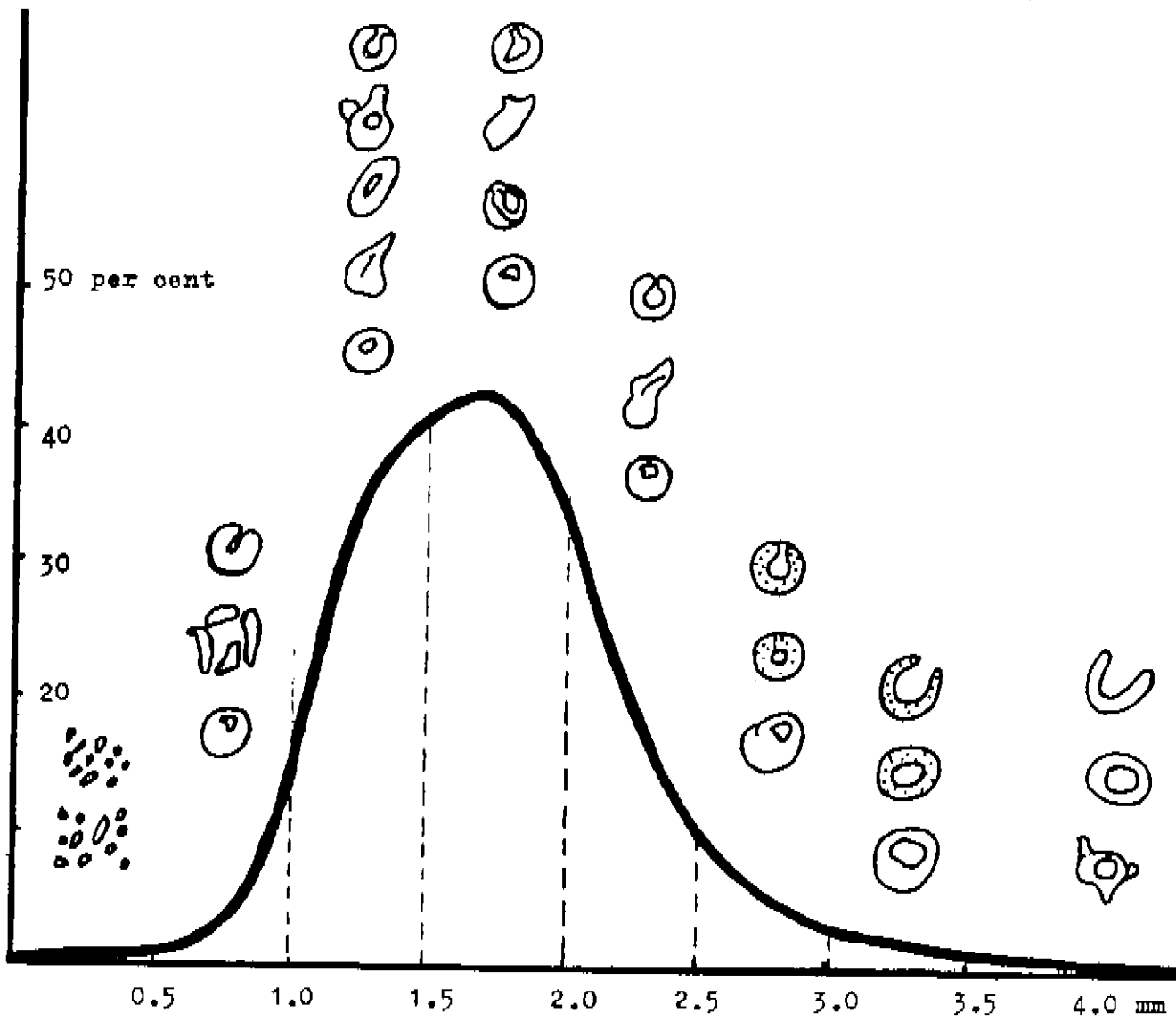


Fig.1. Gravimetric analysis of granular product collected at the bottom of the prilling tower. General appearance of granules and their diameter cross section are shown above the distribution curve.

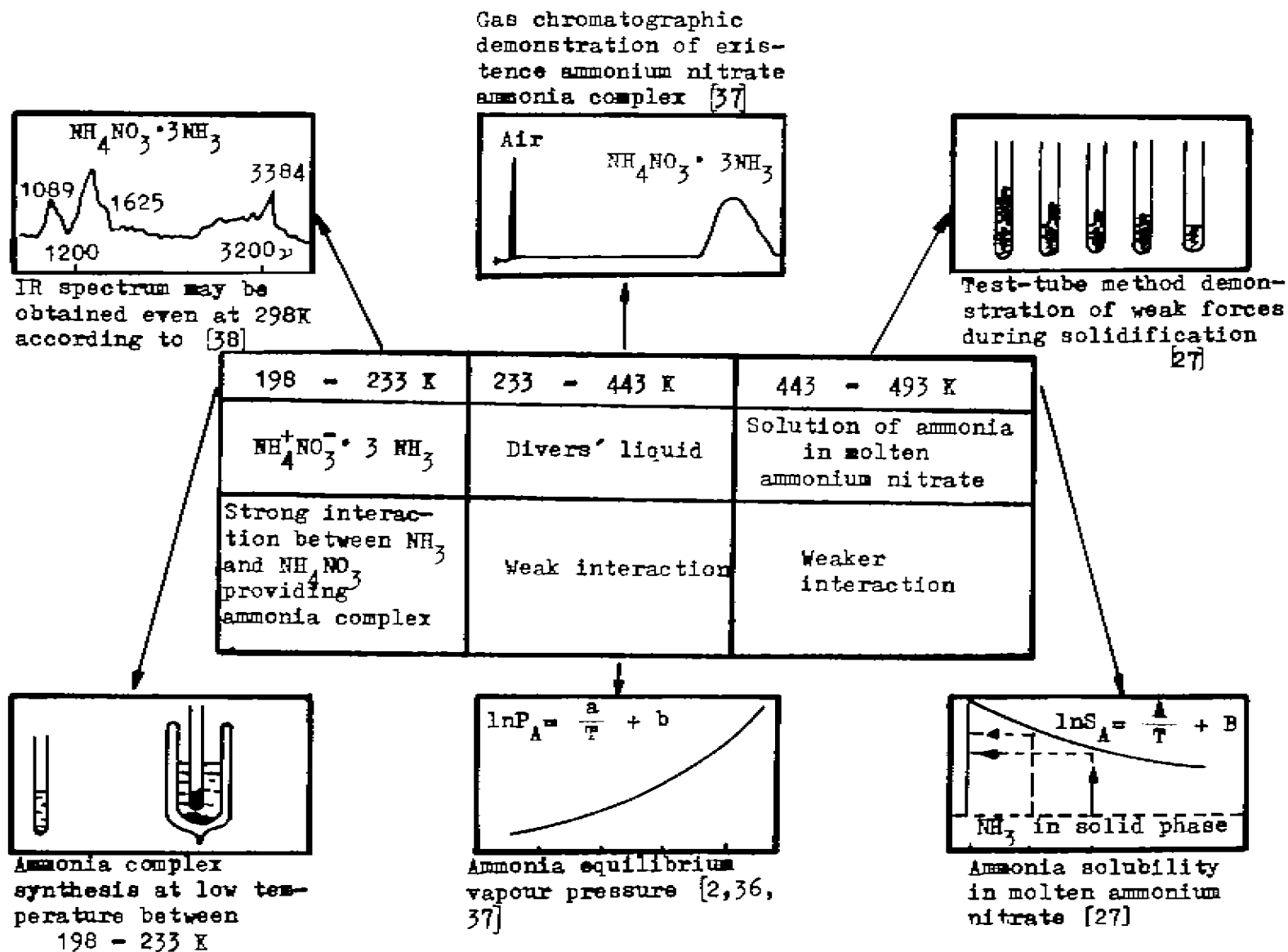


Fig.2. Molecular forces between ammonium nitrate and ammonia as a function of temperature

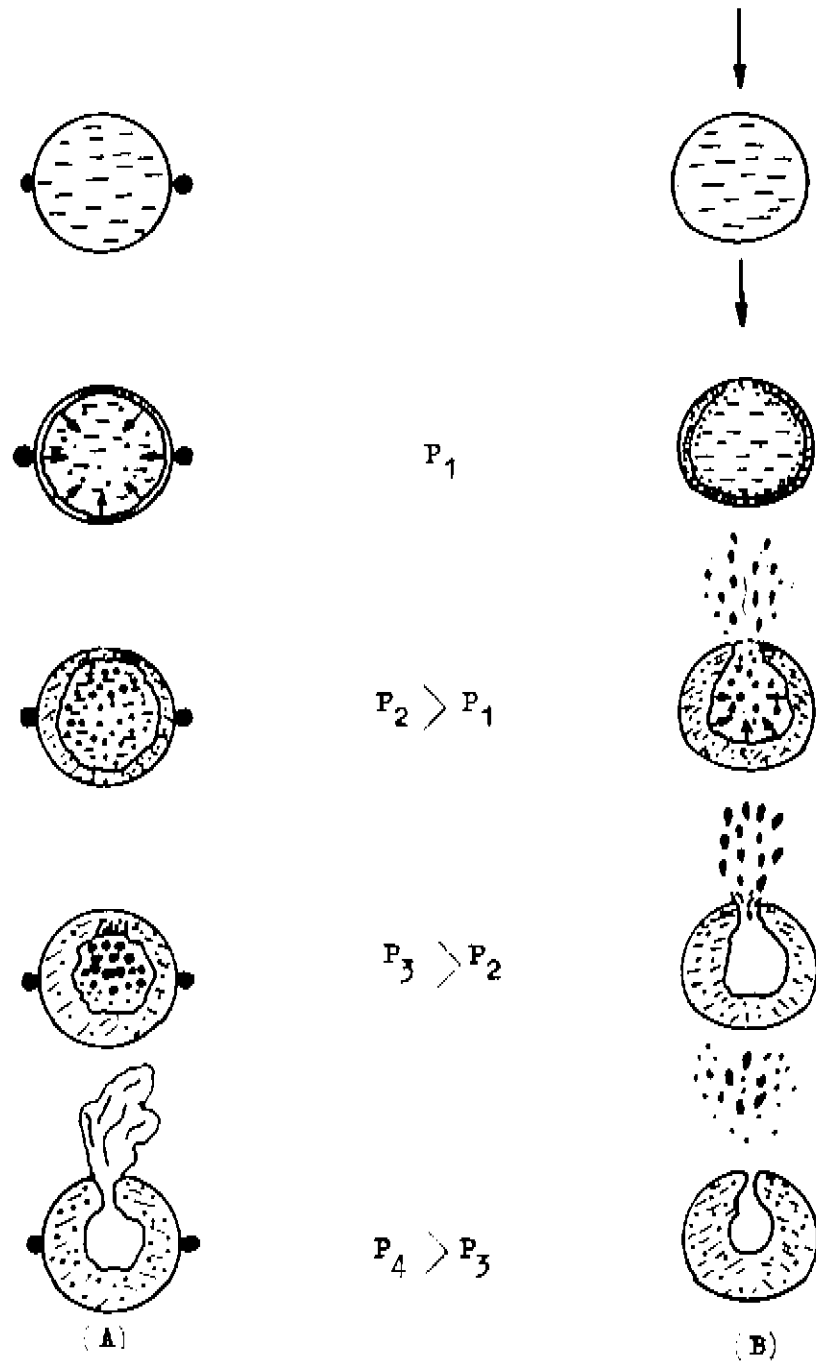


Fig.3. Solidification of drops of ammonia solution in ammonium nitrate hung on a stainless steel loop under static condition (A) and under dynamic condition (B).
 P_1, P_2, P_3, P_4 are the Divers' liquid pressures inside the drops

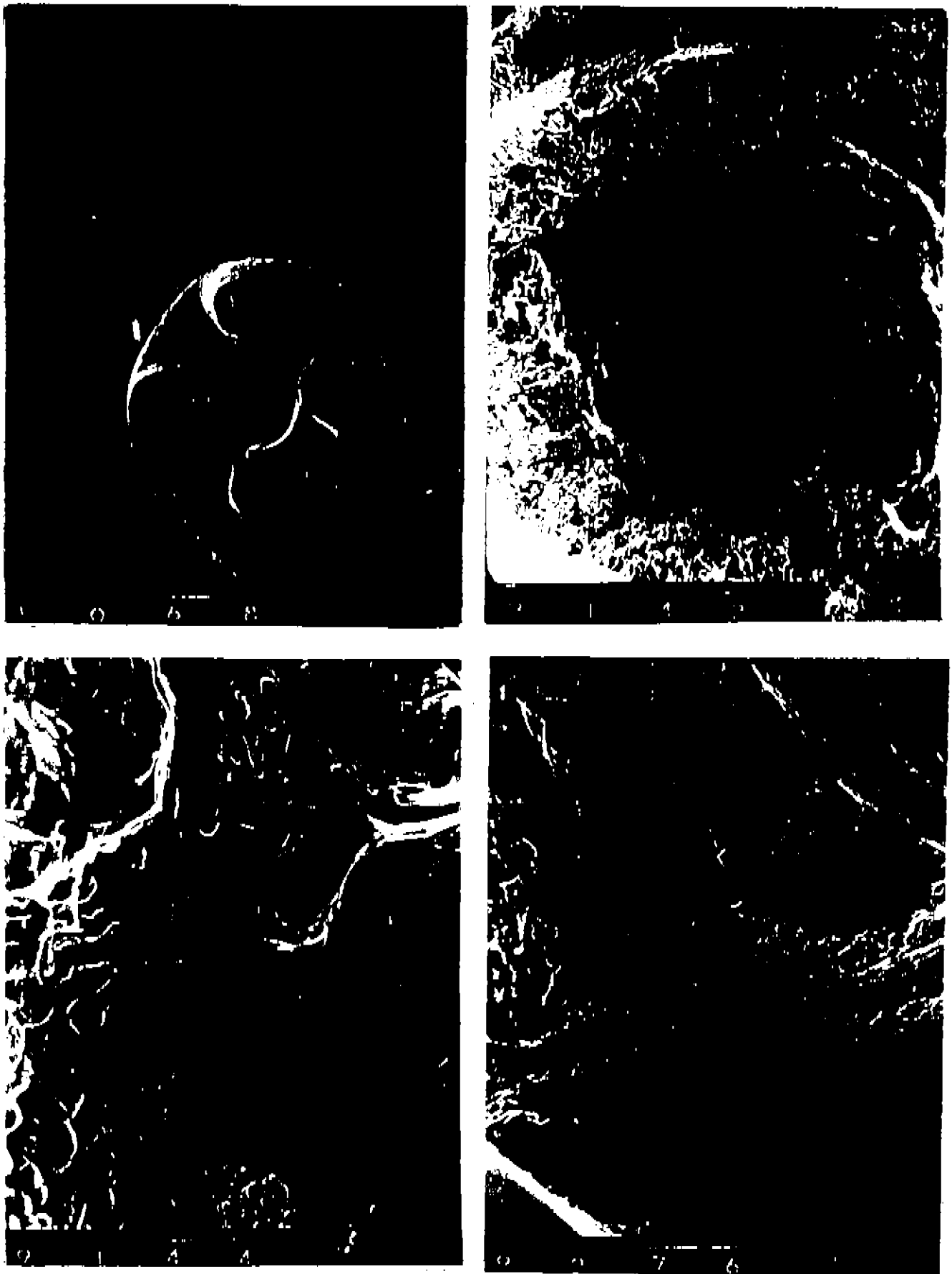


Fig.4. Scanning electron microscope picture of ammonium nitrate granule at the large diameter cross section.

Magnification: 60x, 200x, 600x and 1500x