PARTICLE SIZE ADJUSTMENT OF SPHERICAL AMMONIUM DINITRAMIDE PARTICLES (ADN-PRILLS) PRODUCED BY EMULSION CRYSTALLIZATION

Thomas Heintz, Werner Reinhard, Christoph Birke, Karlfred Leisinger

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

Keywords: ADN-Prills, particle size, emulsion crystallization process

Abstract

During the last years the high performance, low signature and environmental friendly oxidizer ammonium dinitramide (ADN) gained more and more acceptance for defense and space applications. The application of ADN in solid propellant formulations leads to a requirement of spherical particles of two or three different particles sizes. Therefore a coarse particle size fraction in the range of 200-250 µm and medium particle size fraction in the range of 40-60 µm are demanded. A fine fraction of about 5 µm is desirable, but only producible by milling processes.
To achieve these requirements for coarse and medium size (spherical) particles several process parameters of the emulsion crystallization process for ADN, the so-called ADN-Prilling process, were modified. By the variation of process fluids, additives, stirring energy and recrystallization behavior it was possible to generate medium sized ADN-Prills with a mean particle size of 50 µm and coarse ADN-Prills with approx. 200 µm in technical scale. Furthermore targeted seeding during the recrystallization step proved to be a suitable parameter to adjust the particle size of ADN-Prills.

1 Introduction

Ammonium dinitramide (ADN) is the upcoming oxidizer for propellants in defence and space applications. Its advantages, high performance, low signature and environmental friendliness, have been described in different publications [1–4].

From technological and scientific view ADN seems to stand at the border to industrial application. Whereas the low melting point of 93°C and the current price are the remaining drawbacks of the material. The former problem to find a compatible binder system seems to be nearly solved by the investigations of Wingborg et al. [4, 5, 6] and Gettwert et al. [5, 7].

For the application in solid propellants usually bimodal particle sizes are used. By varying the amounts of coarse and fine faction, it is possible to adjust the burning rate, to increase the solid loading and to control the casting viscosity. To obtain a castable propellant formulation with reasonable viscosity and high solid loading, particles with minimum spatial extension are required. For this reason the particles should have a low aspect ratio or more preferably a spherical shape.

The desired particle size of each fraction is in the range of 200–250 µm for the coarse fraction and 20–50 µm for the media fine fraction [5].

If a very fine fraction of 2–5 µm is additionally needed, grinding technologies are preferable. A wet milling technology for producing ADN in this particle size is described in the proceedings of this conference (see Poster 98, Generation of Very Fine Ammonium Dinitramide (ADN) Particles by Bead Milling Technology, Roßmann et al.).

Currently the spherical morphology of ADN-Prills may be achieved by the spray prilling process [8] developed by FOI, Sweden, or the emulsion crystallization process [9] developed by Fraunhofer-ICT Germany. Both processes gain the spherical shape by creation droplets of molten ADN and recrystallize these droplets into spherical solid particles.

The intention of the investigations described in this publication, was to have a closer look to the mechanisms that are determining the emulsion crystallization process. Whereas the technical goal was, to define the process parameters, which are necessary to produce different particle sizes of spherical ADN-Prills reproducibly and in technical scale.

2 Characteristics of the Emulsion Crystallization Process for ADN-Prilling

The emulsion crystallization process for ADN-Prilling is described in [9] in detail. Former experiments have shown that ADN-Prills in the mean particle size range of 100–120 µm typically occur. It was found that the particle size and morphology of the emerging ADN-Prills is influenced by several process- and material parameters. The specific adjustment of the particle size was investigated by varying the following parameters [10]:

- Geometry of the stirrer
- Stirrer speed (rpm)
- Mass ratio between dispersed phase (ADN) and continuous phase (nonpolar liquid)
- Material properties of the continuous phase, e.g. viscosity, surface tension
- Additives (tensides, emulsifiers, emulsion stabilizing (nano-scaled) solids)
- Targeted nucleation by seeding

As indicated in figure 1, the emulsion crystallization process is very complex and the parameters are interacting each other. So it was challenging to isolate the single impacts. For instance the stirrer speed was reduced to lower the shear rate and due to this generate larger particles. But less convection and bigger particles (ADN-melting droplets) are leading to a vertical gradient of the solid/liquid mass ration by sedimentation, which causes inhomogeneous recrystallization behaviour and maybe agglomeration at the bottom of the reaction vessel. To counteract sedimentation it is possible to choose a process liquid with higher viscosity, but this causes higher shear rate and again smaller particles. Overall a lot of experiments were needed to figure out the narrow range of the suitable parameter settings.

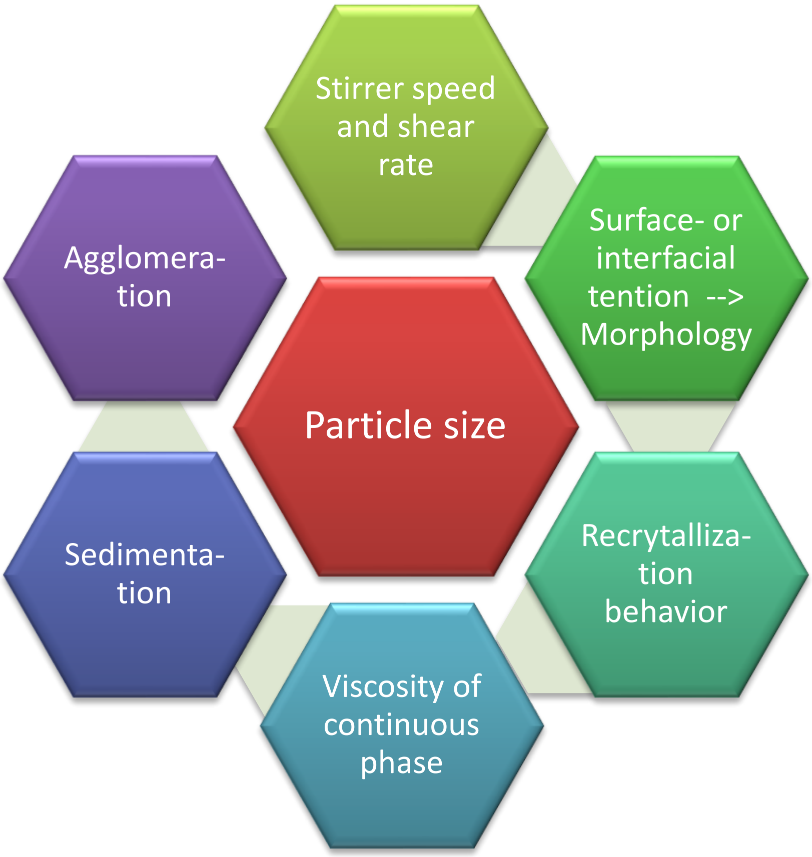

Figure 1: Dependency of process parameters and effects on the ADN-Prilling process

3 Fundamentals of Supercooled Meltings

Supercooling is a thermodynamic phenomenon in which the temperature of a liquid is below its freezing point without becoming a solid. This supercooled melting is a metastable state and may occur in very pure substances, if there is a lack of seed crystals or nucleus where crystallization may start [11]. But heterogeneous crystallization may be triggered by adding seed crystals or mechanical impulse, e.g. shock or vibration.

The phenomenon of supercooled melting has been observed at the ADN emulsion crystallization process, when the emulsified ADN melting droplets where cooled drown to ambient temperature. Big droplets recrystallize at temperatures close below the melting temperature of 93 °C, whereas the smaller the droplets get, the less they recrystallize. Figure 2 shows a microscope picture of this situation. In this transmitted light micrograph picture the solid large prills (>100 µm) appear dark, whereas the small particles (<100 µm) are still remaining in the liquid (molten) state, visible as transparent spheres. The picture was taken at ambient temperature which illustrates the existence of super-cooled ADN-melting droplets, suspended in the continuous phase. The reason for this inhibited homogeneous crystallization is that nucleation energy is needed which leads to a nucleation barrier [12].

The droplet size dependency of recrystallizing has probably several reasons:

- The stochastic lack of seeds in smaller droplets, embedded in the non-polar emulsion phase, prevents from heterogeneous crystallization.
- The high surface- or interfacial-tension of molten ADN that leads to a higher pressure in smaller droplets (Young-Laplace-equation):

  $$p = \frac{2 \cdot \gamma}{r} \qquad (1)$$

  p = pressure inside the droplet
  γ = surface- or interfacial-tension
  r = droplet radius

  The higher pressure inside the smaller droplets prevents from the effect of seed crystals which may exist in the emulsion.
- Less interaction of small droplets during stirring in the high viscous emulsion phase, due to their low mass and diameter.

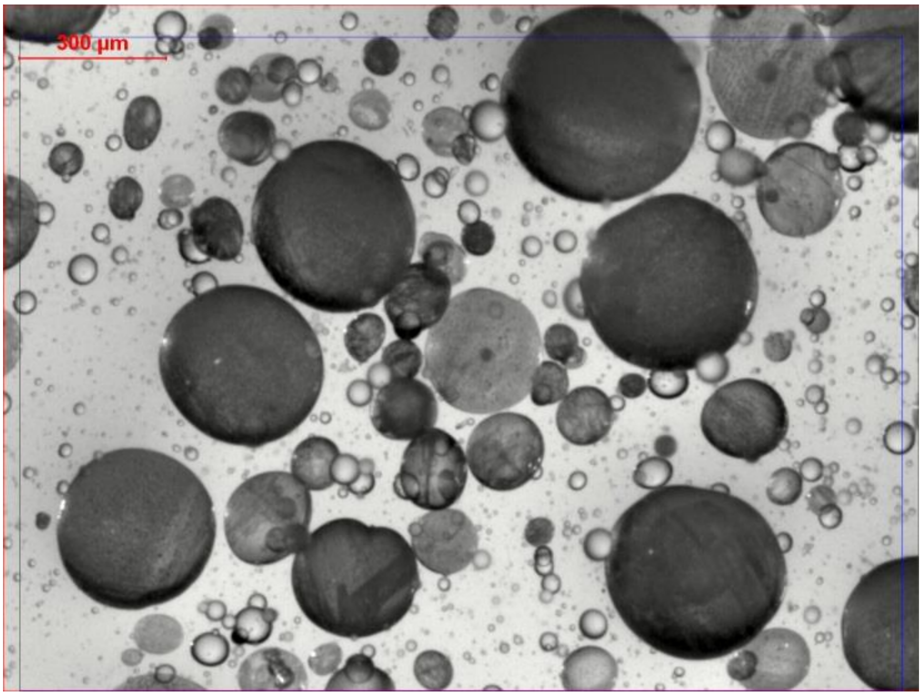

Figure 2: Micrograph (transmitted light) of prilled ADN suspended in process liquid

4 Experimental - Results

The conducted experiments were characterized referring to the particle size and the particle morphology. The particle size distributions were measured by laser light diffraction (Malvern Mastersizer 2000). The microscope pictures were taken by a light microscope (Leica Z16 APO).

4.1 Production of fine Prills

Figures 3 and 4 are showing the current minimum particle size for spherical ADN-Prills. High stirring speed and therefore a high shear rate is leading to a mean particle size of approx. 34 µm.

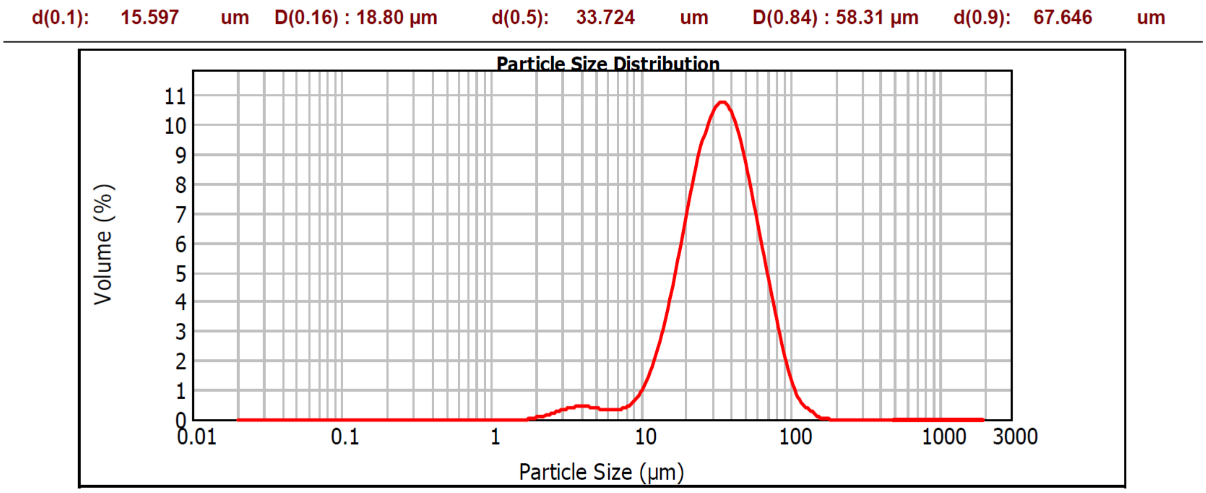

Figure 3: Particle size distribution of fine prilled ADN; mean particle size d(0.5) = 34 µm

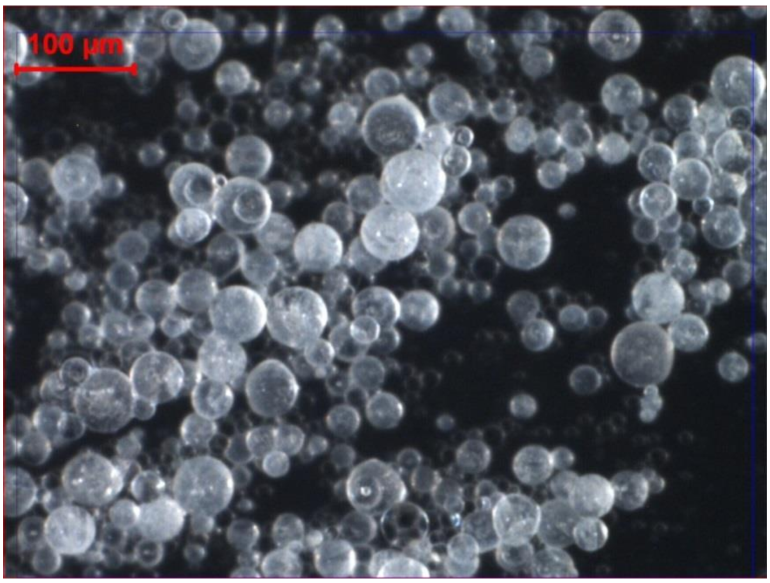

Figure 4: Micrograph (reflected light) of prilled ADN; mean particle size d(0.5) = 34 µm

By varying the stirrer intensity is was possible to adjust the fine ADN-Prills in the range between 34 µm und maximum 57 µm (see figure 5 and 6).

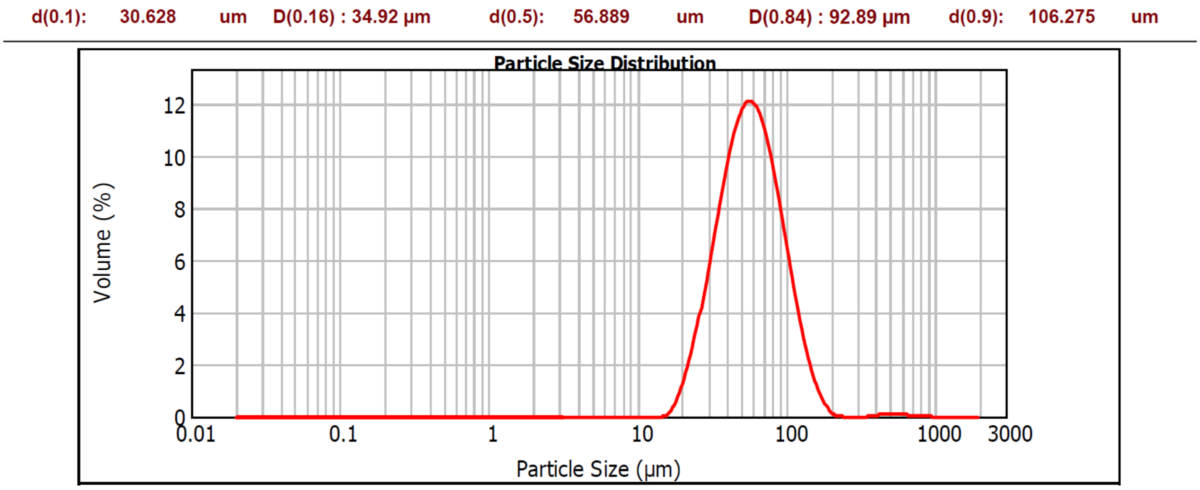

Figure 5: Particle size distribution of prilled ADN; mean particle size d(0.5) = 57 µm

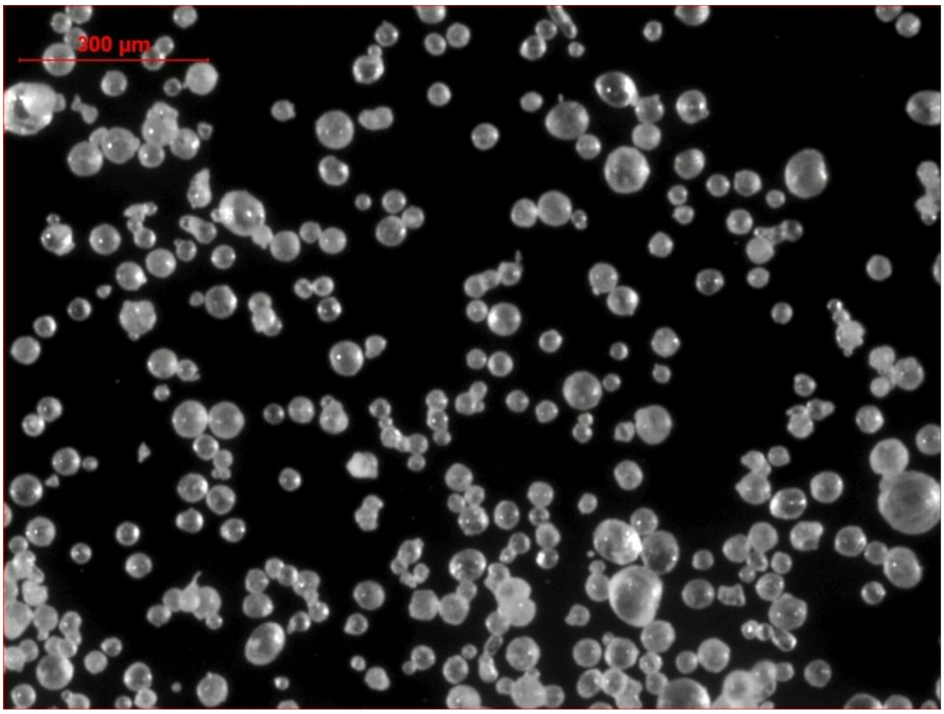

Figure 6: Micrograph (reflected light) of prilled ADN; mean particle size d(0.5) = 57 µm

4.2 Production of coarse Prills

Figures 7 and 8 are showing the current maximum particle size for spherical ADN-Prills. Low stirring speed, high viscos process liquid and targeted nucleation are leading to a mean particle size of approx. 320 µm.

Also coarse ADN-Prills (in the most demanded particle size of approx. 200 µm) can be produced reproducibly in kg-scale. Figure 9 and 10 are showing narrow distributed particles with spherical shape and a mean particle size of 208 µm.

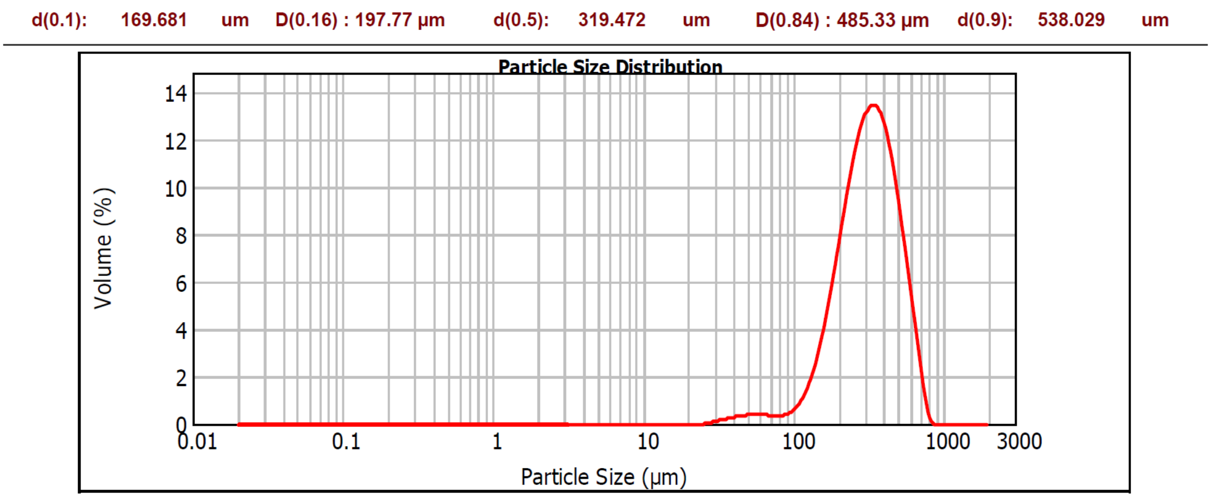

Figure 7: Particle size distribution of coarse prilled ADN; mean particle size d(0.5) = 319 µm

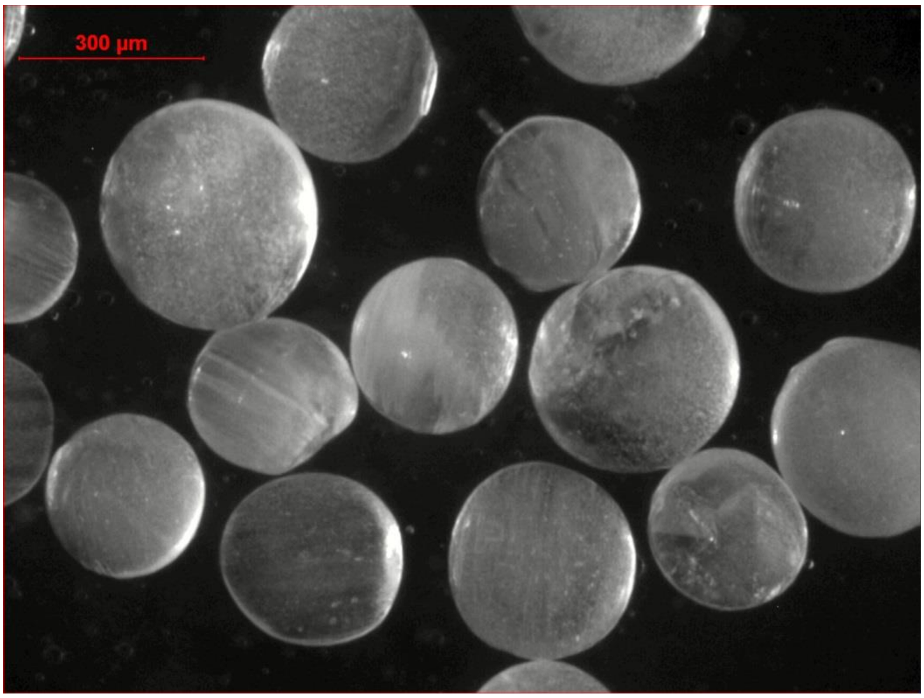

Figure 8: Micrograph (reflected light) of prilled ADN; mean particle size d(0.5) = 319 µm

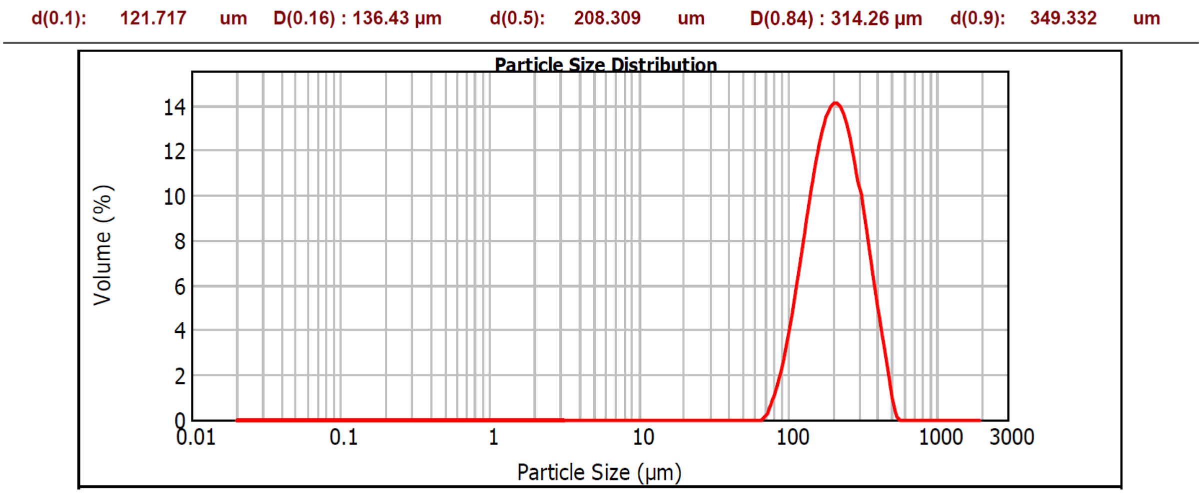

Figure 9: Particle size distribution of prilled ADN; mean particle size d(0.5) = 208 µm

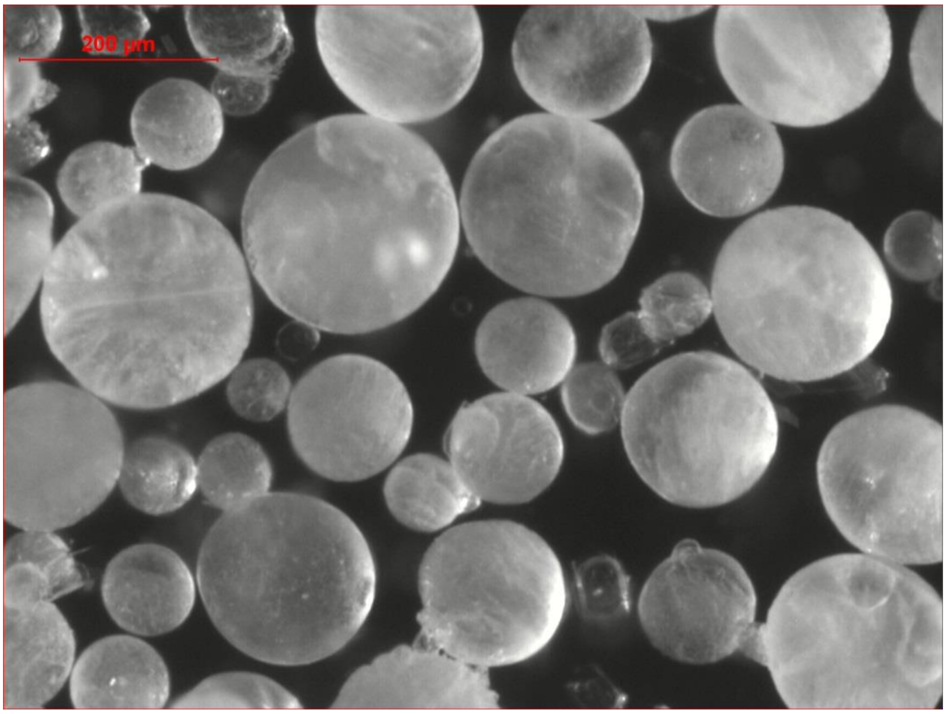

Figure 10: Micrograph (reflected light) of prilled ADN; mean particle size d(0.5) = 208 µm

A high viscous emulsion, which is suitable for the generation of coarse ADN-Prills, leads primarily to supercooled meting droplets, as described in chapter 3. Therefore seeding is a preferable method to initiate the solidification.

It was found that the particle size of the resulting prills can be adjusted by the point in time, or the temperature, when seeding is started. The graph in figure 11 shows the dependency between particle size and the temperature when the seeds were added. The seeding was initiated at 50, 70, 80 and 90 °C. The lower the temperature was, the smaller the particle got. The chosen temperature range is suitable to adjust the particle size in the favorable range for coarse Prills between 150 and 250 µm. It is assumed that longer stirring periods at molten state, as well as the higher viscosity of the emulsion (when seeding is initiated at lower temperature) results in smaller particle sizes.

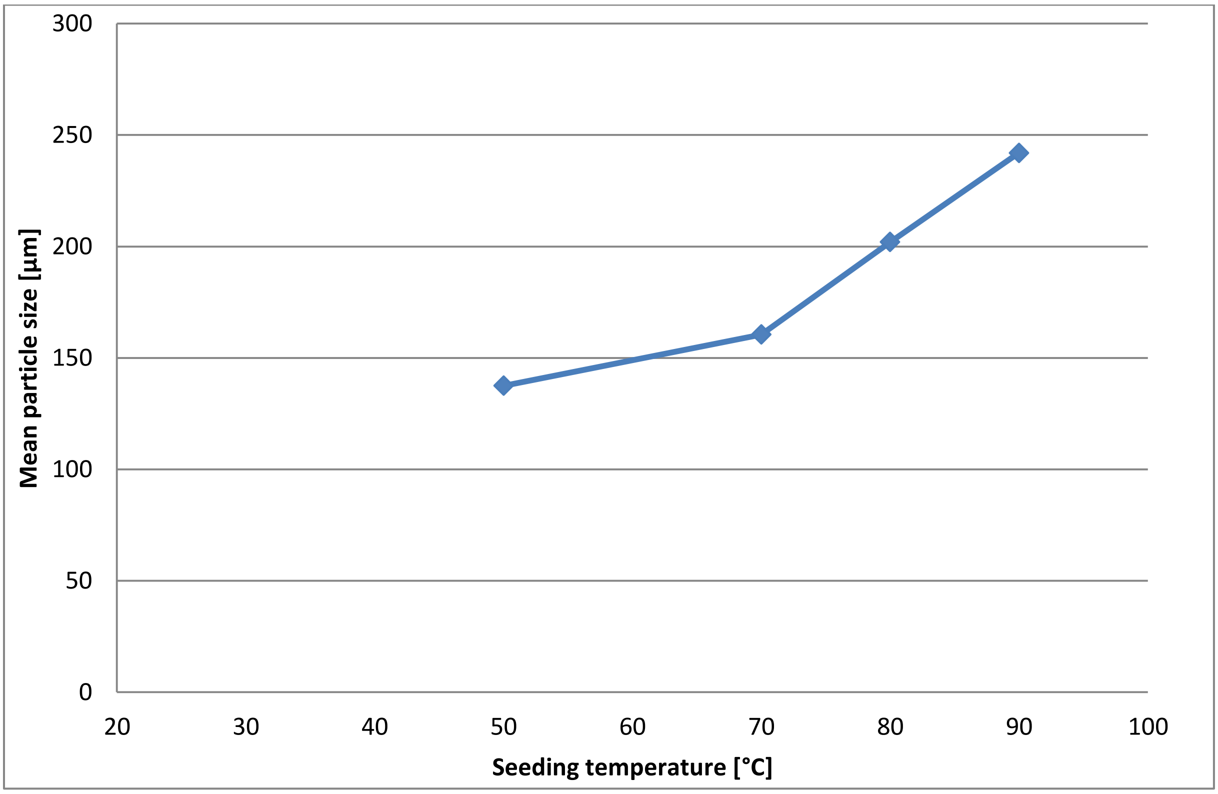

Figure 11: Dependency of particle size and seeding temperature

5 Conclusions and future work

The possible particle size range for producing ADN-Prills could be enlarged down to 35 µm and up to 320 µm. Current particle size ranges for reproducible kg-scale productions are:

- Media fine ADN-Prills: 50–60 µm
- Coarse ADN-Prills: 150–250 µm

In future this ADN-Prills should be tested in bimodal propellant formulations. Important parameters to investigate are casting viscosity and mechanical stability of the formulations. Another interesting questioning is the dependency of the burn rate in relation to the particle size of ADN-Prills.

The large ADN-Prills generated by targeted seeding show an inner layer structure (see figure 12). The cause of this crystal structure shall be investigated by X-ray diffraction methods in correlation with the process parameters of the emulsion prilling process.

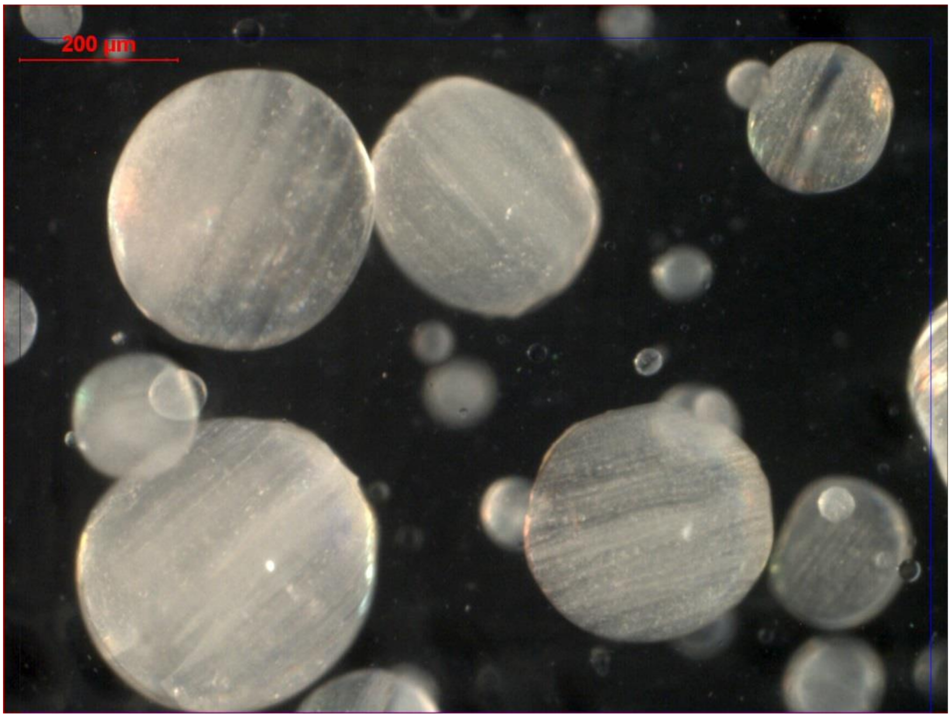

Figure 12: ADN-Prills (approx. 200 µm) with inner layer structure

6 References

[1] Menke, K.; Heintz, T. ; Schweikert, W.; Keicher, T.; Krause, H.: Formulation and Properties of ADN/GAP Propellants, Propellants, Explosives, Pyrotechnics 34 (2009), 3, page 218-230

[2] Menke, K.; Heintz, T. ; Schweikert, W.; Keicher, T.; Krause, H.: Approaches to ADN propellants based on two different binder systems, Energetic Materials - Processing and Product Design, 39th International Annual Conference of ICT, 2008, Karlsruhe, Germany

[3] Nagamachi M., Oliveira, J., Kawamoto, A., Cássia, R., Dutra, L.: ADN – The new oxidizer around the corner for an environmentally friendly smokeless propellant; Journal of Aerospace Technology and Management, Vol 1, no. 2, 2009

[4] Larsson, A.; Wingborg, N.: Green Propellants Based on Ammonium Dinitramide (ADN); Advances in Spacecraft Technologies, ISBN: 978-953-307-551-8

[5] HISP website, URL: http://cordis.europa.eu/projects/rcn/97991_en.html

[6] Wingborg, N.: ADN Propellant Development, 4 th European Conference for Aerospace Sciences (EUCASS), July 4 - 8, 2011, Saint Petersburg, Russia

[7] Gettwert, V., Fischer, S., Menke, K.: Aluminized ADN/GAP Propellants – Formulation and Properties, 44th International Annual Conference of the Fraunhofer ICT, June 25 – 28, 2013, Pfinztal, Germany

[8] Johansson, M., Wingborg, N., Johansson, J., Liljedahl, M., Lindborg, A., Sjöblom, M.: ADN is more than particles and formulations – it is a part of future missile propellants, 2013 Insensitive Munitions & Energetic Materials Technology Symposium, October 7 -10, 2013, San Diego, USA

[9] 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

[10] Heintz, T., Reinhard, W., Birke, C., Leisinger, K.: Adjustment of the particle size of ADN-Prills Generated by the Emulsion Crystallization Process, 44th International Annual Conference of ICT, Energetic Materials – Characterization and Modeling of Ignition Process, Reaction Behaviour and Performance, 2013, Karlsruhe, Germany

[11] Römpp-online encyclopedia; URL: https://roempp.thieme.de/roempp4.0/do/data/RD-11-02179 at 05.05.2014

[12] Römpp-online encyclopedia; URL: https://roempp.thieme.de/roempp4.0/do/data/RD-11-03071 at 05.05.2014