# PULSAR®

## AMMONIUM SULFATE

## 1. SUBJECT OF THE SPECIFICATION

The subject of the Technical Specification is ammonium sulfate obtained as a by-product in the production of:

- caprolactam
- sulphuric acid and oleum from flue-gas desulphurization plants

Ammonium sulfate fulfills quality requirements according to:

- Regulation EC No. 2003/2003 of The European Parliament and Council relating to fertilizers No. 2003/2003 and is designated as „EC FERTILISER"
- PN-C-87002:1985 standard.

## 2. REQUIREMENTS

### 2.1. GENERAL REQUIREMENTS

Ammonium sulfate is off white to gray-beige or gray crystalline solid, free-flowing, soluble in water and without any mechanical impurities. Product contains nitrogen in ammoniacal form (20,8% N) and easily available sulphur (24,2% S, 60,5% as $SO_3$). Product does not form stable lumps. The resulting lumps should be easily crushed under the pressure of the hand.

### 2.2. DETAILED REQUIREMENTS - see Table 1

**Table 1**

| No. | Requirements | | Unit | Limit | | |
|---|---|---|---|---|---|---|
| | | | | PULSAR | PULSAR Mikro | PULSAR Makro |
| 1. | Nitrogen content (N) as dry substance | min | % | 20,8 | | |
| 2. | Water content | max | % | 0,4 | | |
| 3. | Free sulphuric acid content | max | % | 0,1 | | |
| 4. | **Granulation** | | | | | |
| 4.1 | Content of particle size below 0,2 mm | | | max 4% | - | - |
| 4.2 | Content of particle size over 0,6 mm | | | min 70% | | - |
| 4.3 | Content of particle size below 0,8 mm | | | - | min 90% | - |
| 4.4 | Content of particle size over 1,6 mm | | | - | - | min 90% |
| 4.5 | Content of particle size below 1,6 mm | | | - | - | max 5% |

Detailed quality requirements are individually agreed with customers upon signing of commercial contract, and may differ from the above mentioned quality characteristic.

## 3. LABELLING

Product label shall be located in conspicuous location and shall be permanently affixed to the packing. Label text and information should be in a size of type large enough to be readily legible.

For control purposes, a relevant accompanying document must be attached to each batch of the fertiliser shipped in bulk.

Labelling of fertiliser packaging and accompanying document is in compliance with the Regulation (EC) No 2003/2003 of the European Parliament and of the Council of 13.X.2003 relating to fertilisers.

Labelling of packaging contains additional marks due to nature of the product and type of packaging.

## 4. PACKING

Ammonium sulfate may be packed as follows:

- bulk
- polyethylene bags of 25 kg capacity (net weight)
- elastic containers of big bag type containing 500 kg of ammonium sulfate (net weight)

## 5. STORAGE

Ammonium sulfate should be stored in clean, well ventilated roofed facilities while providing protection against moisture and dirt. Packed fertliser may be stored under shelters and in stockpiles, stacks should protected from precipitation by means of insulating materials. In order to reduce caking under pressure, bags should be stacked no higher than 10 layers. Stack height should not exceed 1.6 m. Elastic containers (big bag type) which do not exceed mass of 500 kg of weight may be stored in stacks consisting of maximum three layers.

Improper storage may affect product quality.

## 6. TRANSPORT

Ammonium sulfate shall be transported by any means of transportation while providing clean and dry environment during shipment. Packaging which are not resistant or slightly resistant to moisture must be protected from precipitation. Bags during transport should be stacked no higher than 12 layers. ADR/RID regulations do not apply to this product.

## 7. ANALYTICAL METHODS

### 7.1. TESTING SCHEDULE – see Table 2

**Table 2**

| No. | Test description | Test description as per: |
|---|---|---|
| 1. | Determination of general requirements | 7.4 |
| 2. | Determination of nitrogen content (N) as dry substance | 7.5 |
| 3. | Determination of water content | 7.6 |
| 4. | Determination of free sulphuric acid content | 7.7 |
| 5. | Determination of particle size distribution (PSD) | 7.8 |

### 7.2. LOT QUANTITY

A lot of ammonium sulfate is a daily production output or a single shipment to a customer, however, not less than 20 tons and not more than 500 tons.

### 7.3. SAMPLING

Assuming that the ammonium sulfate manufactured during synthesis of caprolactam is a homogenous substance, primary samples of ammonium sulfate shall be taken in amounts of at least 200 g each.

Take five primary samples out of a single lot of a homogenous product. Primary samples may be taken directly from a belt conveyor during loading, by manually transferring the product to an appropriate vessel in equal time intervals. Transfer the primary samples taken into a clean, dry vessel and mix thoroughly. Next, from thus obtained total sample take at least 0.5 kg of the material and divide into 2 parts; one shall be used for testing, while the other shall be kept as reference for the period of 6 months from date of shipment.

### 7.4. CHECKING FOR COMPLIANCE WITH GENERAL REQUIREMENTS

Check visually for compliance with general requirements.

### 7.5. DETERMINATION OF NITROGEN CONTENT (N) AS DRY MASS

#### 7.5.1. Applicability of the test methods

a) the distillation method is applied in cases of dispute (arbitration method),
b) the formalin method is applied in on-line production monitoring.

#### 7.5.2. DETERMINATION OF NITROGEN CONTENT BY DISTILLATION METHOD

##### 7.5.2.1. Principle of the method

The determination consists in distillation of ammonia from an alkaline solution and absorption in a standard

solution of sulphuric acid. The excess sulphuric acid is titrated with a standardized sodium hydroxide solution in presence of a mixed indicator.

#### 7.5.2.2. Apparatus and instruments

a) Distillation apparatus according to Picture No. 1 (see attachment) which consist of:
- a 1 liter flat-bottomed distillation flask
- a 100 ml dropper
- a catch-drop
- a 7-bulb condenser
- a 500 ml absorption flask

b) two burettes, 50 ml each
c) a 500 ml volumetric flask
d) a 50 ml calibrated pipette
e) Ceramic granules or glass beads

#### 7.5.2.3. Reagents and solutions

a) Sodium hydroxide, solution at concentration of 400 g/l
b) Sodium hydroxide, standard solution at concentration of 0.50 mol/l
c) Sulphuric acid, solution at concentration of 0.50 mol/l
d) Mixed pH indicator prepared as follows: mix 0.2% (m/m) of methyl red alcohol solution with 0.1% (m/m) of methylene blue solution in a ratio 1:1 (v/v)
e) Universal indicator pH paper

#### 7.5.2.4. Test solution preparation

From the test sample, prepared according to item 7.3, weigh approximately 10 g of ammonium sulfate with an accuracy of 0.001 g. Transfer the weighed amount into 500 ml volumetric flask, dissolve in distilled water, dilute to volume with the same solvent and mix well.

#### 7.5.2.5. Determination procedure

Take 50 ml of the test solution and transfer into distillation flask (1). Add approx. 350 ml distilled water and a few glass beads. Using 50 ml burette take 40 ml of sulphuric acid solution at c = 0.50 mol/l and transfer into the absorption flask. Next, add into the absorption flask 80 ml of distilled water and 4-5 drops of the mixed indicator. Close the distillation flask (1) with a rubber stopper provided with catch-drop (3) and dropper (2). Arrange the absorption flask so that condensate tube discharge end is submerged in the sulphuric acid solution. Using dropper carefully introduce 15 ml sodium hydroxide solution at c = 400 g/l into the distillation flask. Close dropper tap, leaving 2 ml of sodium hydroxide solution inside the dropper. Heat the flask by gradually increasing temperature until the liquid boils vigorously. Proceed with distillation until approx. 150 ml of distillate condenses in the absorption flask. Lower the absorption flask so that the condensate tube end is above the surface of the liquid. Check for ammonia presence using pH indicator paper. If the paper indicates no ammonia, flush the tube and the condenser with distilled water, collecting the water in the absorption flask. Titrate the content of the absorption flask with standard sodium hydroxide solution at c = 0.50 mol/l in presence of the mixed indicator until a color change is obtained. Carry out a blank test (prepared as hereinbefore without addition of the test sample) under the same conditions and refer to this in the calculation of a final result.

#### 7.5.2.6. Calculation and expression of results

Calculate the nitrogen content as dry substance ($X_1$) in weight percentage (w/w) using the following formula:

$$X_1 = (V_1 - V_2) \cdot 0{,}007004 \cdot \frac{500}{50} \cdot \frac{100}{m} \cdot \frac{100}{100 - X_3} = \frac{7{,}004 \cdot (V_1 - V_2)}{m(100 - X_3)} \cdot 100$$

where:

$V_1$ - volume (ml) of 0.50 mol/l sodium hydroxide solution consumed during titration of the blank sample

$V_2$ - volume (ml) of 0.50 mol/l sodium hydroxide solution consumed during titration of the test sample

m - mass (g) of the test sample

0.007004 - amount (g/ml) of nitrogen corresponding to 1 ml of 0.50 mol/l sulphuric acid solution

$X_3$ - content of water (% w/w) in the test sample, determined according to item 7.6.

#### 7.5.2.7. Final result of determination

The final results should be an arithmetic mean of the results of at least two consecutive tests, which differ from each other by not more than 0.2%.

### 7.5.3. DETERMINATION OF NITROGEN CONTENT BY FORMALDEHYDE METHOD

#### 7.5.3.1. Principle of the method

The method consists in a reaction of formaldehyde with ammonium sulfate, in which sulphuric acid is released. The sulphuric acid is titrated with a standard solution of sodium hydroxide.

#### 7.5.3.2. Reagents and solutions

a) Formaldehyde, analytical grade, approx. 37% (w/w) solution neutralized with sodium hydroxide solution in the presence of phenolphthalein. Neutralization of relevant amount of formaldehyde should be performed just before the use.

b) Sodium hydroxide, analytical grade; prepare solution at concentration of 0.50 mol/l. Factor of that solution shall be determined by the titration of analytical grade ammonium sulfate as follows: Weigh 33.035 g of $(NH_4)_2SO_4$ into 1 l volumetric flask, dissolve in water and dilute to volume with the same solvent. Pipette 15 ml of that solution into a 300 ml conical flask, neutralize with sodium hydroxide solution at c = 0.50 mol/l in presence of mixed indicator prepared according to item of 7.5.3.2 c), and proceed further as per 7.5.3.3 hereunder. The factor of sodium hydroxide (f) shall be calculated using the following formula:

$$f = \frac{V}{V_1}$$

where:

V - volume (ml) of ammonium sulfate solution

$V_1$ - volume (ml) of 0.50 mol/l sodium hydroxide solution consumed for titration of test sample

c) Mixed indicator: mixture of methyl red and methylene blue prepared according to item 7.5.2.3.d)

d) Phenolphthalein: dissolve 0.1 g of the indicator in 50 ml of ethyl alcohol and dilute to 100 ml with water.

#### 7.5.3.3. Determination procedure

Weigh 10 g of ammonium sulfate with an accuracy of 0.001 g and transfer into a 500 ml volumetric flask. Dissolve in water, dilute to volume with the same solvent and mix. Transfer 50 ml of the thus prepared solution to a 300 ml conical flask, add 3 drops of indicator solution prepared as per 7.5.3.2 c) and neutralize free acid with sodium hydroxide solution. Next, add 10 ml of formaldehyde solution, 5-10 drops of phenolphthalein solution, mix well, and titrate with sodium hydroxide solution until the color of the solution changes through green to dark-pink.

#### 7.5.3.4. Calculation and expression of results

Calculate the nitrogen content as dry substance ($X_2$) in weight percentage (w/w) using the following formula:

$$X_2 = \frac{V \cdot 0{,}007 \cdot 500 \cdot 100 \cdot 100}{50 \cdot m(100 - X_3)} = \frac{V \cdot 700}{m(100 - X_3)}$$

Where

V - volume (ml) of 0.50 mol/l sodium hydroxide consumed for titration

m - mass (g) of the test sample

$X_3$ - content of water (% w/w) in the test sample, determined according to item 7.6.

0.007 - amount (g/ml) of nitrogen corresponding to 1 ml of 0.50 mol/l sodium hydroxide solution

#### 7.5.3.5. Final result of determination

The final results should be an arithmetic mean of the results of at least two consecutive tests, which differ from each other by not more than 0.25%.

### 7.6. DETERMINATION OF WATER CONTENT

**7.6.1. Principle of the method**

Determination of water content consist in drying of the ammonium sulfate sample at temperature c.a. 105 ÷ 110°C for 2 hours. After cooling down, the sample is weighed and water content is calculated based on mass decrement.

**7.6.2. Determination procedure**

Into weighing vessel (previously dried and weighed with an accuracy of 0.001 g) transfer 10 g of ammonium sulfate sample, measured with the same accuracy. Dry in laboratory dryer at 105-110°C for 2 hours. Further cool the vessel with the sample in a desiccator and after that weigh it again with an accuracy of 0.001 g.

**7.6.3. Calculation and expression of results**

Calculate the water content ($X_3$) as weight percentage (w/w) using the following formula:

$$X_3 = \frac{(m - m_1) \cdot 100}{m}$$

where:

m – mass (g) of the sample before drying

$m_1$ – mass (g) of the sample after drying

**7.6.4. Final result of determination**

The final results should be an arithmetic mean of the results of at least two consecutive tests, which differ from each other by not more than 0.08%.

**7.7. DETERMINATION OF FREE SULPHURIC ACID CONTENT**

**7.7.1. Principle of the method**

The method consists in the titration of free sulphuric acid contained in a sample using sodium hydroxide solution in presence of a mixed indicator.

**7.7.2. Reagents and solutions**

a) Sodium hydroxide, analytical grade; prepare solution at concentration of 0.1000 mol/l

b) Mixed indicator: mixture of methyl red and methylene blue prepared according to item 7.5.2.3.d)

**7.7.3. Determination procedure**

Into 500 ml conical flask weigh a sample (10-50 g) of ammonium sulfate with an accuracy of 0.1 g and dissolve in 250 ml of water. The amount of the sample should be chosen so as to contain maximum 0.005-0.05 g of sulphuric acid. If the obtained solution is turbid, filter it and, subsequently, wash the filter with water. Add 3-4 drops of the mixed indicator to the solution tested and titrate with sodium hydroxide solution until the color changes from violet-red to green.

**7.7.4. Calculation and expression of results**

Calculate the free acid content ($X_4$) as weight percentage (w/w) using the following formula:

$$X_4 = \frac{V \cdot 0{,}0049 \cdot 100}{m}$$

where

V - volume (ml) of 0.1000 mol/l sodium hydroxide solution, consumed for titration of the sample

m - mass (g) of the test sample

0.0049 – amount (g/ml) of sulphuric acid corresponding to 1 ml of 0.1000 mol/l sodium hydroxide solution

**7.7.5. Final result of determination**

The final results should be an arithmetic mean of the results of at least two consecutive tests, which differ from each other by not more than 0.02%.

### 7.8. DETERMINATION OF PARTICLE SIZE DISTRIBUTION BY SIEVE ANALYSIS

#### 7.8.1. Principle of the method

The method consists in separation of dry ammonium sulfate on sieves of different sizes, weighing the obtained fractions, and reporting the particle size distribution by fractions.

#### 7.8.2. Equipment

a) A set off test sieves according to DIN/ISO-3310-1 with nominal mesh size of 0.2 mm, 0.6 mm, 0.8 mm 1,6 mm

b) Vibrating screen, laboratory size

#### 7.8.3. Manual determination procedure

Lay the clean, dry sieves one onto another so that their casing are closely fit; put a receiving pan under the bottom sieve. Weigh 100 g sample of ammonium sulfate with an accuracy of 0.01 g and transfer onto the top sieve. Manually shake the sieve horizontally for 5 minutes. Next, weigh the retained mesh fraction on the 0.6 mm sieve with an accuracy of 0.01 g, and the fines fraction of the 0.2 mm sieve collected on the receiving pan with an accuracy of 0.001 g.

#### 7.8.3.1. Determination procedure using vibrating screen

Place the following clean & dry set on the screen: receiving pan and the sieves with gaskets. Weigh 100 g of a homogenized sample of ammonium sulfate with an accuracy of 0.01 g and transfer it quantitatively to the top sieve. Place the sample centrally on the sieve. Mount the cover and fix the set using lock nuts. Turn the screen on for 5 minutes at a vibration amplitude of 1.8 mm. Next, weigh the retained mesh fractions on the sieves with an accuracy of 0.01 g, and the fines fraction of the 0.2 mm sieve collected on the receiving pan with an accuracy of 0.001 g.

#### 7.8.4. Calculation and expression of results

Calculate sieve fractions ($X_5$) as weight percentage (w/w) using the following formula:

$$X_5 = \frac{m_1 \cdot 100}{m}$$

where

$m_1$ – mass (g) of retained mesh fraction / fines fraction

m – mass (g) of the test sample

#### 7.8.5. Final result of determination

The final results should be an arithmetic mean of the results of at least two consecutive tests, differing not more than 2% for the residue on the sieve and 0.2% for the fines fraction.

### 7.9. RESULTS EVALUATION AND TEST CERTIFICATE.

A batch of ammonium sulfate shall be considered to meet the requirements of this Technical Specification if test results conform with the requirements indicated in Table 1. Quality Control Certificates are issued upon customer request.

## 8. REFERENCES

- DIN ISO-3310-1-1992 -Test sieves–Technical requirements and testing–Test sieves of metal wire cloth.
- PN-C-87002:1985 – Artificial fertilisers. Ammonium sulfate.
- PN-C-04501:1971 – Test sieving. Principles and procedures.
- Directive No. 2003/2003 of The European Parliament and of The Council dated 13th October 2003 relating to fertilizers.

## 9. ADDITIONAL INFORMATION

WT-2015/ZA-11 supersedes WT-2013/ZA-11/2.