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(54) Title: METHOD FOR PRODUCING POROUS AMMONIUM NITRATE

(57) Abstract: A method of producing porous ammonium nitrate particles, wherein nearly mono-disperse gas bubbles are injected into molten ammonium nitrate, whereafter the melt is particulated and solidified.



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Method for producing porous ammonium nitrate.

5 Ammonium nitrate (AN) is an important raw material for industrial explosives besides its use as a fertiliser. One type of AN based industrial explosives is ANFO which normally consists of Porous Ammonium Nitrate prills and Fuel Oil. This type is the dominating industrial explosive globally.

10 In ANFO, ammonium nitrate acts as oxidiser and reacts with fuel oil after initiation. The stoichiometric mixing ratio is a blend consisting of about 5.7% FO and 94.3% AN. The oil is normally absorbed in pores in the AN.

The pores/inner voids in ammonium nitrate porous prills (AN-PP) serve two purposes:

15

- First, the volume and size distribution of open pores should be sufficiently able to absorb and retain the proper amount of oil.
- Additional pores/inner voids are required to act as hot spots during detonation to facilitate propagation of the detonation front at a high velocity. The smaller the diameter of the borehole, the more important these inner voids become.

20

The higher the pore volume, the lower the bulk density becomes. Increasing the pore volume by conventional means normally results in reduced mechanical strength.

25 Ideally, an explosive like ANFO and consisting of the elements C, H, N and O should only give N_2 , CO_2 and H_2O as reaction products from the detonation. However, as all ANFO are non-homogeneous, the detonation fumes will also consist of minor quantities of CO, NO and NO_2 .

30 We have found that not only the volume of inner voids/pores of ammonium nitrate porous prills, AN-PP, but also the size distribution of inner voids and crystals influence on the initiation sensitivity, velocity of detonation and composition of the detonation fumes. The smaller the diameter of the borehole, the more important the inner physical properties becomes.

35

In addition, the use of Ultra Low Density AN-PP for ANFO can be useful in certain rock conditions and/or for reducing the amount of ANFO e.g. in the upper part of the borehole

Over the years several methods have been described for manufacture of porous ammonium nitrate prills.

5

According to Romanian patent RO 116072, a synergistic mixture of modifying agents for the structure of the crystals and pore forming drying agents are introduced into the melt of ammonium nitrate at a temperature of 160°C. The total concentration of these additives is in the range of 0.4 to 1.0 %. The porosity is 0.09 to 0.15%, allowing an intake of oil of 15 to 20 %.

10

According to Russian patent RU 2121969 a ratio of 0.05 to 0.15% of molasses is added to the ammonium nitrate before the prilling process. The capacity of oil absorption is 9.7 to 13.5 %. The prills show a high durability and they are claimed to be explosion-proof.

15

The patent GB 1 462 491 offers a process for the production of porous prilled ammonium nitrate, wherein prills with a water content of 2.5 % are dried in a way, that the temperature is below the transition point of phase III to phase IV in a preliminary step. In a second step the prills, now containing 0.3 to 1.5 % of water, are further dried at a temperature exceeding the temperature of that phase transition.

20

Another process for the production of granulated porous ammonium nitrate is described in Russian patent RU 110810, wherein an aqueous solution of aluminum sulphate is added to the melt of ammonium nitrate followed by an addition of an aqueous suspension of a pore forming medium, containing chalk and dispersing agents. A similar principle is described in International patent application WO 0136330. Bubbles of CO₂-gas are generated by a chemical way inside the melt with a decreased pH-value of 3.8, thus lowering the bulk density of the ammonium nitrate prills.

25

Addition of calcinated soda and further additives into the melted ammonium nitrate is described in Russian patent RU 1616048.

30

Porous prills of ammonium nitrate with a bulk density of 0.55 to 0.85 are available after Brazilian descriptions of invention in BR 9600121 and BR 9505880 by addition of chemical reagents inert to ammonium nitrate and generating gas, that will widen existing flaws and bubbles.

35

Addition of 0.2 to 3.0 chalk with a granular diameter of 5-10 μm as pore forming agent is described in Soviet patent SU 767025. An exchange of chalk against other carbonates, e.g. sodium hydrogen carbonate, does not yield the desired results.

- 5 A porous ammonium nitrate is produced following patent description WO 9626158 by wetting non-porous material with water or an aqueous solution of ammonium nitrate up to a water intake of 0.2 to 3.0 %, followed by warming up the mixture to a temperature above the point of phase transition of phase II to phase III and kept at this temperature until the content of water will be 0.2 %. This process yields a porous product with a bulk density
10 from 0.80 to 0.95 g/cm^3 and absorption of oil of 5.8 $\text{cm}^3/100 \text{ g}$.

- The known ways for the production of porous prills of ammonium nitrate are either not able to fulfill the demand for a bulk density of $< 0.65 \text{ g/cm}^3$ and/or the formation of AN with improved fumes characteristics whilst maintaining the handling characteristics of regular
15 AN-PP. Additionally, several of the methods described above will not yield a homogenous distribution of gas bubbles which is a necessary requirement for an even distribution of pores in the solidified product.

- The object of the invention is to obtain a method of producing ammonium nitrate particles
20 with increased pore volume without a significant reduction in mechanical strength. Another object is to obtain porous ammonium nitrate particles with improved blasting properties and a reduction of harmful fumes.

- These and other objects of the invention are obtained by the method as described below,
25 and the invention is further defined and characterized by the accompanying patent claims.

- The invention thus concerns a method of producing porous ammonium nitrate particles, wherein nearly mono-disperse gas bubbles are injected into molten ammonium nitrate, whereafter the melt is particulated and solidified. When micro-bubbles of gas of a narrow
30 size distribution is incorporated into molten ammonium nitrate, an extended system of pores/voids is formed in the inner parts of the resulting prills during the solidifying process.

- The injection of gas is preferably done by physico-chemical ways. The supply of gas to the melt could be done by a nozzle, mainly by a micro-porous membrane. The diameter of
35 the pores of the membrane is 0.01 to 0.5 μm , preferably 0.2 μm . The area of the membrane surface is large enough for obtaining a slow flow of gas passing through, so that the radius of the gas bubbles are mainly controlled by the interface energy of the

three-phase-contact of gas, solid, and liquid melt and wherein the gas pressure is between 50 and 550 mbar, especially about 150 mbar.

- 5 The pore forming gas could be one or more selected among air, oxygen, nitrogen, carbon dioxide, di-nitrogen monoxide, ammonia, argon or substances forming a gas by thermal decomposition above 80 centigrade or mixtures of such gases and substances. Parts of the gaseous phase are preferably completely or partly soluble in the melt. The molten ammonium nitrate could contain additives influencing the crystallisation point, the viscosity
10 or the surface tension.

It is preferred to inject gas into molten ammonium nitrate, containing 1 to 5 % of water and 0.01 to 2.0 % of prilling additives by use of a membrane with pore diameter 0.01 to 0.5 μm submerged into the melt at a temperature of 130°C to 160°C, and thereafter sprayed into
15 a prilling tower.

The essence of the invention is thus the controlled generation of gas bubbles with a narrow distribution of their diameters by physico-chemical means for the production of an
20 additional and modified microstructure in the prills, yielding in an increase in porosity. The presence of an additional micro-structure and porosity improves the blasting properties (sensitivity, velocity of detonation and composition of detonation fumes) under certain blasting conditions whilst maintaining the handling properties of the ammonium nitrate.

- 25 Another benefit of the process is the possibility of increasing the pore volume without significantly reducing the mechanical strength.

According to the claimed method, the porosity of AN is controlled by addition/injection of a gas in the AN-melt prior to prilling. In this way the additional pores consist of fairly
30 spherical inner voids with a narrow size distribution.

The production of prills with 0.5 to 2.5 mm in diameter is carried out by spraying a melt of ammonium nitrate at the top of a prilling tower. The melt may contain various additives for reduction of the melting point, the viscosity or the surface tension. The melt will be
35 sprayed through nozzles of 0.5 to 1.5 mm in diameter with a temperature of 130°C to 160°C. The melt will cool to app. 60°C while falling down and will solidify. The micro-porous structure in the prills will be formed partly during the free fall in the prilling tower but also during subsequent process steps (drying and cooling).

The injection of gas is carried out through micro nozzles, especially by a microporous membrane submerged into the melt, as an example. The material of the nozzles or the membrane is glass, glass frit, ceramics, sintered metal, silicon caoutchouc or
5 perfluoralkane. The diameter of the pores of the membrane is 0.01 to 0.5 μm , preferably 0.2 μm .

The pore forming gas could be air, oxygen, nitrogen, carbon dioxide, di-nitrogen monoxide, ammonia or argon. The necessary amount of gas can be injected into the melt
10 at a low pressure of gas due to the large number of even pores in the membrane. In that way the gas bubbles will not be ripped off by the turbulent current of gas, but their diameters are mainly controlled by the interface energy of the three-phase contact of gas, solid and liquid melt. Gas bubbles with mainly equal radius will appear. The bubbles will not coalesce due to the uniform pressure of curvature, the so-called dejoining pressure,
15 but will remain in an even distribution in the melt. Thus prills of ammonium nitrate with an extended volume of pores are formed.

The idea of the invention will be demonstrated by examples as follows:

20 Example 1

Carbon dioxide was injected into molten ammonium nitrate by a ceramic membrane with an average pore diameter of 0.2 μm , submerged into the melt. The difference gas pressure was 50 to 550 mbar. Small uniform bubbles of gas were generated, and did not escape out of the melt during the solidification of ammonium nitrate in the prilling process.

25

The melt of ammonium nitrate contained 4 % of water and 0.01 % of organic additives (e.g. stabilizer, prilling or coating agents) . Prills were formed with an average diameter of 1.4 mm and a specific bulk density of 0,63 g/cm³.

30 Manufacturing of AN in the same process plant but without the injection of CO₂ yields a product with the same average prill diameter but with a bulk density of 0.70 g/cm³.

35 Example 2

Blasting tests in steel tubes as well as rock have demonstrated that the formation of nitrous fumes (NO + NO₂) is significantly reduced when using AN prills according to the present invention.

Table 1. Data of blasting tests in steel tubes with outer diameter of 54 mm and wall thickness of 2 mm. Initiation by electric blasting cap and 30 g HE primer.

AN-Prills Density [g/cm ³]	Mechanical strength (kg)	NO ₂ (l/kg)	NO (l/kg)	Velocity of detonation [m/s]
0.74	0.55	5	21	2840
0.65	0.52	2	13	3550
0.63	0.51	1	11	3700

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Even if the production process is described especially using prilling for production of the ammonium nitrate particles, other particulation methods are also possible.

Claims

- 5 1. A method of producing porous ammonium nitrate particles, wherein nearly mono-disperse gas bubbles are injected into molten ammonium nitrate, whereafter the melt is particulated and solidified.
- 10 2. A method according to claim 1, wherein the injection of gas is done by physico-chemical ways.
- 15 3. A method according to claim 1 or 2, wherein the supply of gas to the melt is done by a nozzle, mainly by a micro-porous membrane.
- 20 4. A method according to claim 3, wherein the diameter of the pores of the membrane is 0.01 to 0.5 μm , preferably 0.2 μm .
- 25 5. A method according to claim 1 to 3, wherein the pore forming gas is one or more selected among air, oxygen, nitrogen, carbon dioxide, di-nitrogen monoxide, ammonia, argon or substances forming a gas by thermal decomposition above 80 centigrade or mixtures of such gases and substances.
- 30 6. A method according to claim 3, wherein the area of the membrane surface is large enough for obtaining a slow flow of gas passing through, so that the radius of the gas bubbles are mainly controlled by the interface energy of the three-phase-contact of gas, solid, and liquid melt and wherein the gas pressure is between 50 and 550 mbar, especially about 150 mbar.
- 35 7. A method according to claim 1 to 6, wherein the molten ammonium nitrate contains additives influencing the crystallisation point, the viscosity or the surface tension.

8. A method according to claim 1 to 7, wherein gas is injected into molten ammonium nitrate, containing 1 to 5 % of water and 0.01 to 2.0 % of prilling additives by use of a membrane with pore diameter 0.01 to 0.5 μm submerged into the melt at a temperature of 130°C to 160°C, and thereafter sprayed into a prilling tower.

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9. A method according to claim 1 to 8, wherein parts of the gaseous phase are completely or partly soluble in the melt.

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INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C01C 1/18, C06B 31/28, C05C 1/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C01C, C05C, C06B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL, WPI DATA, PAJ

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A	US 2123661 A (IRNFRIED PETERSEN, WOLFEN ET AL), 12 July 1938 (12.07.1938), page 1, line 1 - line 24 --	1-9

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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31/08/2005

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