PROCESSING OF ENERGETIC COMPOSITE PARTICLES BY FLUIDIZED BED TECHNOLOGY

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Abstract

The fluidized bed technology, which has been established at Fraunhofer-ICT is specially modified to work with energetic materials. Furthermore it is possible to use UV-curing polymers as coating materials and nitrogen as an inert process gas.
This fluidized bed technology allows creating various composite particles consisting of different energetic materials. In this work three different examples of energetic composite particles are presented:
ADN-Prills (spherical ammonium dinitramide particles) have been coated with thin layers of GAP (glycidyl azide polymer), which increases the compatibility with isocyanate containing binder systems and the mechanical stability.
Spherical ammonium nitrate particles could be coated with UV-curing polymers, which lead to mechanical stable core-shell structures.
It is also possible to produce composites of mostly HMX (approx. 90 wt. %) and little amounts of FOX-7 or FOX-12, which results in a reduced friction sensitivity of the whole composites.

1   Introduction

The goal of the conducted work is to improve the particle properties of different energetic materials by creating new particles with core/shell or matrix structure. The generation of these composite particles is done by fluidized bed technology. The following improvements are intended to be realized by the new composite particles:
- Improvement of the compatibility (e.g. with isocyanate curing binder systems).
- Protection against environmental conditions (e.g. humidity and radiation).
- Increasing the mechanical stability of the discrete particles.
- Decreasing the material's tendency to agglomeration.

- Reduction of sensitivity.
- Combination of the benefits of two different materials (e.g. low-cost and low-sensitivity).

2 Fluidized bed technology modified for energetic materials

There are two fluidized bed devices (lab-scale and field-scale, see Figure 1) available at ICT, which are suitable to work with particulate energetic materials [1].

Figure 1: Laboratory-scale fluidized bed coating apparatus (Hüttlin, Mycrolab, left) and field-scale fluidized bed coating apparatus (Hüttlin, HKC5, right)

Furthermore two very special modifications concerning the process have been implemented:

2.1 UV-light curing system

Integration of an UV-point light source into the process vessel. The UV-light source is mounted to irradiate the fluidized bed from the top (see Figure 2).

Technical data of the light source: DYMAX, BlueWave 200
Power of light generator: 200 W
Wave length: UVA (320-390 nm) and visible light (390-450 nm)
Flexible light guide: 3 m
Light intensity:
13000 mW/cm^2 (at the output of the light guide)
Approx. 100 mW/cm^2 (10 cm distance from output)
Compare: Sunlight approx. 3 mW/cm^2

The aim of this technique is the application of UV-curing polymers, which generally achieve high mechanical stabilities, as coating materials. Such highly cross linked shells are expected to increase the mechanical stability of the whole composite particles just by coating a less stable core with a thin, high-strength layer.

Figure 2: UV-point light source with orthogonal light guide (left). Fluidized bed vessel with implemented light source (right).

2.2 Inert process gas

Generally the fluidized bed devices are working with dried air as process gas. The lab-scale plant additionally has the opportunity to choose nitrogen as inert process gas. This offers the following advantages:

- Improved safety when processing reactive substances.
- Nearly no humidity in the system when processing hygroscopic substances.
- Improved curing at the surfaces of reactive polymer coatings (reduced stickiness of coating layers).

3 Experimental and results

3.1 Coating of spherical ammonium dinitramide particles (ADN-Prills) with glycidyl azide polymer (GAP)

Table 1 contains the material selection for the fluidized bed coating of ADN-Prills with GAP. Former studies have shown that the energetic binder GAP is suitable for coating ADN [1]. This applies for the fluidized bed processing itself and additionally for the increase of compatibility during the further processing with isocyanate containing binder systems. The usage of tri-functional GAP has the intention to increase the mechanical and chemical stability of the layer by a higher degree of cross linking than di-functional GAP offers. The results are verified by a double experiment (A and B) and adequate characterization.

Table 1: Material selection for ADN-Coating by fluidized bed technology

| Core material | Coating material | | Solvent |
	Binder / prepolymer	Curing agent	
ADN-Prills	di-functional GAP (glycidyl azide polymer)	Isocyanate (N100)	Ethyl acetate
ADN-Prills	tri-functional GAP (glycidyl azide polymer) two complete trails: A and B	Isocyanate (MDI)	Ethyl acetate

The SEM-micrographs (Figure 3 to Figure 5) are showing the ADN-Prills without coating, the ADN-Prills coated with di-functional GAP and the ADN-Prills coated with tri-functional GAP. Both coated samples are showing negligible change in particle-size distribution and morphology. As intended the coating process only affected the particle's surface by adding a thin homogeneous layer on it, which is to be seen at the varied surface structure.
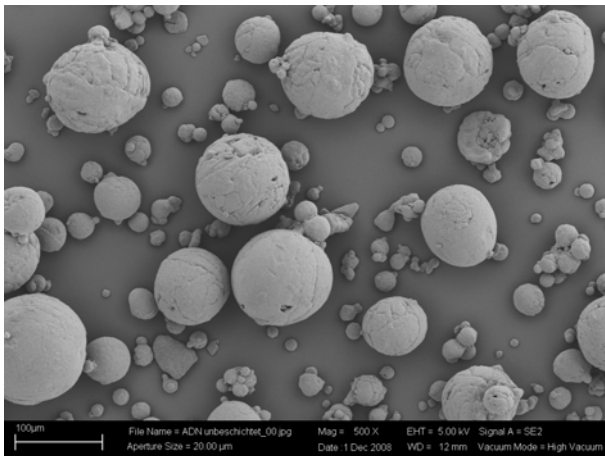

Figure 3: ADN-Prills without coating

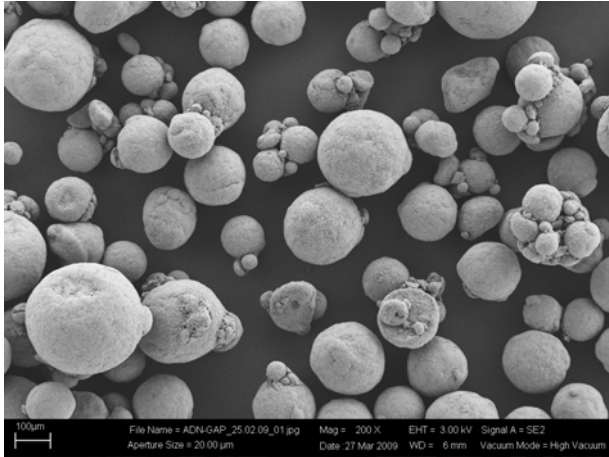Figure 4: ADN-Prills coated with di-functional GAP

Figure 5: ADN-Prills coated with tri-functional GAP

The effectiveness check of the coatings is done by measuring the reactivity between ADN-Prills (coated and not-coated) and an isocyanate containing reference binder system (HTPB/IPDI). As the incompatibility between ADN and isocyanates results in an increased heat of reaction and evolving of decomposition gas, the goal of the investigation was to reduce these both drawbacks verifiable. Due to this, the heat of reaction was measured by microcalorimetry and the evolution of gases by the vacuum stability test equipment [2]. The investigated samples are mixed (50 wt % binder and 50 % ADN-particles) just before the measurements were started, so that the curing reaction is included in the measured time range (7 days at 60 °C). The curves for the heat flow measured by microcalorimetry are to be seen in Figure 6. The series of measurements is supplemented by two curves for comparison:

- The curve of the pure curing reaction of the binder system (lower limit, black graph)
- The curve of the uncoated ADN-Prills in the same binder system (upper limit, pink graph)

The curve for di-functional GAP (blue) is the reference from another investigation series [1]. The two trials with tri-functional GAP (A - green curve and B - red curve) are showing reproducibly a further decrease auf reaction heat and hence an increased compatibility.
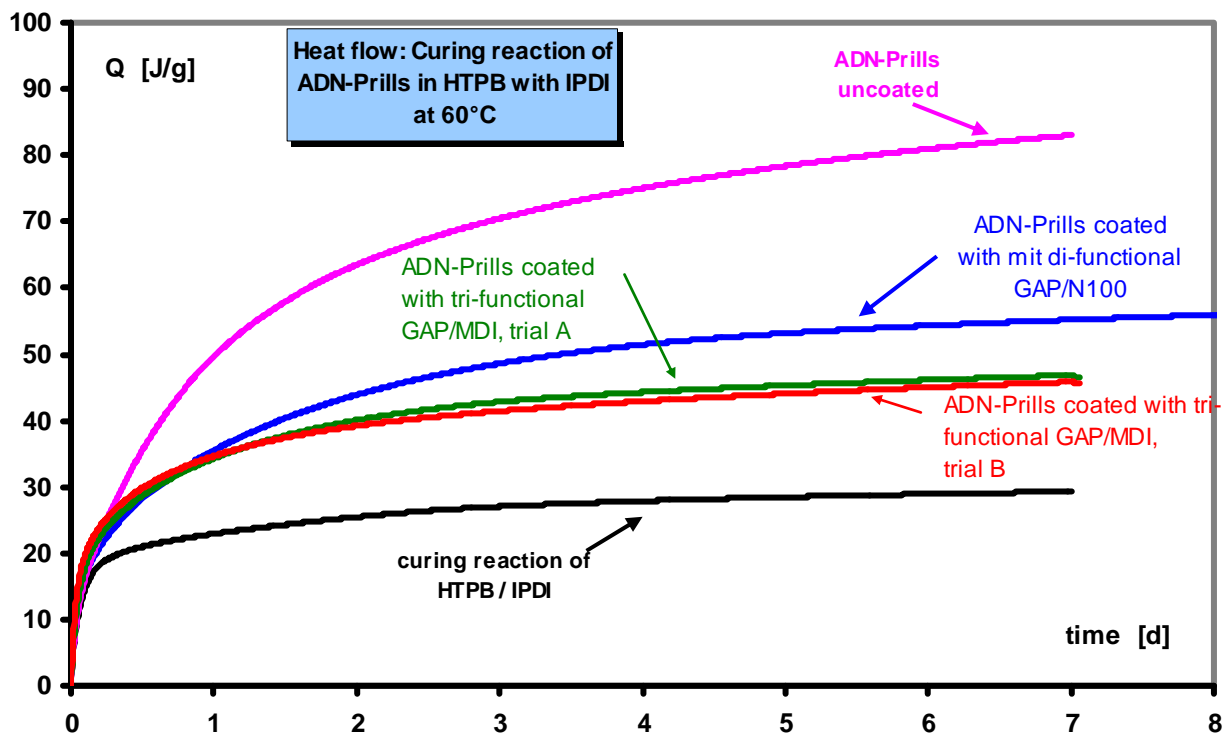
Figure 6: Microcalorimetric measurements of ADN-Prills in HTPB/IPDI; diagram in integrated mode as heat flow.

The similar samples were also investigated concerning evolved gas at the vacuum stability testing device at 60°C for 7 days (see Table 2). Corresponding to the results of the heat flow investigations the vacuum stability test shows the same compatibility improvement. The volume of decomposition gas is lowered more than 50 % compared with the uncoated ADN-Prills.

Table 2: Results of the vacuum stability test for ADN-prills in HTPB/IPDI

Sample	Results of vacuum stability tests 7 d at 60° C	
	volume [cm^3/g]	note, rating
Pure curing reaction, HTPB with IPDI	0.35	reference, min.
ADN from synthesis, EURENCO 20027031	> 5	overpressure, incapable of measurement
ADN-Prills uncoated, made of EURENCO 20027031	3.30	reference, max.
ADN-Prills coated with di-functional GAP/N100	1.35	compatibility increased
ADN-Prills coated with tri-functional GAP/MDI ; trial A	1,30	compatibility increased
ADN-Prills coated with tri-functional GAP/ MDI ; trial B	1,40	compatibility increased

3.2 Coating of spherical ammonium nitrate particles with UV-curing polymers

The following experiments have been conducted with UV-curing polymers as coating materials and by the use of the specially modified fluidized bed apparatus (see chapter 2.1 and

2.2). The chosen material was a urethane oligomer (meth) acrylate monomer blend from the company DYMAX.

In Figure 7 the spherical ammonium nitrate particles, produced at Fraunhofer-ICT by atomization of an AN-melting, are illustrated in three different zoom factors. The ANparticle have a slightly rough surface caused by the adhesion of fine overspray droplets, which are typical for the atomization process of meltings. By means of fluidized bed coating, with this highly cross linking UV-curing polymer, a very smooth surface and a mechanical stable core-shell structure can be achieved (see Figure 8). Again the particle morphology and the particle size distribution are not influenced by the process. The mean particles crushing strength measured by a special measuring device of the company etewe [3] could be increased from 21,9 N/mm^2 to 31,9 N/mm^2 only by adding 3 % of the coating material.
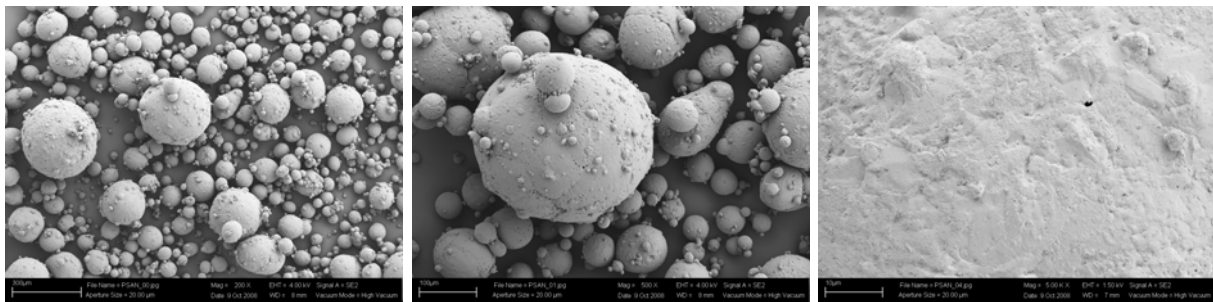

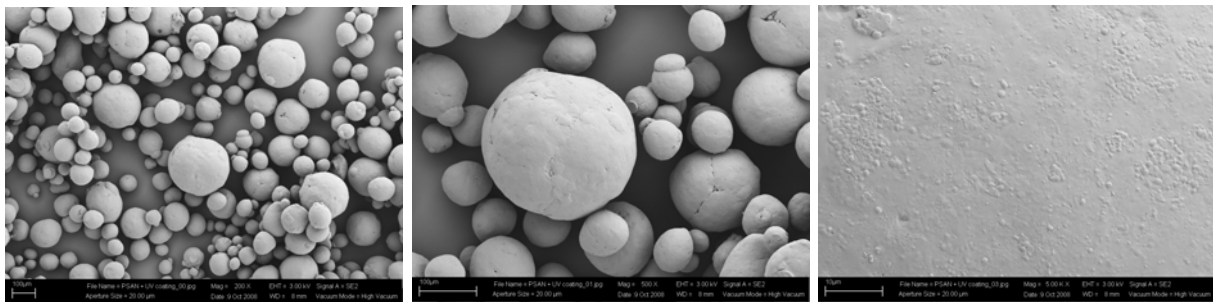Figure 7: Spherical ammonium nitrate without coating; mean particle crushing strength 21,9 N/mm^2

Figure 8: Spherical ammonium nitrate coated with 3 % UV-curing polymer; mean particle crushing strength 31,9 N/mm^2

3.3 Creation of composite particles consisting of HMX/FOX-7 or HMX/FOX-12

The fluidized bed technology makes it also possible to produce composite particles of mostly HMX (approx. 90 wt. %) and little amounts of FOX-7 (1,1-diamino 2,2-dinitro ethylene) or FOX-12 resp. GUDN (N-guanylurea-dinitramide). The intention of this work is to give the advantages (e.g. low sensitivity) of a special and high pricing material (e.g. FOX-7 or FOX-12) to a standard material (e.g. HMX) by coating its surface and changing its morphology. The benefit should be to receive the properties of special materials by using only approx. 10 % of it in the designed composite particle.

Figure 9 (left) is showing the microscope image of uncoated HMX. The composite particles with 10 % FOX-12, mostly on the surface, are shown in the right picture. Due to abrasion of fine HMX and simultaneous adhesion of FOX-12 a rounding of the composites has occurred.
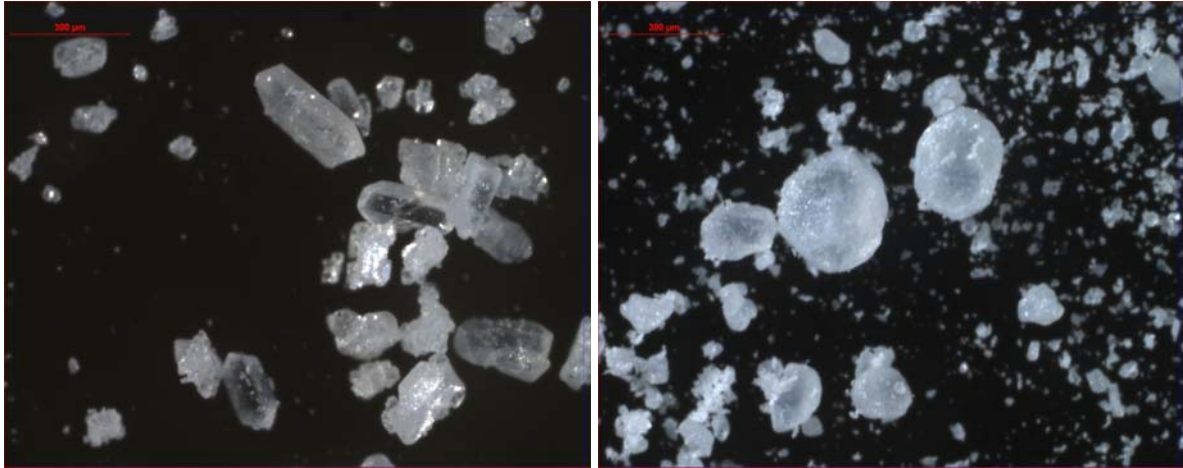
Figure 9: Light micrographs of HMX original; Typ B Class 1 (left) and composite particle of HMX and FOX-12 (right)

Another example for generation energetic composite particles is illustrated in the SEM micrographs Figure 10 and the light micrograph Figure 11. The same HMX core material has been treated with a mixture of dissolved FOX-7 and the energetic polymer GAP (glycidyl azide polymer). The emerging polymer layer, which includes the FOX-7, reduces the abrasion of HMX. Due to this the original morphology of HMX is more conserved (Figure 10) and less fine HMX is to be seen in the light micrograph (Figure 11).

The investigations have shown that several designs of composite particles are producible, depending on the choice of materials. The sensitivity tests result in a decrease of friction sensitivity of the composite particles (e.g. HMX original: 128 N is reduced to HMX/FOX7/GAP: 240 N).
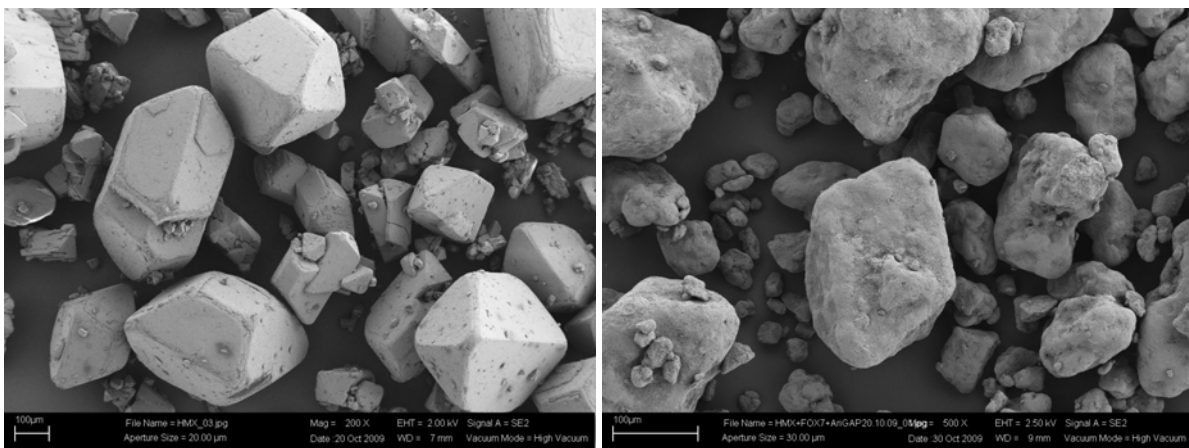

Figure 10: SEM micrographs of HMX original; Typ B Class 1 (left) and composite particle of HMX/FOX-7/GAP (right)
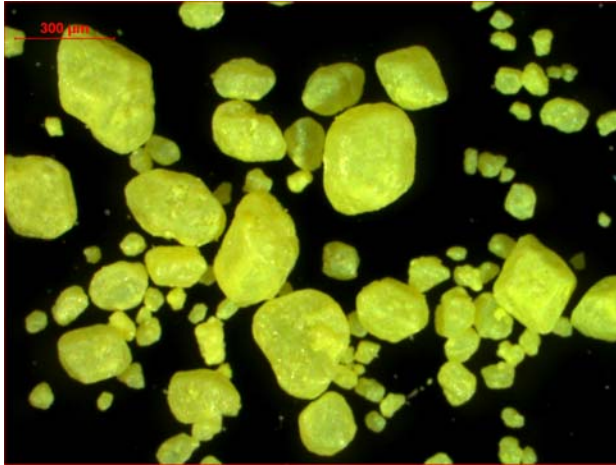
Figure 11: Light micrograph of composite particle consisting of HMX/FOX-7/GAP (compare Figure 10, right)

4 Conclusions

The fluidized bed technology, which has been established at Fraunhofer-ICT, offers the possibility to generate tailored particulate (energetic) products for the need in defence applications (e.g. solid rocket propellants, high explosives, foamed propellant charges). This technology allows combining a huge repertory of energetic materials, by spraying dissolved (resp. dispersed) energetic materials onto the fluidized bed, consisting of solid core energetic particles. Furthermore it is promising to add stabilizing or burn rate modifying substances. A prospective benefit may be the possibility to lower the sensitivity of explosive particles, whereas the challenge is to do this economically by using only little amounts of high-priced special materials.

5 References

[1] 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)

[2] Bohn, M.A. (ed.): Heat Flow Calorimetry on Energetic Materials; Proceedings of the 6th International Heat Flow Calorimetry Symposium on Energetic Materials, 2008, p. 247-260 Fraunhofer ICT, Pfinztal-Berghausen

[3] 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