CONTINUOUS PRODUCTION OF SPHERICAL AMMONIUM DINITRAMIDE PARTICLES (ADN-PRILLS) BY MICROREACTION TECHNOLOGY

Thomas Heintz, Andreas Fuchs

Fraunhofer - Institut Chemische Technologie (ICT)
Joseph-von-Fraunhofer-Str. 7, 76327 Pfinztal, Germany
E-mail: Thomas.Heintz@ict.fraunhofer.de

Abstract

The production of spherical ammonium dinitramide (ADN) particles (so called ADN-Prills) is established at ICT as a batch process, using the emulsion crystallization technique. This paper presents how this know-how is transferred to the micro reaction technology. The goal was to develop a continuous working ADN-Periling process. The advantages of this continuous process for ADN are:

- Less thermal stress, as the ADN only remains for a very short time in the heating zone.
- A more safety process, because there is only less amount of ADN in the heating zone.
- The possibility to scale-up the process.

The conducted work has shown that it is possible to generate spherical ADN-particles with an adequate particle size by combining the micro reaction technique and the ADN emulsion crystallization process.

1 Introduction

ADN (ammonium dinitramide) is a promising oxidizer, which could be used for example in solid rocket propellants in the near future. ADN is more powerful than ammonium nitrate and less polluting than ammonium perchlorate. The disadvantage of ADN is its incompatibility with polymer binders systems containing isocyanates as curing agents. During propellant formulation and curing ADN reacts with these isocyanates by formation of decomposition gases. To avoid this, at ICT different investigation on coating of ADN by using fluidizing bed technology have been conducted [1]. The goal of this work was to confer ADN particles a suitable protection against the contact to curing agents.
The further processing of ADN particles by fluidized bed technology, or without coating in isocyanate free curing systems, makes it necessary to reshape the irregular shaped ADN crystals (directly from synthesis) into spherical particles, so called ADN-Prills [2]. Generally spherical particle have a higher packing density, good free flowing properties and a preferable surface to volume ratio. The spherical morphology is also suitable to work with in fluidized bed coating devices, because sharp edges are difficult to coat.
The primary prilling process, developed at ICT in the nineties, was a batch process [3]. In this work the original prilling process is modified into a continuous working process. The advantage of a continuous process is an increased safety and more parameters which can be set to change the properties of the ADN-Prills.

There are several advantages of spherical ADN particles compared with needle-shaped or flaky ADN crystals:

- Spherical or compact particles have a higher bulk density, which is an advantage at further processing. The solid particle concentration in a given volume can be increased.
- The particles have better free flowing properties. So the viscosity in a suspension or propellant formulation is reduced compared with the irregular shaped particles.
- The particles get a smaller surface in relation to their volume. Therefore the reaction surface of the particles gets also smaller.

- Because of less specific surface the spherical particles are more suitable to be coated with a protection layer.
- Spherical particles have a lower tendency to agglomeration, which benefits the materials handling and the safety during this work.

The following improvements of the continuous (microreactor supported) prilling process in comparison to the primary batch prilling process are expected:

- The particle size can be influenced by the geometry of the microreactor.
- It is possible to create small particle size distributions.
- The safety of the process is increased, because there is only a very small amount of ADN in the actual heating process zone.
- The process is thermally gentle to ADN. The duration of ADN in a hot ambient is much shorter than in the batch process. In an optimized process ADN is only in hot conditions for a few seconds and cools down again very fast.

The prilled ADN particles were characterized by the following methods:

- Light microscopy to get an overview of the manufactured particles and the agglomeration rate.
- REM to see the morphology on the particle’s surface.
- Laser light diffraction technology to characterize the mean particle size and particle size distribution.

2 The ADN-Prilling process using the microreaction technology

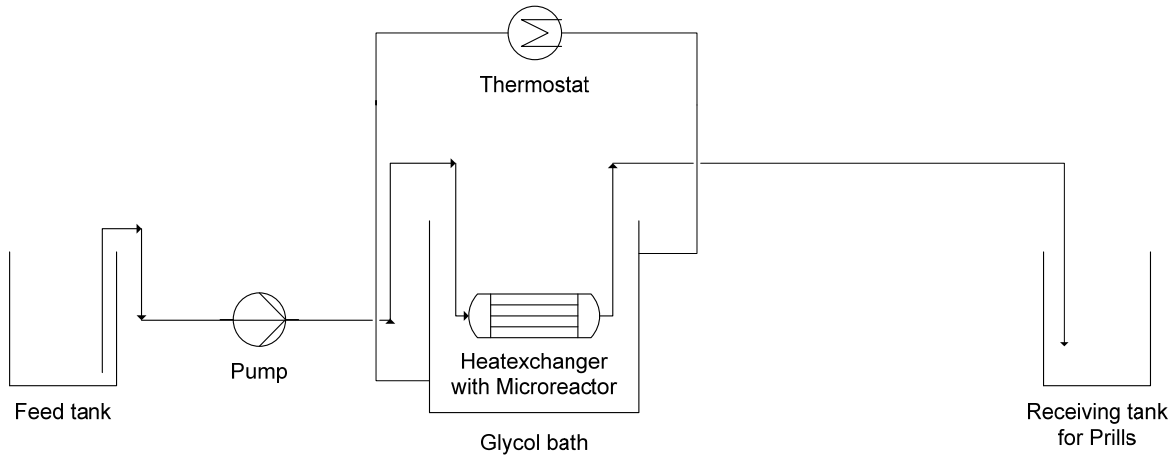

Figure 1: Trial composition of the prilling process

Figure 1 shows schematically the experimental set-up for a continuous ADN-Prilling process using the microreaction technology [4]. To get the ADN particles in a spherical form decane is necessary as anti solvent (continuous phase of the emulsion [3]). A surfactant is also necessary to lower the surface tension, resp. interfacial tension, and so the particle size. An anti-caking agent is needed to reduce agglomeration. This mixture is what the feed tank has to be filled with. The processing components are a glycol bath, a thermostat, a heating coil, a microreactor and a tube pump. With the tube pump the ADN containing suspension can be transferred from the feed tank through the heating coil in the glycol bath, through the microreactor and than in the receiving tank. In the heating coil the ADN crystals melt and get a spherical morphology because in fluidic state a sphere is the energetic optimized form. With the microreactor at the end of the heating coil it is possible to reduce the mean particle size and the particle size distribution of the molten ADN droplets. The molten ADN gets pushed through the very small cross-section with many baffles in this microreactor and gets spitted into smaller liquid particles. After passing the microreactor the molten ADN-Prills are cooled down below the melting point in the receiving tank. But it is not sufficient to cool down ADN to recrystallize it again. Additionally it is necessary to stir the ADN-Prills in the receiving tank for a while. With the combination of cooling down the prills and provide mechanical energy

it is possible to ensure the recrystalisation. The stirrer in the receiving tank also prevents from agglomeration.
Before the trials with ADN were started, some preliminary tests with sodium acetate as dummy material have been conducted.

The parameters which can be varied are:

- The temperature of the thermostat.
- The flow rate of the continuous phase (decane with additives) charged with ADN.
- The kind of microreactor.
- Amount of anti-caking agent.
- Amount of tenside.
- The charge of ADN in decane.

After cooling and recrystallizing the decane is decanded and the prills stay in the receiving tank. The solid ADN-prills have to get washed with heptane, because the vapour point of the remaining decane is very high and can hardly be removed in a vacuum drier. The advantage of heptan is its lower vapour point. In the vacuum drier heptane vaporizes easily and the prills get a free flowing and dry powder.

3 Experimental and results

The first trials have been done with sodium acetate particles. This material is not explosive but has some similar characteristics in its consistence to ADN. Therefore it was used as a substitute for ADN. The trials with sodium acetate were used to figure out the process parameters. After this the trials with ADN were started.

3.1 Results of light microscopy

Figure 2 shows the spherical sodium acetate particles that are produced by the continuous prilling process using the microreaction technology.

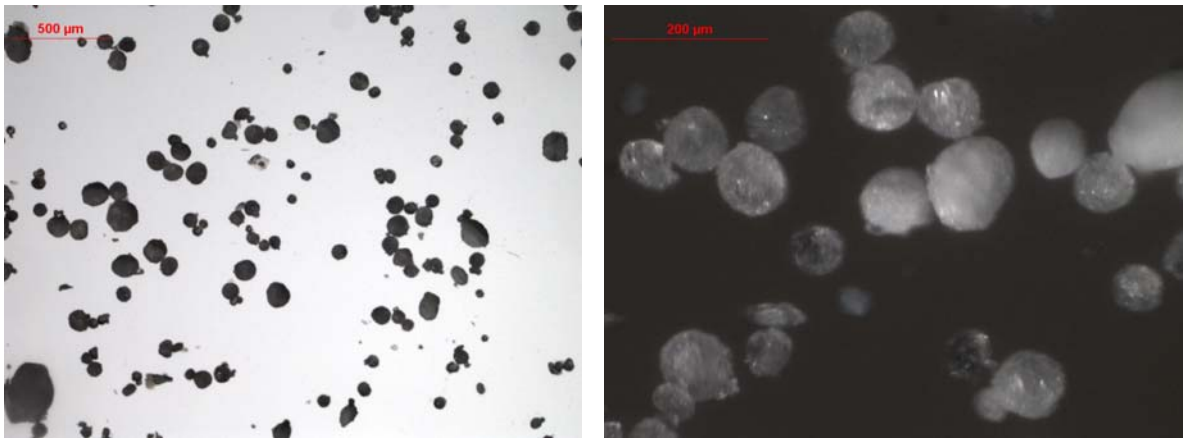

Figure 2: Spherical sodium acetate particles produced by the continuous prilling process

With these results it was agreed that it is possible to create also spherical ADN particles with the microreaction technology by using the figured out parameters. Figure 3 shows the original ADN particles, as they arise from synthesis, and its irregular morphology.

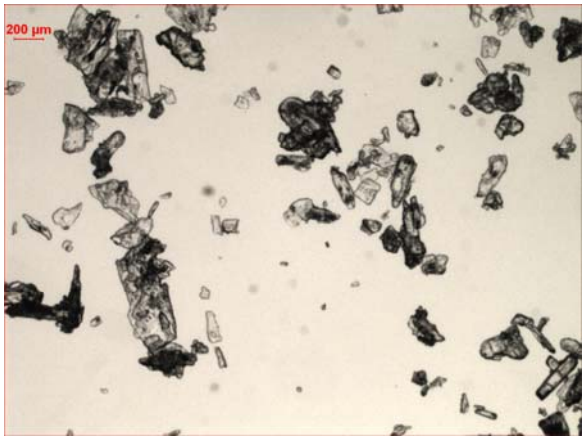

Figure 3: Original irregular shaped ADN (feed material)

On the microscopy pictures Figure 4 it is to be seen that it is possible to generate ADN-Prills with spherical morphology. The overview picture shows that the agglomeration rate is at a low level.
Another difference between the original ADN and the prilled particles is also the transparency. The original particles seem to be much more transparent than the prilled ones.

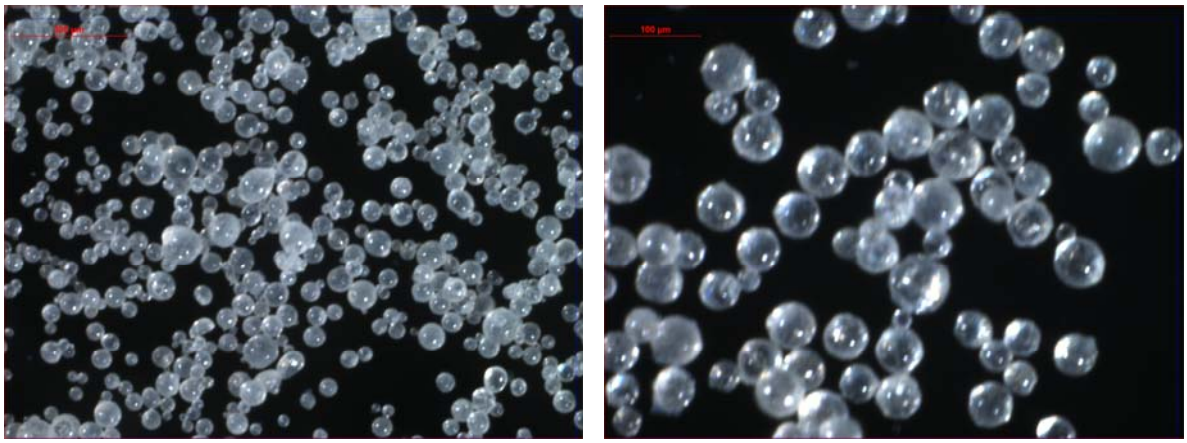

Figure 4: ADN-prills generated by the continuous prilling process

3.2 Results of SEM microscopy

The SEM investigations are showing similar results as the light micrographs. The following pictures (Figure 5) are showing the original particles of sodium acetate. Figure 6 shows the prilled sodium acetate particles with spherical morphology and a few porosities on the surface.

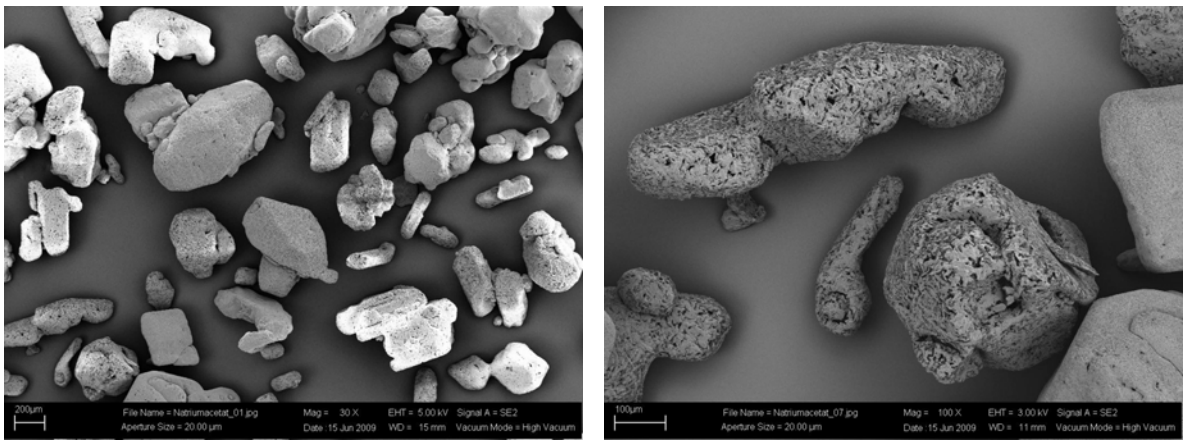

Figure 5: SEM micrograph of original sodium acetate

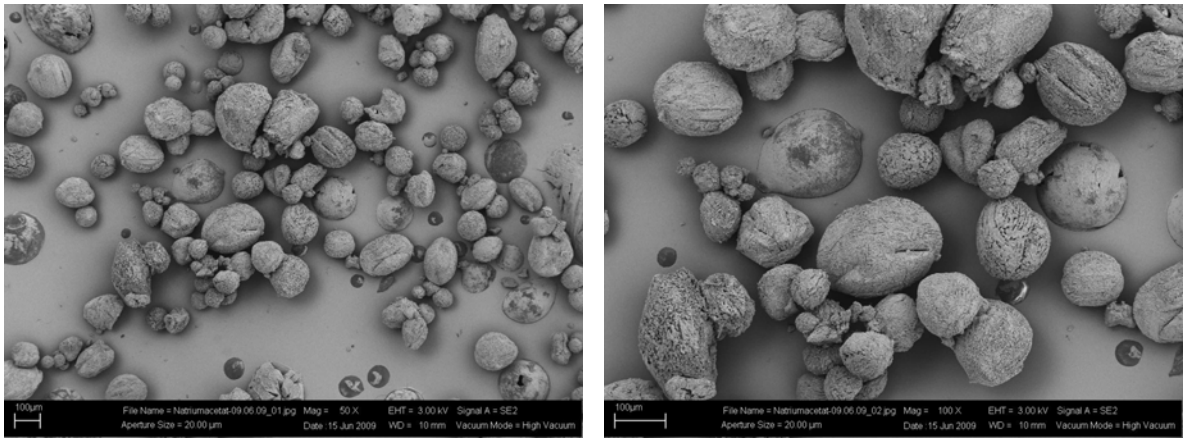

Figure 6: SEM micrograph of prilled sodium acetate

The results of ADN reshaped by the continuous prilling process are to be seen in Figure 7. On the surface of the ADN-prills probably some anti-caking agent can be found, which is added to avoid agglomeration.

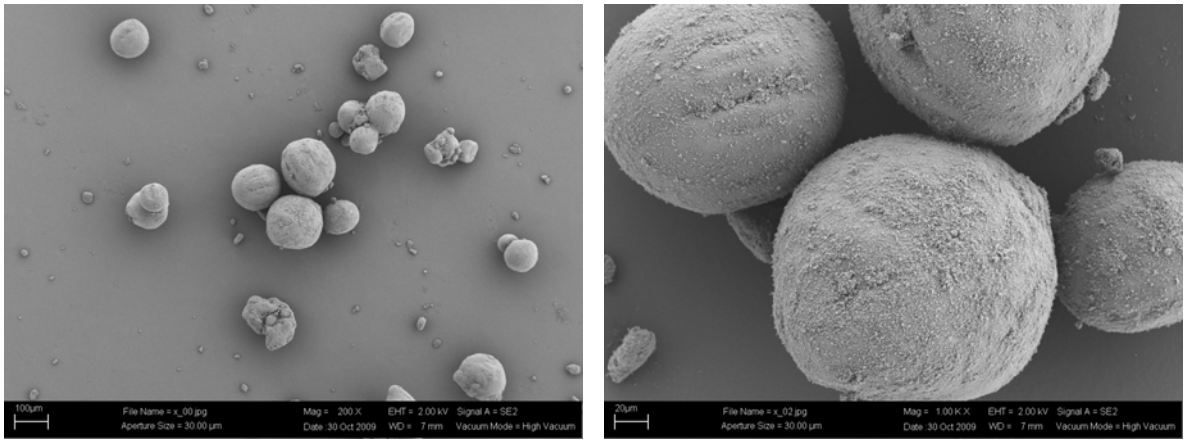

Figure 7: SEM micrograph of prilled ADN

3.3 Process parameters and mean particle size

Table 1 contains the results of mean particle size measurement and the used parameters of the conducted ADN-Prilling trials by using microreaction technology.

Table 1: Results of mean particle size measurement of the conducted ADN-Prilling trials and the used parameters

Feed-temperature [°C]	Flow rate [ml/min]	Ratio anti-caking agent to decane [g/200ml]	Ratio surfactant to decane [g/200ml]	Microreactor or tube type	Mean particle size [µm]
125	13	0,9 (milled)	0,9	800 µm tube	76
120	9	0,3	0	Microreactor	168
120	13	0,3	0	Microreactor	118
120	13	0,9	0	None	141
125	13	1,8 (milled)	2	800 µm tube	81
120	13	0,9	0	Microreactor	141
125	13	0,9 (milled)	1,8	800 µm tube	157
125	13	0,9	0,9	800 µm tube	122 agglomerated
125	13	0	0	800 µm tube	373

The ratio of ADN to decane was always set to 5 g ADN in 100 ml decane. A relation of more than 5 g/100 ml blocks the system very fast. A relation less 5 g/100 ml is not efficient. The feed temperature has been set to at least 120°C. Below that temperature the risk of blockage has been high. In this case the ADN particles did not melt probably and blocked the microreactor.

Testing a 300 µm and an 800 µm tube without internal mixing structures, instead of the microreactor, has shown that the smallest diameter that could be used was an 800 µm tube.

The chosen microreactor was made of glass, containing passive mixing structures [4]. These mixing structures, resp. baffles, should smash the melted ADN into smaller droplets.

The results in Table 1 are showing a very wide range of particle sizes. There are mean particle sizes of less than 100 µm and even some with more than 300 µm. With the microreaction prilling technology it may be possible to choose the size, which is optimal for a specific application. This may be one of the major advantages of this process.

The results are showing that the flow should be set at 13 ml/min to get a reproducible small particle size. Beyond this flow rate the problem of blockage increases very fast, because of the less dwell time in the heated section. If the dwell time is too short the particles do not melt and block the system. Below this flow the particles get bigger, because the application of energy by the microreactor decreases.

At a temperature of 125°C the risk of blockage can be reduced compared with 120°C. At 125°C and using the 800 µm tube the mean particle size and particle size distribution can be reduced. A feed temperature higher than 125°C is not preferable because of safety reasons.

Adding a surfactant is also beneficial to reduce the particle size, because the interfacial tension between ADN melting and decane is reduced.

Adding milled anti-caking agent, comminuted by a mixer mill, is more effective than to use it unprepared, because there are more primary particles and less agglomerates of the active substance. So it is much more efficient to avoid agglomeration of the ADN-prills.

4 Conclusions and future work

The results have shown that the morphology of ADN particles can be changed by application of the microreaction technology. The continuous produced particles get a spherical morphology and an adequate mean particle size.
In further investigations the blockage of the heating tube and the microreactor must be minimized. This problem may be reduced by designing a more vertical configuration of the tube and the heated section. The sedimentation of ADN in the process sequence must be avoided.
Creating smaller particle sizes will be one of the goals. The target will be producing free flowing particles with mean sizes lower than 75 µm and a narrow particle size distribution.
Another possibility could be to stabilize ADN chemically by embedding stabilizing additives into the prills [5].
But mainly it is to find out if it is possible to produce higher yields of ADN. At the moment the amounts are about 10 g. To produce 500 or 1000 g ADN-Prills in one day should be possible.
Concerning the product characterization it is interesting to investigate of the particle's crushing strength [1].

5 References

[1] Heintz, T., Pontius, H., Aniol, J., Birke, C., Leisinger, K., Reinhard, W.: Ammonium Dinitramide (ADN) - Prilling, Coating and Characterization; Propellants, Explosives, Pyrotechnics; 3/09, Volume 34, June 2009, p. 231 – 238

[2] Heintz, T., Pontius, H., Aniol, J., Birke, C., Leisinger, K., Reinhard, W.: ADN - Prilling, Coating and Characterization, 39. International Annual Conference of ICT, Energetic Materials – Processing and Product Design (2008)

[3] Teipel, U., Heintz, T., Krause, H.: Crystallization of spherical Ammonium Dinitramide, Propellants, Explosives, Pyrotechnics 25, 2000, p. 81 – 85

[4] Boskovic, D. ; Türcke, T. ; Mendl, A.; Löbbecke, S.: Fast and Save Production of Liquid Explosives in a Continuous Pilot Plant Employing Microreaction Technology, 40. International Annual Conference of ICT, Energetic Materials – Characterisation, Modelling and Validation, (2009)

[5] Heintz, T., Pontius, H., Teipel, U.: Stabilized spherical particles of ammonium-dinitramide (ADN), 35. ICT-Jahrestagung, Energetic Materials - Structure and Properties (2004)