A Study on The Structure of Porous Granular Ammonium Nitrate by Scanning Electron Microscopy

I. The Structure of Porous Granular AN Manufactured by Fluidized-Bed Process

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Porous granular ammonium nitrate (AN) is a principal raw material of ANFO explosive. Its structural characteristics and type and magnitude of surfactant used will no doubt have significant influence on the oil absorption, one of the key technical performances of granular AN. By means of a scanning electron microscope (SEM), the author for the first time in China has made a comprehensive observation of the outer and inner structures of various kinds porous AN granules manufactured by different processes, investigated the rule of their granulation, and summarized some preliminary achievements in this respect. As the first part of the report, this paper mainly presents the research work on the structure of porous AN granules manufactured by fluidized-bed process.

1. Introduction

Of the modern commercial explosives developed since the 1950s, ANFO represents the world's leading explosive both in production and consumption. AN is the main ingredient of ANFO explosive, amounting up to 95-96% by weight. Most countries adopt porous AN granules to ensure that ANFO explosive can be directly processed by mixing the ingredients at room temperature and be mechanically charged into boreholes on-site so that the maximum technical and economical benefits can be achieved.

Owing to some restrictive reasons, explosives in china had been manufactured from crystalline (or powder) ammonium nitrate up to the early 1970s. It was crushed, heated and mixed with other ingredients by an edge runner and then processed in a fixed plant to make up an explosive. But in fact main technical problems associated with the production of porous granular AN had already been solved by Changsha Institute of Mining Research in collaboration with Shijiazhuang Chemical Fertilizers Plant in the late 1960s. A decade later, based on the research achievements and pilot-plant production for several years, mass production of porous granular AN normally commenced and a number of manufacturing plants with a total capacity of 200,000 T/Yr of porous granular AN were constructed and put into production.

It is known from all information availabl both at home and abroad that up to now, there have been two main processes of manufacturing porous AN granules namely, the granulating towerheat drying process and the fluidized-bed process. The former has been employed by many countries because of its high efficiency and low cost while the latter which is unique in China has the advantage of low capital cost and simple equipment.

Evidently, the porous AN granules manufactured by the above mentioned two processes would differ in their structures, since their granulation, dehydration and even the mechanism of the formation of their porous structure are substantially different. Furthermore, such difference in structures would exert various influences on their properties.

In order to reveal the outer and inner structures of the porous AN granules, to get some insight into their granulating procedures and to recognize the relationship between their structures and performance, a comprehensive observation has been made of various porous AN granules by the use of a scanning electron

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microscope (SEM), and a comparison was also made between the porous AN granules and dense AN prills.

This paper provides the first part of a series of papers in this field and is particularly dealing with the achievements about the porous AN granules manufactured by fluidized-bed process.

2. Sampling and Research Method

Samples were taken from Shijiazhuang Chemical Fertilizers Plant where porous AN granules are manufactured by fluidized-bed process. As far as the quality and properties of the product, and the production history of the plant are concerned, all samples from this source may be considered to be fully representative for studying the structure of this type of porous AN granules as well as their related theoretical problems.

The model and technical parameters of the scanning electron microscope used here are as follows:

Model:	JSM35C
Accelerating voltage:	Generally 20kv, occasionally 15kv
Magnification:	Whole-size examination 30x-100x
	Local examination 300x-1500x
	Crystal grain examination 5000x-6000x

Granules 1. 5-3. 0 mm in diameter and having a fairly regular appearance were selected from the samples for examination. Examinations involving the following two conditions were taken at each magnification level.

(i) The outer structure. The sample granule was examined with its original product appearance and structure unaltered.

(ii) The inner structure. The sample granule to be examined was cut along its axis into halves with a sharp blade, the half having a more smooth cleavage was chosen for examination.

Five or six samples were prepared for each condition. Examinations and photographing were carried out at three magnification levels.

For lack of conductivity necessary for SEM examination and also based on general requirements for structure study, the dried AN granule samples should be vaccum-pumped and gold-plated or platinum-plated by a cathodec-sputtering coating machine before examination.

3. The General Principle of Fluidized-Bed Process and Quality Specifications of AN Granules Manufacturing

The samples examined here were taken from batches of porous AN granules manufactured by fluidized-bed process. As the principle and operating parameters of this process have been well described in many other literatures, this paper will only high-light the typical flowsheet and the equipment adopted in the fluidized-bed process developed by Shijiazhuang Chemical Fertilizers Plant and Changsha Institute of Research. [1]

At the bottom of a tapered-cone-shaped fluidizing granulating equipment, a hot air current is introduced. It passes through a perforated plate in the equipment, making the AN material placed on this plate move up and down continuously and form a fluidized bed. A complete cycle of manufacturing AN granules within the fluidized bed may be described as follows: Firstly, some small AN grains (30 mesh) are charged onto the plate as solid seed crystal and are kept in fluidized state. Then, a molten AN mixed with a surfactant (0. 05% by weight of stearylamine acetate) is sprayed over the fluidized bed of small grains through an atomizing nozzle by the aid of compressed air. Upon contacting with the fluidized bed of grains, the atomized droplets of molten AN adhere to and accumulate on their surface repeatedly. At the same time, the moisture contained in the adhered dropletsis continuously evaporated by the uprising hot, dry air current, thus resulting in the formation of fine-grained aggregate of spherical granules with a low water content. When the weight of a granule increases to such an extent that the pneumatic classification due to fluidization-gradient caused by the hot air current is inadequate to support its uprising motion, it will settle down through the perforated plate onto the bottom of the bed and from there discharges through the outlet of the equipment as finished product.

According to the standards set for the porous AN granules by Shijiazhuang Chemical Fertilizers Plant, the quality specifications of the product are as follows: [1]

Water content	<0. 3%
Oil absorption	0. 8%
Granular size	0. 5-2. 5 mm in diameter
Bulk density	0. 80-0. 85g/cm^3

4. The Outer Structure of Porous AN Granules

As is determined by the principle of the manufacturing process, all large granular products are composed of tremen dous number of small particles which adhere and collect altogether. In the present study, these large granular products are defined as macrograins, and the small particles constituting the macrograins are defined as crystal units for the convenience of structure study.

Whole-size examinations were made of various samples and corresponding photoes were taken for the study of their outer structures, indicating that macrograins were usually spheroidal or ellipsoidal granules (according to some photoes, usually the ratio of the longer axis to the shorter one was about 1.1) with irregular and unsmoothed surfaces, upon which the crystal units were widerspread and adhered to one after another like fish roes, exhibiting an undulate appearance (see photo 1). This uneven distribution of crystal units over the granular product surface can be explained by the fact that, before growing to be finished granules, the seed crystal and crystal grains at various stages of their growth move and seethe irregularly within the fluidized bed and hence during seething, the probabilities and also the positions of collision and adherence between the atomized droplets are quite different from each other.

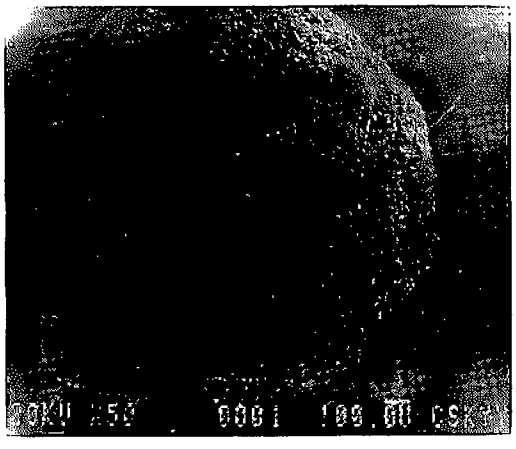

Photo 1. A SEM picture taken from a whole-size examination of AN macrograin for outer structure study (50X)

Owing to the distribution profile of crystal units over the surface of macrograins, this kind of structure may be called "bayberry" type structure.

If some magnified photoes were taken of part of the granule surface, it could be further found that although all crystal units generally adhere to and condense on the granule surface by filling the vacancies one after another,they are unlikely to fill up all the vacancies in proper sequence for the reasons described previously, resulting in uneven aggregation, arbitrary shapes of crystal units with various particle sizes. In consequence, the interstices between crystal units and their distribution are changing very complicatedly (see photo 2)

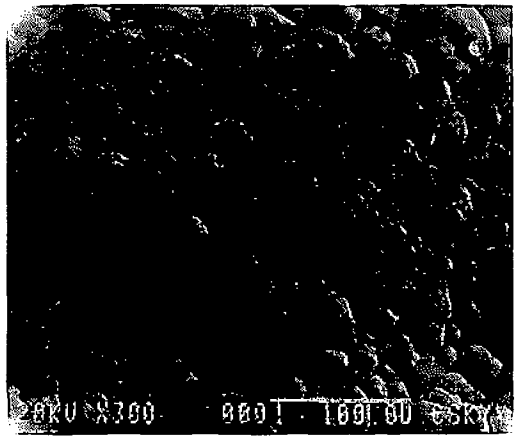

Photo 2. A magnified SEM picture taken from a local examination of AN granule's surface for outer structure study (300X)

The magnified photoes taken of local surface of several samples show that almost there is no crystal unit which takes a strictly spheroidal shape. In fact, all the crystal units take spheroid-like or ellipsoidal shapes. This is probably due to one or more of the following effects.

(i) The molten AN droplets tend to condense in the form of spheroid because of the surface tension. The addition of stearylamine acetate as a surfactant, however, tends to suppress the surface tension and to some extent hinders the droplets from condensing in the form of spheroid.

(ii) During granulation in the granulating tower, the droplets are surrounded by a free space and are subjected to equal external effects in all directions. However, this is not the case when they are absorbed on the surface of the seedcrystal where,owing to the unevenness of heat transfer

and radiation, uneven growth of host crystal and other crystal grain, a time-lagging effect may occur in various parts of the droplet surface and in all directions.

(iii) During the short period from its absorption onto the seed crystal surface to its condensation as a crystal unit, the atomized droplet evidently will be subjected to a series of very complicated fluid-dynamical effects. These include the influences of hot air currents which not only cause each macrograin as a whole to rise and descend, to seethe and flow relatively, but also exert gravity, centrifugal and relative flow upon the individual uncondensed droplets on the surface of the granule.

(iv) The constraint effect of volume and shape of the interstices left between the condensed crystal units upon the condensation of latter uncondensed droplets.

The sizes of some crystal units visible in the magnified photoes taken of local granule's surface were measured. The approximate ranges of their dimensions are as follows :

Unidirectional dimension : Max 55-100μm
Min 5-20μm
Average 20-30μm

Ratio of diameter to length : Spheroidal 1. 0
Egg-shaped 0. 5-0. 6
Ellipsoidal 0. 7-0. 9
(in majority)

Interstices between crystal units :
Max 10-30μm
Min 0. 3μm
Average 1. 5-3. 0μm

5. The Inner Structure of Porous AN Granules

It is not difficult to imagine that the inner struture of a granule or macrograin may be deduced to some extent from the characteristics of its outer structure, as is evidenced by the Photoes taken of the cross section of the granule (see photo 3).

Photo 3 shows that the density or compactness of aggregation of crystal units forming the macrograins varies with position over the surface of the granule, giving rise to interstices of various sizes and orientations.

It should be noted that somewhere in the center of the granule or macrograin there may exist irregular

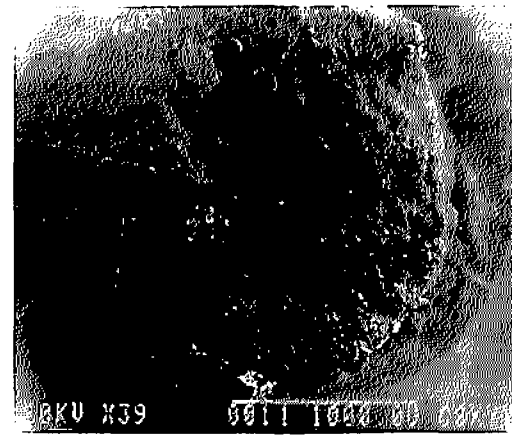

Photo 3. A SEM picture taken of the entire cross section of an AN granule for inner structure study (39X)

secondary blocks of aggregation (unidirectional dimension ranges from 200 to 400 μm) in which some irregular interstices are interlinked with each other, the width of these interstices is about 15-25μm.

In order to study the inner structure of a granule or macrograin, magnified photoes were taken of part of its cross section, revealing the shape characteristics of the crystal units inside the AN granule and the layered aggregation structure of the crystal units along this cross section (see Photo 4).

Although the structural characteristics and aggregation behavior of the crystal units inside a macrograin have much in common with those on the

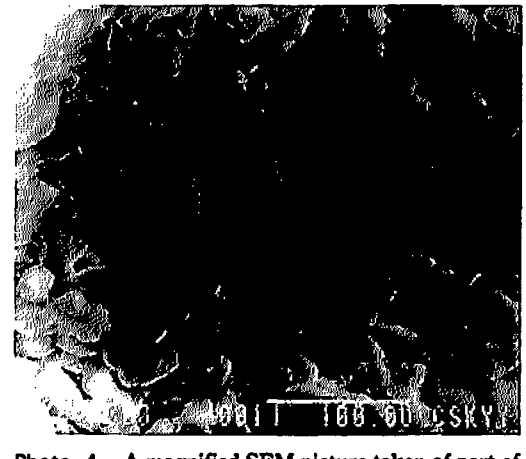

Photo 4 A magnified SEM picture taken of part of the granule's cross section for inner structure study (300X)

surface of it, they still differ in the following two aspects:

(i) The crystal units inside the macrograin become small in size, with the maximum unidirectional dimension being 40–45μm, the minimum 5–12μm and averagely 15–35μm. As compared with the corresponding values of the outer crystal units, the lower limit of their minimum unidirectional dimension is 5μm, but the maximum and average of the inner crystal units account for only 50% and 60–75% respectively of those of outer ones.

(ii) All the crystal units aggregated on the macrograin surface are free-growing as individuals while only a minority of the inner crystal units with small dimensions are able to develop. In this way, most of them grow to be pod-shaped or dumbbellshaped twin crystals, or overlap to form layered flat crystal grains having an irregular appearance.

The first case can not yet be reasonably interpreted while the second may be explained as follows.

Generally, only the outermost layer of crystal units on the macrograin surface, where they face a free space, can grow freely to form individual grains. When a new atomized droplet is absorbed onto the surface of such a crystal unit, a new solid-liquid interface will set up in accordance with the general principle of granulation by fluidized bed process [2] and the liquid droplet will interlink and bridge up with the original crystal units by interface energy. Probably this may cause the solidified crystal units to partly remelt instantaneously at the contact points due to heat transfered from the hot molten droplets. These will condense at last, forming a new outermost layer while the original outermost layer becomes the second outer one. Obviously, it is the formation of such interlinking and bridging at the solid-liquid interface, the partial remelt of the crystal units and the condensation of the liquid-remelt system that directly lead to the growth of twin crystal units. By repeating this process more than twice on the same crystal unit, it will grow to be a flat crystal grain having an irregular appearance, with its traverse dimensions greater than its thickness. By repeating this process many times on a large number of crystal units on various planes, a layered aggregation structure will eventually be formed by many vertically overlapping layers of flat crystal grains.

However, some small crystal units located in the depressed zones between larger ones are not able to be in contact with the latter absorbed droplets and so do not undergo the above mentioned process. They grow freely to be individual grains.

Since each granule or macrograin consists of a tremendous number of irregular crystal units and the granulating process is influenced by a number of complicated accidental factors, some extremely irregular interstices will occur inevitably inside the granule, as is shown in photo 4. These interstices are distributed three-dimensionally and inter-connected with each other with a width of 2.5–7.5μm. Additionally, in some parts there exist some irregular cavities, the maximum transverse dimension of which may reach 80μm × 15μm with a considerable depth. All these cavities, if any, also inter-connected with one after another.

6. The Structure of Crystal Units

It is the author's opinion that the macro-structure of granules, that is, the aggregation behavior of crystal units, and the distribution of interstices are the two key factors affecting the porosity and oil absorption of porous granular AN product, while the shape and structure of crystal units seem to be less important. The objective basis of this opinion is that the size of the vast majority of these crystal units is less than 50μm. It is fine enough to meet the quality requirements for explosive manufacturing, as compared with the size of crystalline (or powder) AN (generally +160 mesh or greater than 100μm, very rarely up to 200 mesh or 75μm), which is heated and crushed by an edge runner for manufacturing traditional AN explosives. In consequence, the structure of crystal units will not in the least influence the above mentioned two quality indicators even if all of them are dense, individual grains.

In spite of this, some crystal units on the surface of and inside the finished granules were still examined and several photoes were taken at the magnification of 1000X–6000X, so as to further understand their inner structures in detail (see Photoes 5, 6, 7, 8 and 9).

Note: the cracks on the faces of the crystal units in photoes 5 & 7 were not originally present but most probably, were caused by local crystal transformation and melt of crystal due to excessive heat from too long

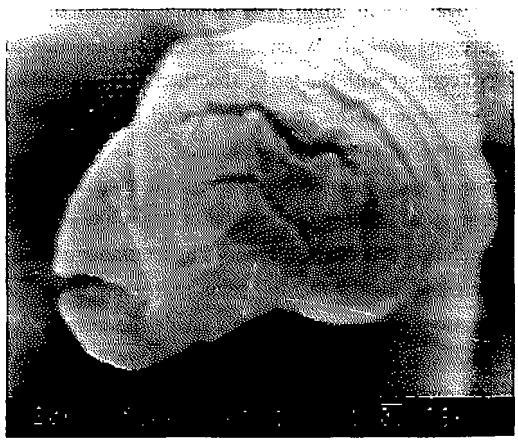

Photo 5

Photo 6

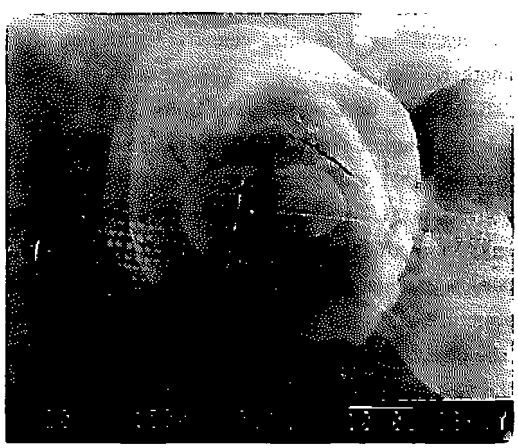

Photo 7

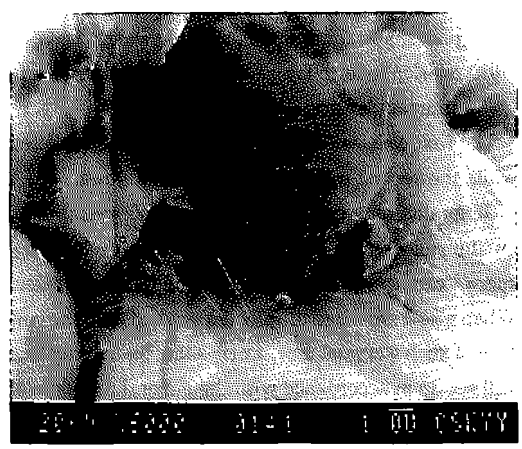

Photo 8

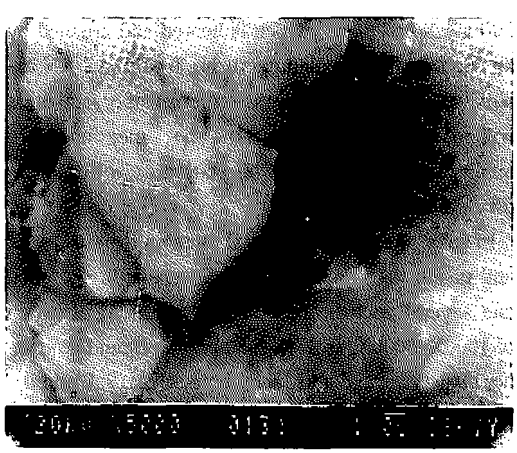

Photo 9

Phptoes 5. 6. 7. 8 and 9. Magnified SEM pictures taken of individual crystal units in granules or macrograins for studying the sturucture of crystal units (800X-6000X)

electron focussing during high magnification (>1500X) of samples. Such cracks increase both in magnitude and width with the time. This phenomenon was previously reported abroad.[3]

After examining and analyzing these photoes taken at various angles, the author has found the following noteworthy information.

(i) In an unstrict sense, of all crystal units, not a single one is a spheroidal or ellipsoidal grain with a regular shape and smooth surface, even if their unidirectional dimesion is as small as 10μm, Photo 7 clearly shows some foldings and undulation on the surface of a crystal unit, like veins protruding from the skin below.

(ii) Strictly, a large crystal unit may not be considered to be just a single one. By a large crystal unit here is not meant the pod-shaped or dumbbell-shaped twin crystal but nearly all those having many smaller dendritic crystals (generally the unidirectional size of which is less than 15μm) (see photoes 5, 6, and 7).

(iii) Photo 6 shows the growth of small dendritic crystal somewhere on the surface of a large crystal unit. In some cases, one crystal unit even grows from the datum plane of another large one, as can be seen in the center of photo 8. All this shows that their crystal units actually are not just loosely and locally sticking to one after another in some positions as they seem to be, but are linking altogether something like the four limbs being linked to the body. This once again confirms the conclusion that the crystal is growing up in the course of interlinking, bridging, remelting, and re-condensation of atomized droplets at the points of their adhesion.

(iv) Photo 9 shows some depressed stains on the surface of some crystal units, probably caused by corrosion or the like.

7. Calculation of Granulating Capability

Some technical parameters with regard to the fluidized-bed granulating process employed by Shijiazhuang Chemical Fertilizers Plant are as follows.

The grain size of seed crystal:30 mesh, two average grain sizes of 0.4mm diameter (−35 mesh) and 0.3mm diameter (+48 mesh) are chosen for calculation.

The grain size of AN granules product:0.5mm (+32mesh) −2.5mm (−7 mesh), these two values are chosen as lower and upper limits respectively for practical calculation.

Based on the results of this study on the outer and inner granule structures using SEM examination and photographing, the practical parameters of crystal units representing the data of inner structures may be obtained as follows.

For calculation, the average diameter of crystal units is taken to be 30μm. The average width of the interstices between the crystal units is taken to be 4μm, with the exception of those special cavities. So the actual overall diameter of the space occupied by each crystal unit is 34μm, including its surrounding space. The calculation results based on the above mentioned parameters are listed in Table 1.

A T-shaped nozzle with a capability of 10 ton/day is

Table 1

finished granule dia. (mm) \ Seed crystal dia. (mm) \ results		vol. of a granule (mm^3)		vol. of a 30 −μm crystal unit (mm^3)	number of crystal units in one granule ($\times 10^4$)	
		overall	excluding seed crystal		overall	excluding seed crystal
0.5	0.4	0.0208	(−0.0107) 0.0101	0.0006×10^{-4}	34.6667	16.8333
	0.3	0.0208	(−0.0045) 0.0163	〃	34.6667	27.1667
2.5	0.4	2.6042	(−0.0107) 2.5935	〃	4340.3333	4322.5
	0.3	2.6042	(−0.0045) 2.5997	〃	4340.3333	4332.8333

used to spray the molten AN in Shijiazhuang Chemical Fertilizers Plant. The amount sprayed per unit time is about 0. 1157kg/sec for each nozzle provided that the nozzle is well matched with other auxilliary equipment and under normal operating conditions all the time.

For each 30-μm diameter crystal unit taking a spheroidal shape, the volume occupied is about $4.5\times10^{-12}cm^3$. If the unit is considered as a dense crystal and its density is 1. 5g/cm³, then its weight is about $6.75\times10^{-12}g$.

In general, the molten AN with a concentration of 90% by weight is sprayed at 120-125℃ during production. Thus the amount sprayed per unit time may be converted into the capacity of producing solid AN crystal units. i. e. $0.1157\times90\%=0.1041kg/sec$

The number of crystal units produced per second therefore could be calculated to be 15.42×10^{12} provided that the average diameter of the crystal units formed is 30μm and that each T-shape nozzle is in normal operating condition.

Finally, when seed crystal of various sizes is used. The number of finished AN granules formed by the T-shape nozzle with the above-mentioned capability could be calculated and the results are listed in Table 2.

All the calculations were done on the assumption that the equipment should be in normall operating conditions. taking no account of other unexpected interferences and losses.Apparently, the actual values would be less than those calculated above.

Table 2

Numbey of granules produced per sec. / Seed crystal condition / Dia of finished granales (mm)	diam. of seed crystals (mm)	
	0.4	0.3
0.5	9.1×10^1	5.68×10^1
2.5	3.57×10^5	3.56×10^5

8. Summary and Conclusions

Using a scanning electron microscope, the structure of porous AN granules manufactured by fluidized-bed process has been studied and analyzed comprehensively, including the formation and aggregation of granules or macrograins, the shape, size and growth of crystal units, the width and distribution of interstices inside the granules. A series of quantitative data were obtained by measurements and calculations. All these may help to take full advantage of the technical performances and characteristics of this kind of AN granules, and further improve the fluidized-bed process.

From the description above, it could be concluded that:the porous AN granule. 0.5-2.5mm in diameterand produced by the fluidized-bed process, is composed of 35×10^4-43×10^6 crystal units 30μm in diameter. Such a spheroidal or ellipsoidal granule (or macrograin as it is defined in this paper) takes a "bayberry" type of outer structure, inside which are distributed irregular interstices of 4μm in width all these interstices are interlinked with one after another. The tremendous surface foldings, the huge number of crystal units, the widespread distribution and interlinkage of interstices inside, all these will afford this kind of AN granules a great specific area. Furthermore, the addition of 0.05% by weight of stearylamine acetate into the molten AN during granulation could prevent caking and improve absorbability, yielding porous granular ammonium nitrate of high absorption.

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ブリル硝安の構造についての走査型電子顕微鏡による研究

聶　森林

ブリル硝安の構造上の特性や使用される界面活性剤の種類·量は，その油吸収特性に大きく影響する。筆者は中国で最初に走査型電子顕微鏡により製法の異なる種々のブリル硝安の内部及び外面的な構造を観察し，それらの造粒特性について研究した。

本論文は，この第1報として流動床法で製造されたブリル硝安の構造について論じたものである。

（中国有色金属工業総公司　長沙鉱山研究所）