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# Particle Design of Energetic Materials

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**Abstract:** The crystal quality and the internal microstructure of crystals have a great influence on the sensitivity of energetic materials. Besides, the particle size and the particle size distribution are of great importance to the processing technology of energetic materials. Particle properties can especially be influenced by applying different crystallization techniques, such as cooling crystallization, membrane crystallization, emulsion crystallization and others. The objective of the investigations was to determine the interrelationship between the properties of the gained crystals and the process parameters. Special attention was directed to the qualitative and quantitative examination of crystal defects and their dependence on the experimental conditions. Besides, the morphology and structure of crystals were calculated by molecular modelling. The effect of crystal defects on the sensitivity of the material was tested on different collectives of particles having varying amount of crystal defects.

**Keywords**: product design, particle quality, crystallization, FOX 7, HMX, ADN

## Introduction

Particulate energetic materials and systems produced with such particulates, such as solid propellants, propellant powders and explosives, have assumed an ever more important role in industry. Important material properties of these materials, including burn rate behavior and sensitivity, are decisively affected by particulate properties such as particle morphology, size and size distribution.

Particles are generally manufactured using well-known solids formation techniques such as crystallization, precipitation, size-reduction, spray drying or deagglomeration [1, 2]. Although a large amount of information exists on these different processing techniques, there are still gaps in our understanding of how to completely control the particle formation process or reliably predict processing phenomena and the properties of the particulate products.

A number of subjects related to particle technology and the design of particulate products require further investigation, including the characterization and experimental determination of various particle properties, the simulation and modeling of process operations involving dispersed products and, in particular, the relationship between product properties and the properties of dispersed systems and particles.

## Product design of particles

The aim of product design is to develop final products with a defined set of properties that can be economically commercialized in an environmentally acceptable manner [3, 4]. The design of particulate products and dispersed systems is complex because obtaining the desired end product properties requires achieving an optimal combination of the chemical and physical properties of each component of the system. An essential problem in product design is to achieve selectively and reproducibly the desired material characteristics that meet the demands required of the particulate product or dispersed system of energetic materials under development. Such characteristics may include:

- insensitivity,
- defect free particles,
- absence of gas or fluid inclusions,
- high density,
- high purity,
- surface and adhesion properties,
- wettability, particle-binder interactions,

- high packing density,
- high performance,
- rheological behavior,
- stability,
- low propensity to form fine dusts,
- filterability,
- low tendency to agglomerate.

Many of these product material properties are currently optimized empirically based on process and product requirements. The product properties are strongly dependent on the physical properties of the incorporated powder and on the dispersity characteristics of the system. The functional relationship between the product properties and the dispersity properties for chemically identical products can be described *via* the property function:

$$\xi_i = f(\kappa_j) \tag{1}$$

This equation postulates that the product properties $\xi_i$ are largely dependent on the dispersity properties $\kappa_j$.

For particulate products and dispersed systems, important dispersity properties include:

- particle size,
- particle size distribution,
- morphology,
- polymorphism,
- crystallinity,
- internal structure, porosity,
- particle density, bulk density.

One of the main challenges in the field of particle technology is attaining a better understanding of the relationship between the product properties $\xi_i$ and the dispersity properties $\kappa_j$ for different types of products and product applications.

By considering the process function, particles with defined dispersity properties can be manufactured using a variety of processing technologies, including methods such as crystallization or spray drying.

The dispersity properties of particulate products represent, through the property and process functions, a connection between the feedstock, the chosen processing method and the required application oriented product properties of the final product (see Figure 1). Besides appropriate chemical design of the feedstock, when designing particulate products one or more suitable processing

methods with appropriate process parameters must be selected and the required dispersity properties must be set to create an end product with the required material properties.

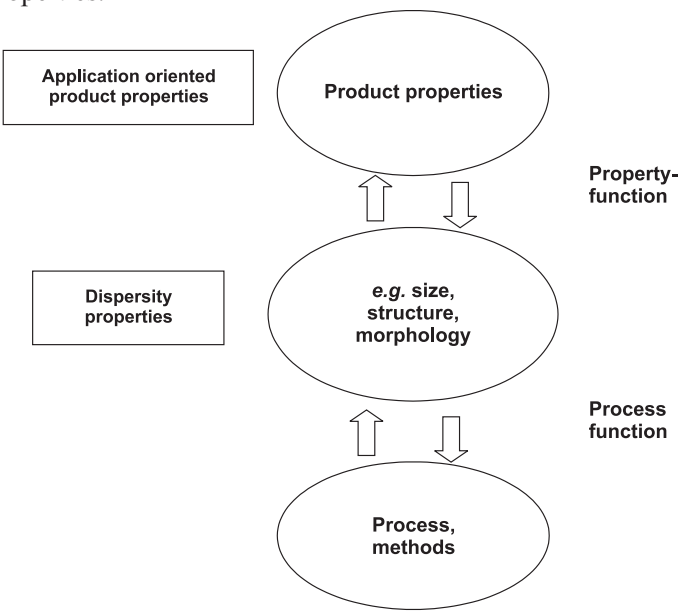



**Figure 1.** Product design in particle technology.

## Crystal defects and flaws

In addition to "hot spots" in the binder [5, 6] and interactions between particles and binder, another property that significantly influences the sensitivity of energetic systems is the crystal quality of the particulates. When describing the product quality of particulate materials, one distinguishes between flaws within the crystal [7-11] and the crystal's surface properties. Inner flaws that can significantly impair the crystal quality include point defects (Schottky or Frenkel defects), screw and edge dislocations, two dimensional defects (*e.g.*, twin formation) and three dimensional defects (*e.g.*, fluid or gas inclusions).

Defects are essentially a deviation in the perfect periodicity of a crystal. In an ideal crystal all the atoms assume a configuration corresponding to the global energy minimum. However, a real crystal does not exhibit a global energy minimum, but instead adopts configurations corresponding to numerous local energy minima. Because crystal defects have a significant effect on the physical properties of

a crystal (*e.g.*, the internal stress distribution), they also have a significant influence on the sensitivity of energetic materials. Figure 2 shows an example defect in the FOX 7 crystal.

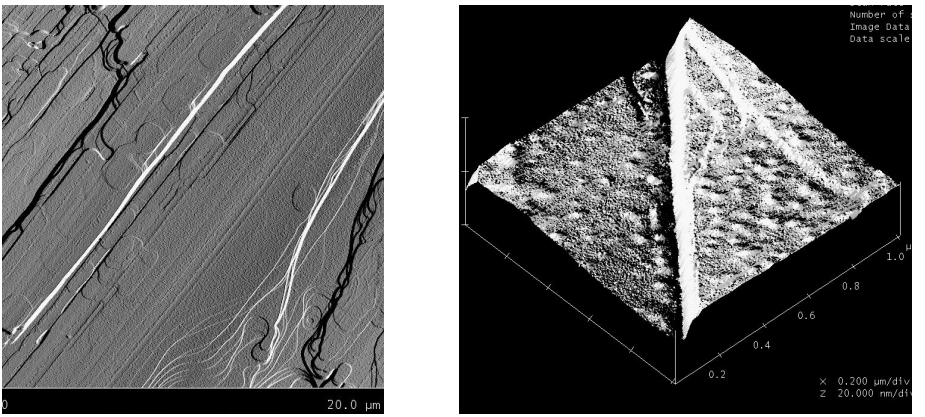



**Figure 2.** Defect at the surface of a FOX 7 crystal.

Because crystal defects are related to the crystal's formation history, optimizing the crystallization method offers the possibility to minimize crystal defects. Figures 3 and 4 show FOX 7 crystal surfaces; surface defects are clearly visible in the crystal depicted in Figure 3. In contrast, Figure 4 shows crystal growth layers of FOX 7 produced using optimized crystallization conditions.

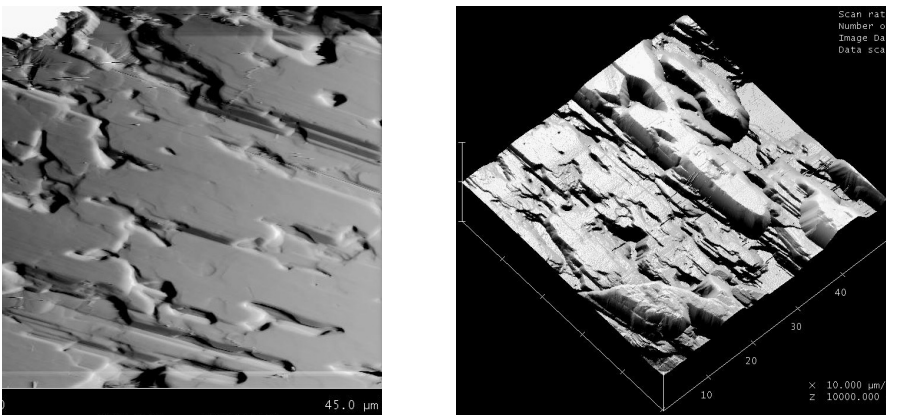



**Figure 3.** Surfaces of FOX 7 crystals.

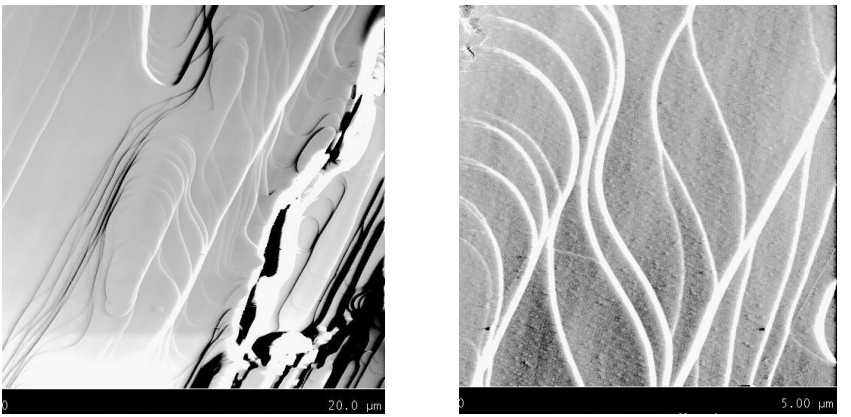



**Figure 4.** Crystal growth layers (FOX 7).

At high suspension concentrations and local regions of high supersaturation, nucleation may occur in liquid bridges. After crystallization, this causes the transition to solid bridges (see Figure 5) and the agglomeration of particles.

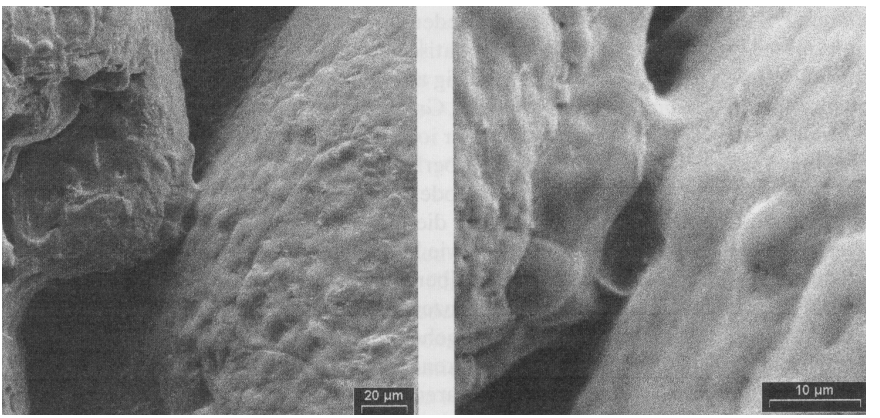



**Figure 5.** Solids bridges.

Subjecting the agglomerated crystals to mechanical energy (*e.g.*, through processing) leads to their deagglomeration and can also produce crystals with sharp edges (as also occurs in particle grinding), a condition which leads to a clear increase in the material's sensitivity.

## Product design *via* crystallization

The starting point for many particle formation processes is a fluid phase sufficiently supersaturated with an active component. As a result of transport processes, chemical reactions and other processes, nucleation occurs leading to the formation of clusters. Typically, nucleation is categorized either as primary (both homogeneous and heterogeneous) or secondary nucleation. During suspension crystallization, nucleation is followed by crystal growth of the dispersed phase in the supersaturated solution. Besides the decisive particle growth stage, critical steps in the product design process include: homogenization or stabilization of the dispersed system, or suppressing aggregation of the dispersed phase, depending on the specific application requirements of the end product.

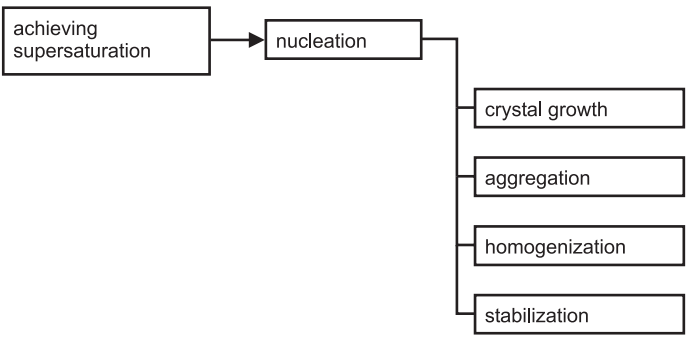



**Figure 6.** Product design *via* crystallization.

### Particle design *via* molecular modelling

Besides particle size and particle size distribution, other important dispersity properties include morphology, polymorphism and crystal structure. The morphology and structure of crystals are largely determined by the type of interactions that occur between the crystal surface and the surrounding fluid [12]. In the last few years, computation programs have been developed and become commercially available that allow the morphology of various crystalline materials to be calculated. The inner crystalline structure and distance and symmetry positions of the elementary cells are known exactly for many energetic materials. There are various theories for describing the relationship between the inner crystalline structure and outer crystal form, such as the Bravais-Friedel-Donnay-Harker model [13], which allows the crystal structure to be pre-calculated based on pure geometry, and the Hartman-Perdok method [14],

which, besides geometrical parameters, includes the effect of energetic interactions. Another method of modelling the crystal structure is the "Attachment Energy" method [15-17]. The surface deposition energy $E_{Att}$ is the energy released when a layer deposits onto the crystal surface.

$$\Delta E_{Att} = E_{Cry} - E_{Sliece} \tag{2}$$

Here, $E_{Cry}$ is the lattice energy and $E_{Sliece}$ is the energy of a layer of infinite thickness. The growth rate of the crystal surface is directly proportional to the surface deposition energy $E_{Att}$, so that surfaces with low deposition energy grow more slowly and therefore have the greatest influence on the crystalline morphology.

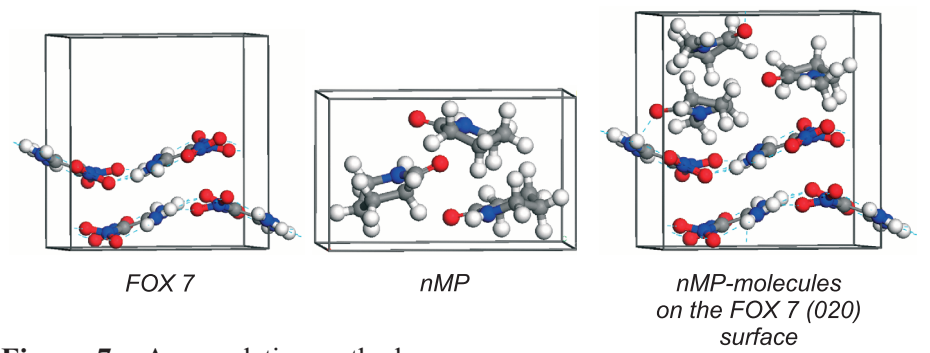



**Figure 7.** Accumulation method.

The environment in which crystallization takes place (*i.e*,. the solvent) has a decisive influence on the crystal habit. Use of different solvents leads to formation of various morphologies of a material. This influence on the crystal growth process is still not fully understood or amenable to modelling. A well-known method from the literature describes the incorporation of solvent into the crystal lattice structure (Build-up method; see Figure 8).

One newly developed method, instead of simulating the substitution of molecules at the crystal lattice points, describes the accumulation of solvent on the crystalline surface and calculates the crystal habit on the basis of interactions between the crystal surface and solvent (see Figure 7).

$$\Delta E = -(E_{Cry} + E_{Solvent} - E_{Cry+Solvent}) \tag{3}$$

This method allows one to simulate more realistically the growth of the crystal habit and its dependence on the solvent. Figure 8 shows an example of the solvent influence on FOX 7 crystals.

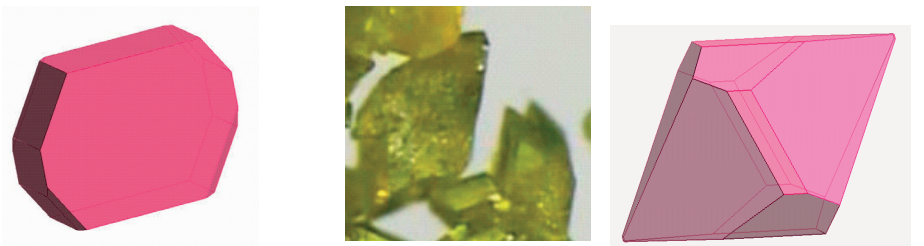



**Figure 8.** Solvent influences (Fox 7).

**Crystallization of 1,1-diamino-2,2-dinitroethylene (FOX 7)**

Cooling crystallization was used to recrystallize FOX 7. It is clear from Figure 9 that due to its various surfaces, FOX 7 crystallizes at a range of different crystallization rates and surface defects form on those crystal surfaces in which the growth process is hindered.

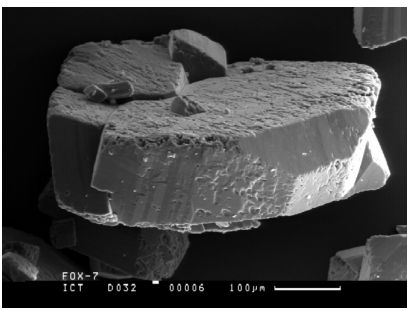
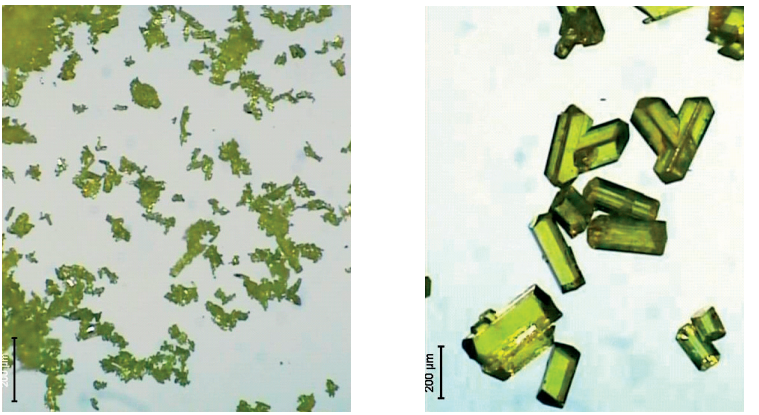



**Figure 9.** FOX 7 crystal.

All of the following experiments were conducted using a cooling gradient $dT/dt$ of 10 K $h^{-1}$. Pure 1-methyl-2-pyrrolidone (nMP) and an nMP/water mixture were used as solvents. It was found that using pure solvent and a certain portion of water as antisolvent yielded crystals ranging in size $x_{50,3}$ from 40 to 50 $\mu$m. Using solvent mixtures (*e. g.* acetonitrile, $\gamma$-butyrolactone, dimethylformamide

(DMF)), particles with sizes ranging from 100 $\mu$m ≤ $x_{50,3}$ ≤ 400 $\mu$m can be produced *via* cooling crystallization (see Figure 10).

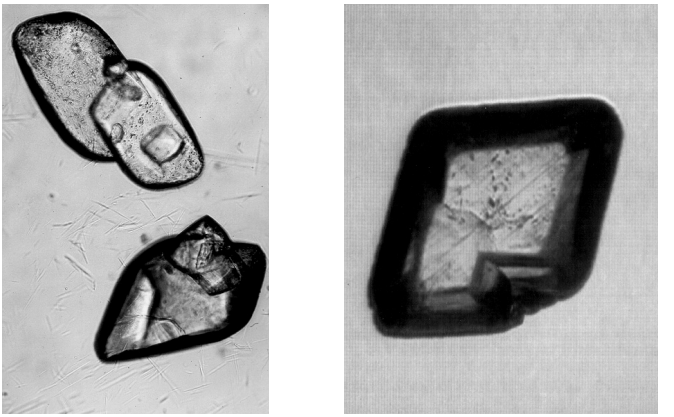



$x_{50,3}$ = 55 $\mu$m $x_{50,3}$ = 306 $\mu$m

**Figure 10.** FOX 7 crystals (cooling crystallization).

**Crystallization of insensitive HMX**

Using a modified cooling crystallization process, insensitive HMX (I-HMX) was produced. Figure 11 shows the original HMX and I-HMX.



HMX I-HMX

**Figure 11.** HMX crystals.

Using this special crystallization process, HMX with a significantly higher particle density was produced. The higher density is directly attributable to the reduced number of inner crystal defects in the molecules. Model PBX test slabs were produced using this HMX and subjected to gap tests. The I-HMX exhibits an insensitivity nearly a factor of two better than conventional HMX based on the shock wave loading test (Figure 12).

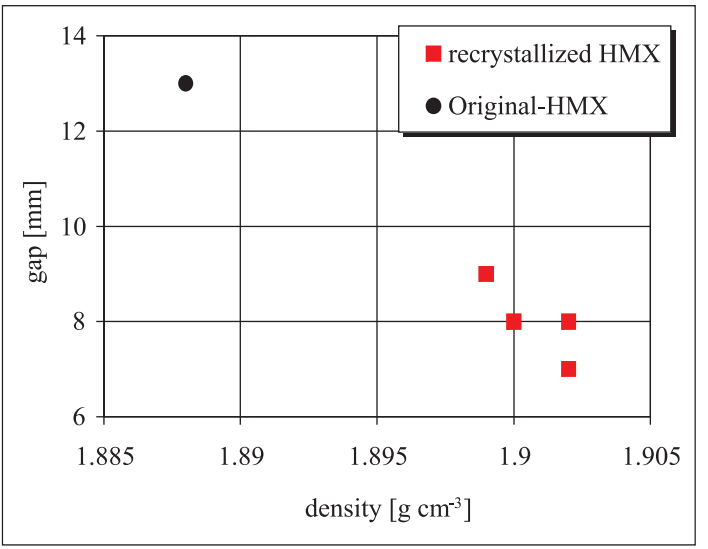



**Figure 12.** Gap test results, original HMX and I-HMX.

**Product improvement using ultrasound to initiate nucleation**

The use of ultrasound to initiate precipitation leads to a significant improvement in the quality of the end product and a narrower particle size distribution [18, 19]. Primary homogeneous nucleation is a process that occurs under thermodynamically unstable conditions. For many materials, a solid phase forms only under conditions of supersaturation. The point at which nucleation begins depends on the concentration of foreign material, the type of secondary material and the amount of mechanical energy applied to the system. When ultrasound is used during the cooling crystallization process, the onset temperature for nucleation is nearly independent of the temperature gradient and significantly higher than in the absence of ultrasound. In addition, the particle size distribution is significantly narrower when nucleation is initiated *via* ultrasound. The particle size distribution can be

described in terms of the distribution coefficient $\lambda_i$:

$$\lambda_i = \frac{x_{84,3} - x_{16,3}}{2 \cdot x_{50,3}} \tag{4}$$

where $x_{i,3}$ is the particle size for a volume sum distribution of i%.

**Particle manufacture via the membrane crystallization process**

Membrane crystallization is a new crystallization process that offers an interesting alternative to cooling or steam crystallization, especially for energetic materials [20-22]. This method is especially interesting for use with thermolabile products, because the process can be carried out at low temperatures. In addition, the energy balance for membrane crystallization is considerably more favorable compared to cooling or steam processes. Like other processes, membrane crystallization occurs in an oversaturated solution, in which the solvent is transported through a semi-permeable membrane, thereby becoming more concentrated at a nearly constant process temperature. The membrane must be chosen so that it provides a selective barrier to the active ingredient while allowing the solvent to penetrate the membrane (see Figure 13). Membrane processes are typically pressure driven methods, such as reverse osmosis or micro or nano-filtration [23]. After transport of the solvent through the membrane to form a highly concentrated fluid phase, nucleation begins and is followed by the desired crystal growth stage.

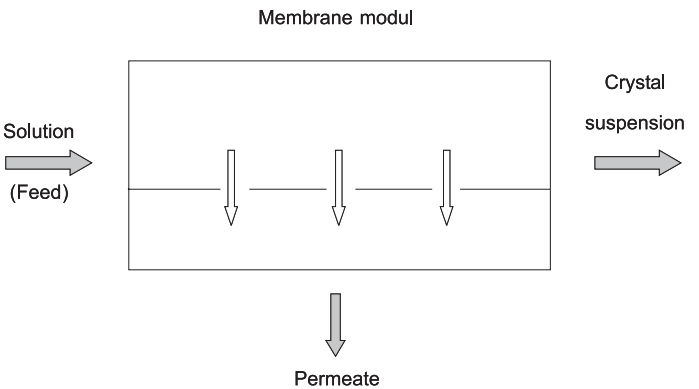
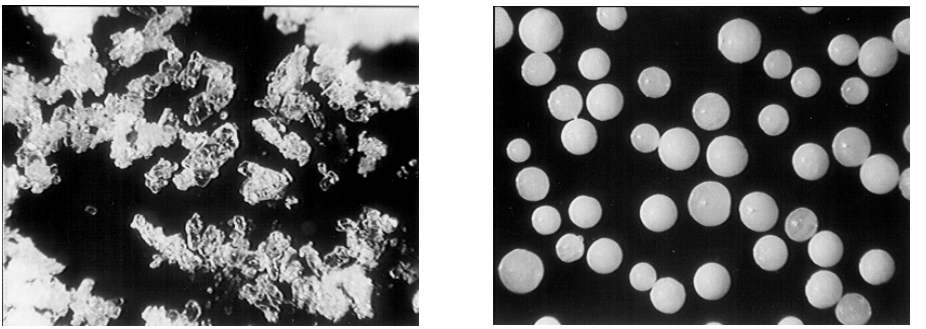



**Figure 13.** Membrane crystallization.

## Product design of spherical Ammonium Dinitramide (ADN)

Emulsion crystallization is particularly suitable for producing spherical particles of materials that melt at temperatures accessible with conventional processing technologies. The emulsion crystallization process consists of two linked process steps. The first step is production of an emulsion consisting of molten material dispersed in an inert continuous phase. The droplet size of an emulsion can be controlled by choosing the appropriate emulsification method and equipment. Various dispersion and size reduction processes exist, using equipment such as rotor-stator mixers (gear rim dispersers and colloid mills) or static mixers.

The second step in emulsion crystallization, which is decisive to the process, is the transition of the fluid dispersed phase into solid particles. For materials with particularly sluggish nucleation behavior, in addition to application of a sharp temperature gradient, some combination of mechanical energy input, particle-particle and/or particle-wall interactions or addition of seed crystals is necessary to initiate the nucleation process. The possibility of producing ammonium dinitramide (ADN) *via* the emulsion crystallization process is demonstrated in Figure 14.



a. Synthetic product b. Emulsion crystallization product

**Figure 14.** Crystallization of ammonium dinitramide (ADN).

Figure 14a shows the product after synthesis and 14b depicts the spherical ammonium dinitramide after the emulsion crystallization process [24]. Afterwards, the continuous and dispersed phase of the suspension are separated and the product is dried.

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