

Production of Particles of Explosives

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Herstellung von Explosivstoffpartikeln

Bei Festtreib- und Explosivstoffen kommt dem partikulären Füllstoff eine besondere Bedeutung zu. Die Rekristallisation der Explosivstoffpartikel erfolgt je nach stoffspezifischen Eigenschaften in unterschiedlichen verfahrenstechnischen Prozessen. Neben der Zerkleinerung, der Sprühkristallisation und der Kristallisation aus Lösungen finden auch neue Verfahren wie die Kristallisation unter Einsatz komprimierter Gase und die Emulsionskristallisation immer mehr Anwendung.

Synthèse de particules explosives

La substance de charge particulaire joue un rôle important dans les explosifs et les propergols solides. La recristallisation des particules explosives se déroule suivant différents processus techniques en fonction des propriétés de la substance. Parallèlement au broyage, à la cristallisation par pulvérisation et à la cristallisation à partir de solutions, de nouvelles méthodes telles que la cristallisation utilisant des gaz comprimés et la cristallisation en émulsion trouvent des applications de plus en plus fréquentes.

Summary

The particulate properties of the particles in solid propellant and explosive charges are of very special importance. Depending on the properties of the substances involved, recrystallization of particles of explosives is carried out using different process technologies. Alongside milling, spray crystallization and crystallization out of solutions, new procedures such as crystallization using compressed gases and emulsion crystallization are finding increasing application.

1. Introduction

Solid propellants and explosives often consist of heavily laden polymer systems. In these systems, the particulate components which can comprise up to 90% by weight of the total are especially important. The particulate properties of energetic materials and/or oxidizers require special methods depending on the type of application.

The formation of these particles, by recrystallization or other means, is a production step which follows after the synthesis of the compound and before the processing steps giving a finished solid propellant or explosive charge (see Fig. 1).

The properties of the synthesized particulate components can be controlled by using different process technological

procedures for their preparation and recrystallization. In this way an explosive with, for example, better working properties or a larger specific area (to influence the burning characteristics) can be obtained. With particle production procedures tailored to the product in question, explosive particulates with a variety of specific properties can be made:

- Different mean particle diameters
- Narrow particle size distribution
- Well-defined particle shape, morphology
- Low-defect (or defect-free) crystals
- Higher purity.

The following sections present various different procedures for the production of particulate explosive materials.

2. Particle Preparation Procedures

Different processing techniques are used in the production of explosive particles depending on the physical properties of the explosive material and the desired characteristic values, such as the mean particle size, of the product:

- Milling (size reduction)
- Crystallization out of solutions
- Crystallization using compressed gases
- Emulsion crystallization
- Spray crystallization (spray drying)
- Coating of particulate systems.

2.1 Size Reduction

In size reduction procedures the structural elements of a solid are broken down with mechanical forces, increasing the dispersivity of the mass. Because of interactions that are difficult to quantify and which depend on a number of physical properties such as hardness, structural constitution and the way in which the material is stressed, size reduction

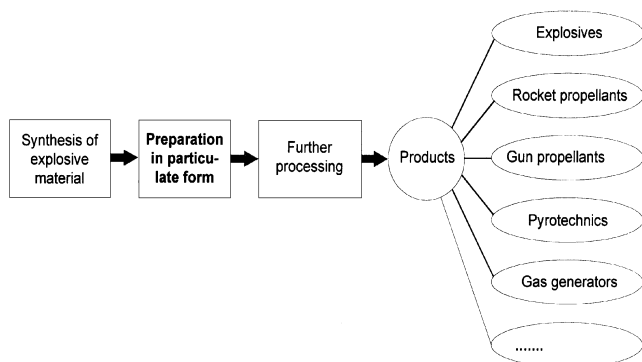


Figure 1. Steps in the production of energetic materials.

remains largely an empirical science. Theoretical characterization is today possible only on a phenomenon-by-phenomenon basis. As a result, a large number of different devices based on different operating principles have been developed. The following types of size-reduction devices are suitable for use with explosive materials:

- Rotor-stator mills
- Colloid mills
- Ball mills
- Vibration mills
- Jet mills.

For safety and other reasons, wet milling is the preferred method of size reduction for components of explosives. Another advantage of wet milling is that less energy input is required per unit of product than for dry milling. This is because the liquid, with its higher viscosity, promotes the transfer of forces to the particles being milled more effectively than does air.

The rotor-stator device shown in Figure 2 can mill RDX, HMX or CL-20 in aqueous suspension down to particle diameters as low as $x = 5 \mu\text{m}$.

The rotor-stator system shown consists of a 6-bladed rotor and a stator having 8 inclined slits. The rotor rpm n can be varied in a range of $3000 \text{ min}^{-1} \leq n \leq 20\,000 \text{ min}^{-1}$, providing maximal circumferential velocities of $u = 16.8 \text{ m/s}$. The particles and the continuous phase of the suspension flow into the device axially and are then propelled tangentially outward through the slits. Figure 3 shows CL-20 particles milled in a rotor-stator device. Their mean particle size is $x_m \approx 5 \mu\text{m}$.

From Figure 3 it is clear that particles resulting from a size-reduction process do not have a homogeneous surface structure. Small secondary particles or crystal fragments adhere to the primary particles. During the size reduction process the particles are subjected to high shear and impact forces which cause altered stress states to build up in the interior of the crystals. Furthermore, size reduction often results in a broad size distribution curve making a subsequent grading step necessary. Figure 4 shows the volume sum

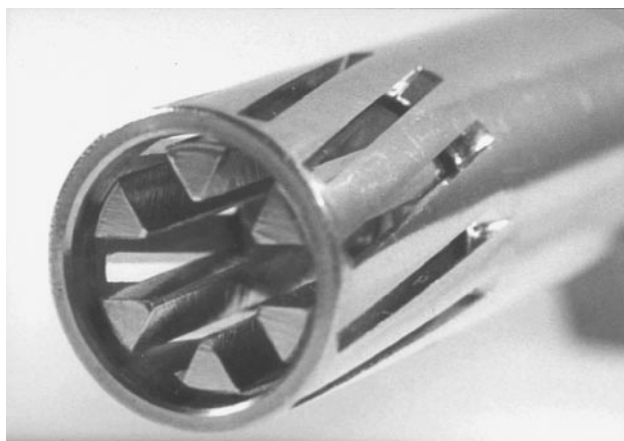


Figure 2. Rotor-stator milling device.

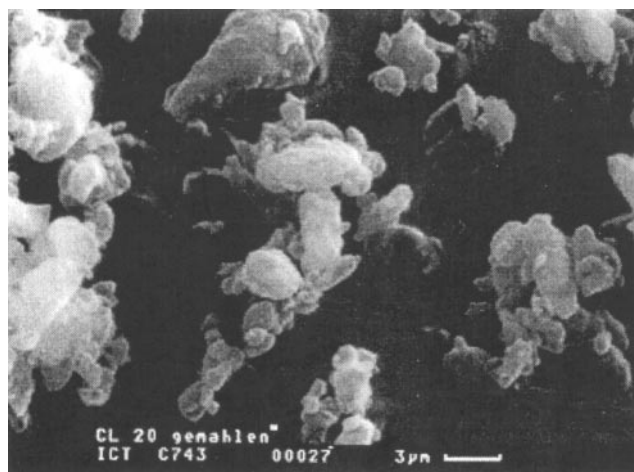


Figure 3. CL-20 wet-milled in rotor-stator system.

distribution $Q_3(x)$ and the volume density distribution $q_3(x)$ curves for octogen after a batch ultrasonic size-reduction procedure.

The median particle diameter $x_{50.3}$ is $4.8 \mu\text{m}$ and the dispersivity k , a measure of the breadth of the size distribution and hence a value which reflects the homogeneity of a particulate, is 0.456 as calculated from its definition in VDI guideline 3491⁽¹⁾:

$$k = \frac{x_{84.3} - x_{16.3}}{2 \cdot x_{50.3}} \quad (1)$$

$$k < 0.14 \rightarrow \text{monodisperse}$$

$$0.14 \leq k \leq 0.41 \rightarrow \text{quasi-monodisperse}$$

$$k > 0.41 \rightarrow \text{polydisperse}$$

The jet mill is one device enabling dry milling of explosive materials. In a jet mill the material to be milled is suspended in an expanding gas stream moving at sonic or supersonic speeds. The particles are reduced in size by impact and

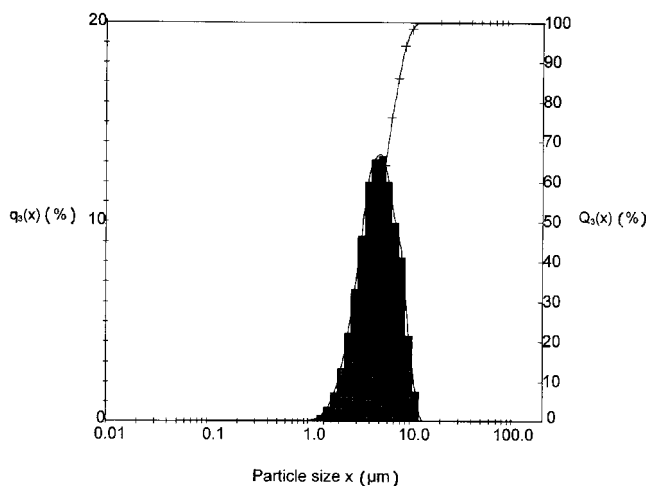


Figure 4. Volume sum distribution $Q_3(x)$ and volume density distribution $q_3(x)$ of octogen after ultrasonic size reduction.

attrition (particle-to-wall and particle-to-particle interactions). Jet mills can operate with very small chambers and hence with low product volumes. The in-process residence time of the particles is also very low. These characteristics make jet mills especially suitable for the preparation of the finest of particles of explosive materials. An additional advantage is that jet mills are self-cooling, because of the gas stream used. Jet mills are especially suitable for milling ammonium and potassium perchlorates, for which particle sizes of approximately 3 μm can be achieved.

2.2 Crystallization out of Solutions

Compared to size reduction in which the particles are subjected to high levels of mechanical stress, crystallization procedures for the preparation of particles of explosives offer substantial advantages. The crystals can be grown relatively slowly and free of stress, and, after completion of the crystallization process, they have a well-defined crystalline shape and structure.

Crystallization is a basic technique in process technology; it can be brought about by cooling a saturated solution or evaporation of solvent components, depending on the solvability properties of the solid to be crystallized. Crystallization procedures can be classified according to the method used to achieve the required supersaturation, as follows:

- Crystallization by cooling
- Evaporation crystallization
- Vacuum crystallization
- Displacement crystallization.

The choice of an appropriate crystallization procedure depends on the shape of the solubility curve for the particular product/solvent system. If solubility increases with temperature, then supersaturation should be achieved by cooling. If the curve is very flat, then solvent evaporation will be required in addition.

As a result of the surface interactions between crystal and solvent, the resulting crystal habit is highly dependent on the choice of solvent. This means that with crystallization,

crystals optimized for their further processing can be engineered. Figure 5 shows octogen crystals that were recrystallized using different solvents.

Crystallization comprises two important mechanisms:

- Nucleation
- Crystal growth.

Nucleation occurs when the solution equilibrium is disturbed under supersaturated conditions. Molecules or ions from the supersaturated solution attach themselves to the surfaces of the crystal nucleus and cause it to grow. Certain properties of the crystal can be influenced by carefully controlling the growth process. It is thus possible, for example, to grow crystals that are free or almost free of defects. Figure 6 shows the results of a gap test with PBX made up of HTPB and octogen crystals (approx. 70 wt%) recrystallized in propene carbonate.

The internal quality of the crystals increases with increasing density, i.e. denser crystals have fewer defects. Figure 6 shows clearly that recrystallized HMX particles are substantially less sensitive, as a result of a reduced crystal defect rate.

2.4 Crystallization Using Supercritical Fluids

Crystallization procedures using compressed gases are another method with which it is possible to crystallize components of explosives.

These new techniques are especially suited to the production of low-defect particles in the submicron range with narrow size distributions. The unusual properties of highly compressed gases make it possible to produce particulates with any of a wide range of characteristics⁽²⁾.

Three different such procedures are available for the production of particles of explosive materials:

The **RESS process** (Rapid Expansion of Supercritical Solutions) is used with explosive materials that are soluble in a supercritical fluid, either alone or in the presence of a modifier. Particles are formed through the rapid expansion of the solution as it flows through a nozzle. The pressure p and the temperature T are sharply reduced by the rapid expan-

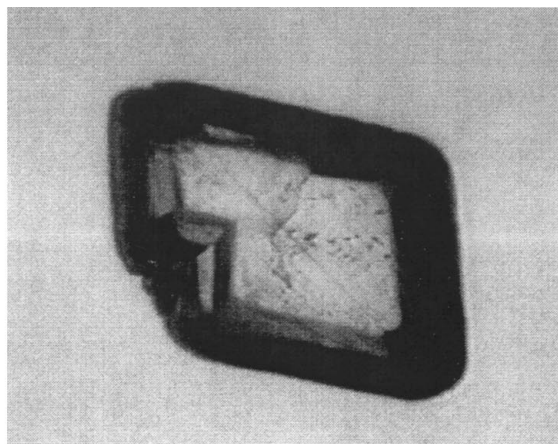
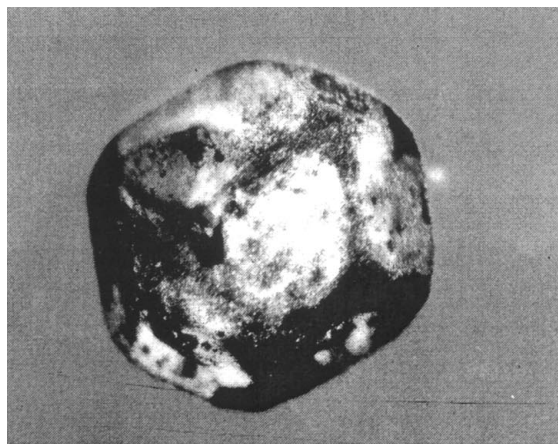


Figure 5. Octogen crystals.

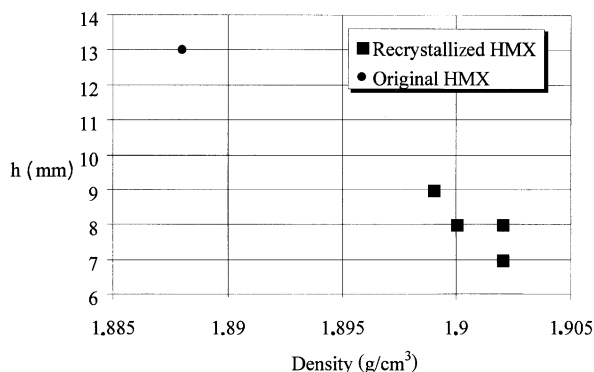


Figure 6. Gap test results for HMX crystals recrystallized in propene carbonate.

sion, causing very high local levels of supersaturation and nucleation in the free jet. The primary application of this process, which is characterized by the rapid expansion in the nozzle, is in the production of fine particulates with narrow size distributions. Because no solvent in the classical sense is involved, and because crystal formation is relatively rapid, solvent-inclusion crystal defects are avoided. Figure 7 shows a schematic representation of the RESS pilot plant.

The gas is brought to supercritical conditions in the pump/heat-exchanger section where it is compressed and re-cooled, shown at the right of the diagram. The supercritical fluid then takes on previously prepared explosive material in the extractor (B1), and the resulting supercritical solution is sprayed out of a nozzle. Figure 8 shows two photographs of TNT particles, in both cases crystallized with supercritical carbon dioxide.

The TNT particles crystallized statically in CO₂ (Fig. 8a) show the needle-like crystallization pattern typical of TNT. With the rapid expansion in the RESS process (Fig. 8b), the degree of development of the crystal habitus can be

observed. The median particle size of the TNT particles is $x_{50.3} = 10 \mu\text{m}$.

Figure 9 shows NTO particles which were also recrystallized in a RESS process with supercritical CO₂.

With NTO it is also possible to generate primary particles in the submicron region, but the tendency of NTO to agglomerate needs to be investigated in future studies.

If the explosive material is *not* soluble in a supercritical fluid, then the compressed gas can be used as an **anti-solvent** which initiates recrystallization of the explosive out of a solution involving a classical solvent. In this process, the absorption of the compressed gas by the solvent causes the liquid phase to expand. This increase in the specific volume of the solution, i.e. reduction of the solution's density, causes a decrease in the solvent power of the solvent, which in turn causes particles of explosive material to precipitate. Two procedural variants based on this phenomenon are in use.

- The heavily laden solution is first placed in a crystallization chamber and the compressed gas is admitted thereafter.
- The solution and the compressed gas are sprayed into a crystallization column at the same time, preferably in a countercurrent flow pattern. The diffusion of the gas into the solution droplets is then very rapid, resulting in precipitation of fine particles of explosive. This variant is known as the **PCA process** (Precipitation with a Compressed Fluid Anti-Solvent).

2.4 Emulsion Crystallization

Emulsion crystallization is particularly suited to recrystallization of fusible propellant and explosive materials. The oxidizer ammonium dinitramide (ADN), which melts at

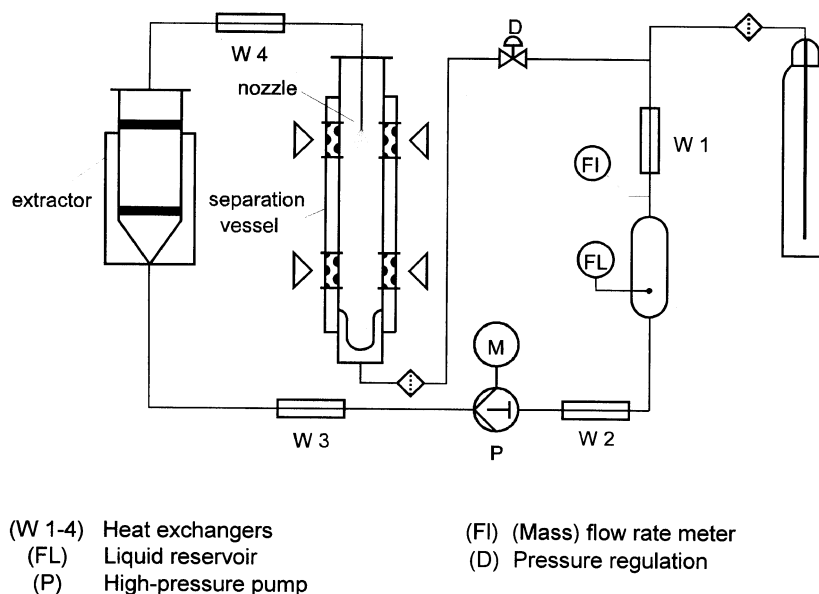
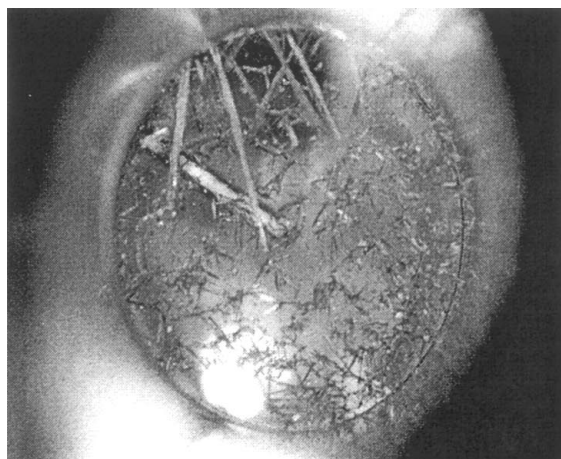


Figure 7. RESS pilot plant.



(a) Statically produced



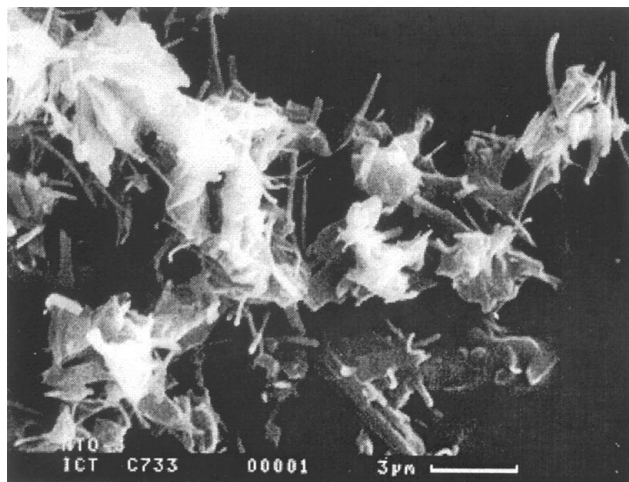
(b) Produced by RESS process

Figure 8. TNT particles.

about 92°C, can be formed into spherical particles with this process⁽³⁾.

The emulsion crystallization process comprises two main steps, as described below for ADN:

- (1) Preparation of a liquid/liquid, multi-phase system with molten ADN as the disperse phase in a continuous phase in which it is insoluble and immiscible. Atomization and emulsification are accomplished by mechanical means, for example with a rotor-stator system (see Fig. 2) or a suitable agitator.
- (2) Crystallization of the emulsified droplets to solid spherical ADN particles. Because ADN exhibits a strong tendency toward supercooling, mechanical energy input is also required in this step. Beyond simple cooling below the melting point, recrystallization of ADN droplets must be promoted by mechanical energy or particle-particle interactions. Such local application of energy then initiates the crystallization process.

**Figure 9.** RESS process NTO particles.

Emulsion crystallization can be used to produce ADN particles in the $5 \mu\text{m} \leq x_{50.3} \leq 800 \mu\text{m}$ range.

2.5 Spray Crystallization or Spray Drying

Spray crystallization is also a two-step process. In the first step the liquid is atomized and in the second the droplets are dried and spherical particles crystallized. Using a two-fluid nozzle with concentric gas and liquid phase outputs, the mean droplet diameter x_m can be regulated as follows:

$$x_m \approx 0.58 \cdot \sqrt{\frac{\sigma}{w^2 \cdot \rho_g}} + 1.6 \cdot \left(\frac{\dot{V}_F}{\dot{V}_G} \right)^{1.5} \quad (2)$$

where:

- σ the surface tension of the liquid
- \dot{V}_F the volume flow rate of the liquid
- ρ_g the density of the gas
- \dot{V}_G the volume flow rate of the gas
- w the speed of the gas relative to the liquid.

The relative speed w is also a function of the pressure across the atomizer. If the output flow velocity is reduced (for example by a decrease in the liquid head in the feed system) then the relative speed w increases, leading to smaller particle sizes. Figure 10 shows a schematic diagram of a plant for the production of phase-stabilized ammonium nitrate (PSAN).

The spray crystallization plant consists of a crystallization tower with the main component part (atomization sprayer) and a cooling jacket. Downstream of the tower is a cyclone for particulate removal, and above the tower is a melting pot with stirrer.

With spray crystallization techniques, phase-stabilized ammonium nitrate can be produced with various different additives, such as zinc oxide, copper oxide or nickel oxide, or without additives as **SCAN** (**S**pray **C**rystallized **A**N) in the

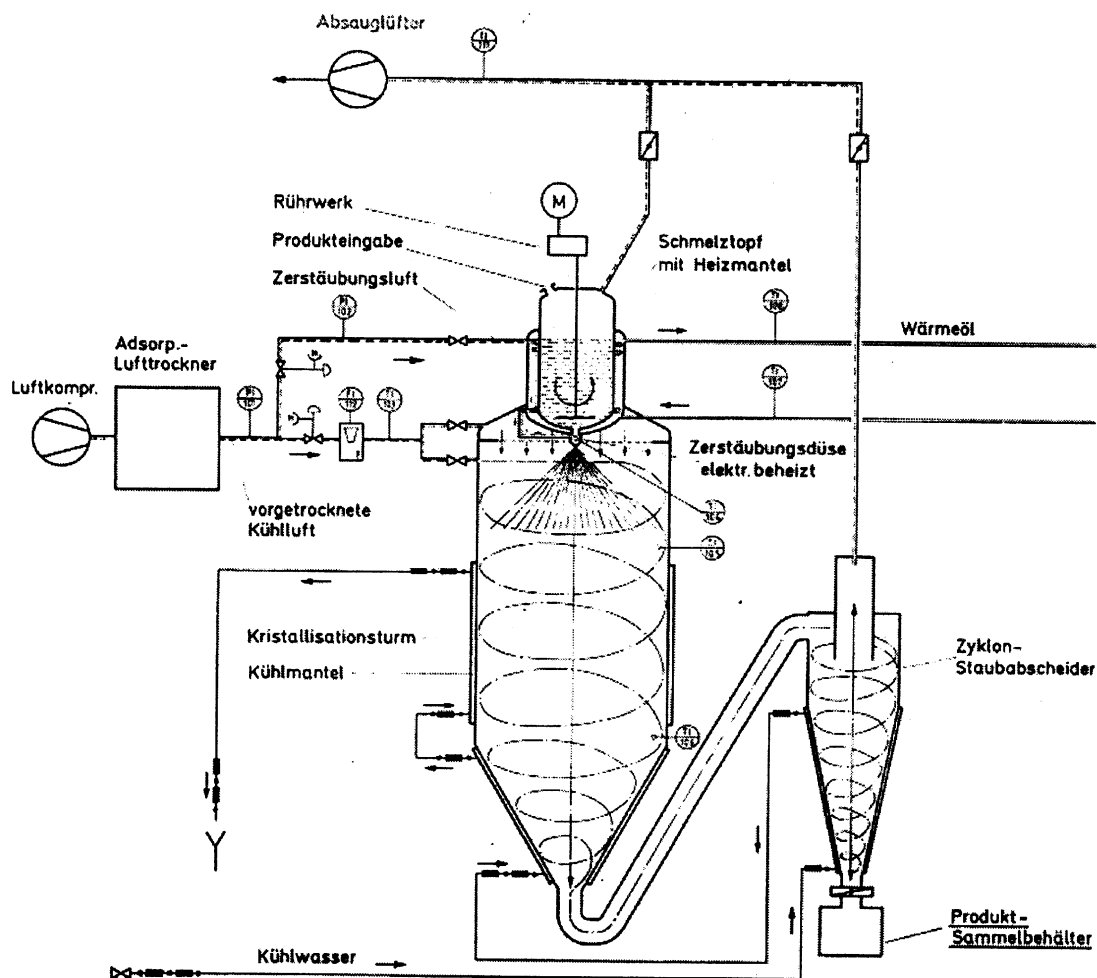


Figure 10. Spray crystallization PSAN production.

form of spherical particles with mean sizes of $x_m = 20 \mu\text{m}$, $x_m = 50 \mu\text{m}$, $x_m = 160 \mu\text{m}$ or $x_m = 300 \mu\text{m}$.

3. References

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