

## Ultrasonic Assisted Preparation of Nano HMX

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### **Abstract:**

*Size reduction of high energy materials such as 1, 3, 5, 7-tetranitro- 1, 3, 5, 7-tetraaza cyclooctane (HMX) has considerable influences on improving their explosive characteristics. In this study, nanosized HMX particles were produced using ultrasonically reprecipitation method by applying water as a safe and accessible antisolvent instead of unsafe conventional methods. SEM photographs revealed that much uniform and low agglomerated spherical morphology can be obtained at low concentration of HMX- acetone solution with low temperature antisolvent. These results are achieved from SEM and TEM photographs and Digimizer - Winks software.*

**Keywords:** Ultrasonically reprecipitation, Nano-size HMX, Size reduction, High energetic materials

### **1. INTRODUCTION**

Materials size reduction has been done by different methods to improve their characteristics. These methods are invented in a wide range from utilization of high-pressure mill [1] to crystallization with ultrasonic vibration [2, 3].

1, 3, 5, 7-Tetranitro-1, 3, 5, 7-tetraazacyclooctane (HMX), is an explosive high energy material which has numerous applications such as military and commercial applications. The microstructural properties of an energetic material strongly influence the combustive and explosive behavior of the formulations [4, 5]. These differences can be attributed in part to the strong influence of the heat and mass transport rate which are affected by many factors. Among these, the particle size of the energetic materials [6] and the homogeneity of the formulations play the major role. Very fine particle size with a homogenous formulation can shift the

balance from transport control state to the chemical kinetic control state [7]. Because of this matter, recent efforts are motivated to create nanoscale energetic materials. The behavior of nanoscale materials is quite different from micro-size energetic materials in many ways. They have higher burning rates, lower impact and friction sensitivity and, lower temperature of the maximum energy release compared to the conventional energetic materials with larger size [8,9] Some techniques like using supercritical fluid [13,14], sol-gel, high speed air impaction, micro emulsion, vacuum co-deposition [10,11] and reprecipitation at the room temperature [12] have been used to create nanoscale energetic materials. In this study, preparation of nanosize HMX by ultrasonically reprecipitation has been reported.

#### **1.1. Sonocrystallization**

Crystallization is a complex process including

multiple interacting processes. In the conventional salting-out crystallization, the entire process from solution with a suitable concentration to supersaturation, nucleation of solution and crystal growth, generally requires many hours with blend of mechanical agitation and addition of precipitant dosage. By mechanical agitation, microscopic mixing is mainly provided.

Sonocrystallization is the use of power ultrasound to control the crystallization process [13]. It is applied as a mechanical aid to blend and cavitate the medium during the salting-out process and is able to induce nucleation in lower supersaturation than conventional agitation. In this process, cavitation has the main role. Power ultrasound creates cavitation in liquid media. This impact happens by change in the sonic power in the suction phase of the ultrasonic oscillation. During this phase, small voids are made by vacuum in the liquid. The suction phase is followed by a pressure phase where these voids collapse inward. The reaction occurs in a 200 nm ring surrounding the collapsing bubble [15]. The reaction occurs upon high velocities and simultaneous blending. In the extremely small volume, the kinetic energy is converted into the thermal and potential energy (pressure). Therefore, the fluid becomes heated and the spherical pressure shock waves are generated. The order of magnitude of the shock wave pressure is a multiple of the pressure caused by sonic waves; it can be higher than 1000 MPa [16]. Furthermore, local hot spots with the temperature of 5000-25000 K can occur.

The explanation for creating the nano-structured products is that the fast kinetics do not permit the growth of the nuclei, and in each collapsing bubble, a few nucleation centers are formed whose growth is limited by the short collapse [17, 18].

Comminution by ultrasonic in aqueous phase is ideally suited for comminuting energetic materials. Apart from that, the short stay in comminution zone without any confinement is very advantageous for these sensitive materials.

#### *1.1.1. Advantages of Sonocrystallization*

By using ultrasound, a non-invasive way for

improving of crystal properties is provided, mainly by controlling the size distribution and habit of crystals. By varying the power and duration of sonication the crystal size distribution can be tailored to optimize downstream processing. The following advantages are considered for Sonocrystallization:

- low agglomeration
- improved crystal purity and secondary physical properties of the product
- with ultrasound, some reactions begin without any requirements to additives.
- Powder filling operations can be more trouble-free because the crystals flow much better (due to rounding) than those produced conventionally.
- Doubling of the bulk density is possible, which is very essential for using the explosive materials [19, 20].

## **2. EXPERIMENTAL**

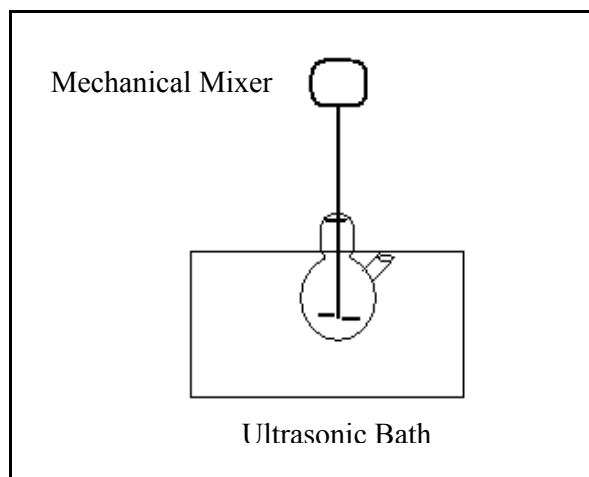
### **2.1. Materials**

Sonication experiments were performed in an ultrasonic bath (Bandelin Sonorex-PK100). The internal dimensions of the bath were: length: 24 cm, breadth: 14 cm, height: 10 cm. The bath had a power rating of 320 W. Water was taken in the ultrasonic bath as a cavitation medium and filled up to a height of 9 cm. The experimental set up figure has been presented in Figure 1.

The crystal morphology has been studied by Scanning Electron Microscope (SEM) instrument of Philips-XL30 and Transmission Electron Microscope (TEM) of Philips-CM 120. For obtaining particle size distribution from SEM photos, Digimizer and Winks softwares were used. To gather the precipitates, Kokusan (model H-108N) centrifugation device was used.

### **2.2. Reprecipitation of HMX**

1 mL of HMX in acetone (solvent) with defined concentration was dropped into 25 mL of antisolvent



**Figure 1:** Schematic of the experimental set up



**Figure 2:** SEM photograph of tearing of the prepared sample in the presence of  $\text{CHCl}_3$  as antisolvent. This tearing happens because of low thermal consistence.

containing 0.5 mL ethanol as dispersant agent. Antisolvent will reprecipitate the particles which were solved in the solvent. This system is stirring by a mechanical mixer with the speed of 2000 rpm. This solution was in a 100 mL flask placed in the ultrasonic bath which was filled by water as the cavitation medium. Sonication time was 15 min and the mentioned procedure was same for all of the experiments.

To find the optimum condition for preparation of

nanosize HMX crystals, some important items such as antisolvent type, initial HMX acetone concentration, sonication time and antisolvent temperature were applied at different forms and quantities.

### 3. RESULTS AND DISCUSSIONS

#### 3.1. Effect of the antisolvent type

The average particle sizes obtained from SEM photographs are presented in table 1. This part of the experiments was completed with 0.01% HMX-acetone solution at the room temperature. While taking SEM photographs, samples prepared in presence of DMSO, chloroform and n-heptane were torn by the collision of electrons, but the sample prepared by water, didn't get any tearing. It can be concluded that the thermal resistance of this sample (which is a very important characteristic for high energy materials) is higher than the others. Figure 2. shows tearing of nanosize-HMX sample when  $\text{CHCl}_3$  is used as the antisolvent. For DMSO and  $\text{CHCl}_3$ , nano size HMX particles were completely beside each other with no space between them, but particle size distribution (PSD) was more uniform for DMSO experiment. The lowest agglomeration was seen with n-heptane. For water antisolvent, HMX nanoparticles were near to each other with some spaces among them. So, both PSD and particle size were in better state.

#### 3.2. Effect of the initial concentration of HMX-acetone solution

In other part, different concentrations of initial HMX-acetone as solvent were utilized which are shown in table 2. Antisolvent was water at the room temperature. By applying lower concentrations, in addition to the lower average particle size, the agglomeration and PSD were considerably more uniform than higher concentrations.

#### 3.3. Effect of sonication time

The items detected as optimum ones, are applied at

**Table 1:** Average particle size for different organic and inorganic antisolvents

antisolvent	n-Heptane	Water	Chloroform	DMSO
Average particle size (nm)	85.0	49.0	41.0	30.0

**Table 2:** Effect of the solvent concentration

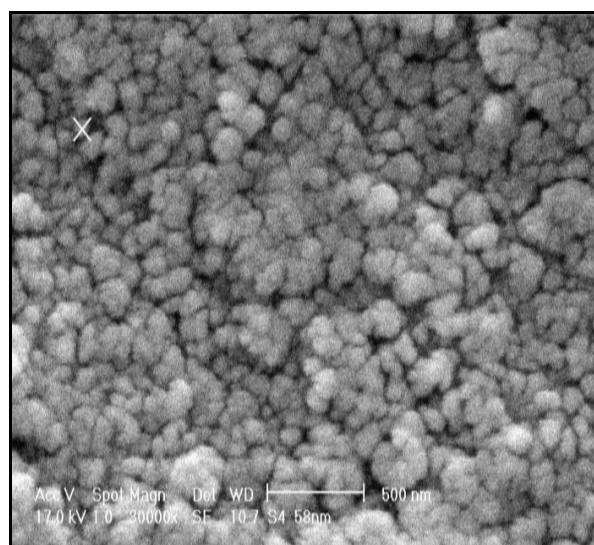
HMX-Acetone Conc.	0.01%	0.05%	0.1%	0.5%
Average particle size (nm)	49	49	83	>400
morphology	Spherical	Spherical	Spherical	Hexagonal

**Table 3:** Effect of the sonication time

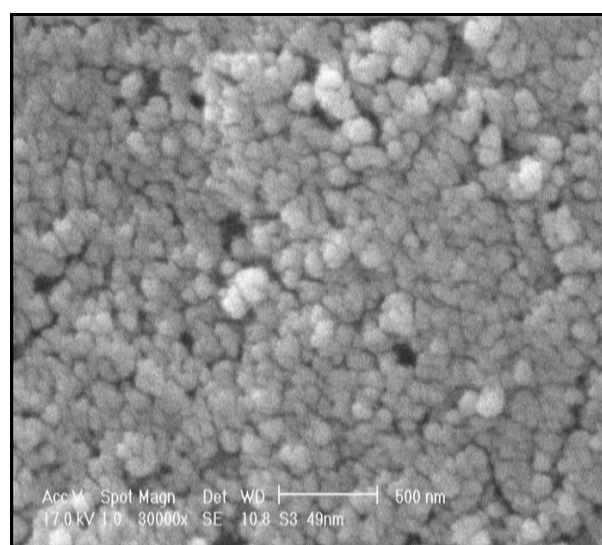
Sonication Time (min)	5	10	15	20
Average particle size (nm)	73	67	49	48

**Table 4:** Optimized parameters

HMX-Acetone Concentration	Antisolvent	Antisolvent Temperature	Sonication Time
0.01%	Water	0-2°C	15 min



a.



b.

**Figure 3:** SEM photographs of HMX nano-particles prepared by reprecipitation. Common preparation condition for both of them: 1 mL of 0.01% HMX-acetone solution dropped in to 25 mL stirring water of 2000 rpm as antisolvent. The system was sonicated for 15 min. For a. Water used at the room temperature and for b. water used at 0-2°C. Actually sample b. is precipitated in the optimum condition extracted from experiments.

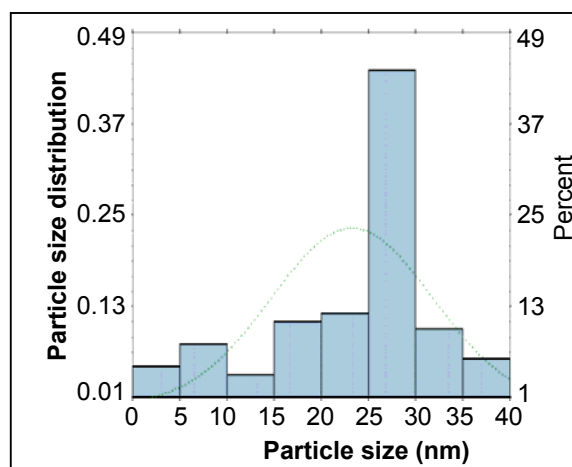
room temperature for this system by implementing different sonication times according to table 3. For sonocrystallization, insonation provides microscopic mixing by vibration, cavitation and travel of ultrasound wave. Satisfactory mixing is achieved much more rapidly than in the conventional mixing. By increasing the sonication time from 5 to 15 min, the average particle size and agglomeration decrease. This outcome completely confirms the mechanism of sonication in deagglomeration and preparation of particles with small size. When sonication time is more than 15 min, it's effect is not substantial.

### 3.4. Effect of antisolvent temperature

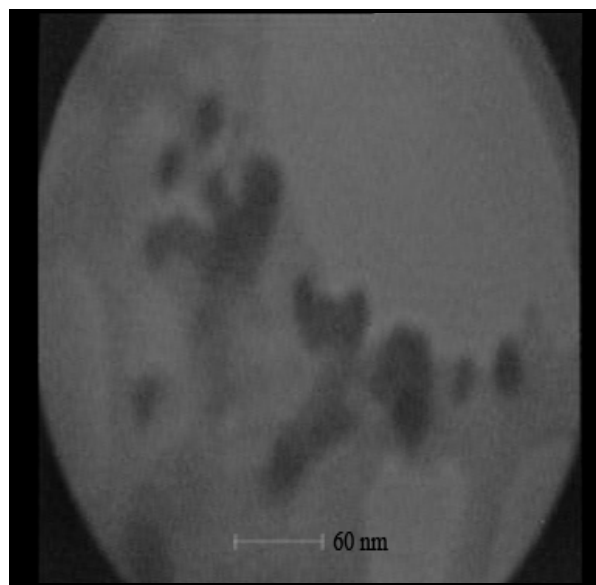
The lower temperature was one of the other factors which were expected to have an obvious influence on decreasing the average particle size and agglomeration. For this purpose, in the solution of 0.01% HMX acetone, antisolvent was water with 0-2 °C. Actually this experiment was done under the optimized condition including antisolvent type, HMX acetone solution concentration, sonication time and antisolvent temperature which were acquired in this study. Figure 3-b is the nanoparticles prepared in the optimized condition, which demonstrates more uniformity with spherical particles in comparison with other samples. Most of the particles have the diameter of 27 nm. In figure 4 particle size distribution is discernible and Figure 5 shows the TEM photograph of this sample. The finalized parameters are listed in table 4.

## 4. CONCLUSIONS

Various size reduction methods have been used to prepare nanoparticles with the improved characteristics. Because of high sensitivity of the explosive materials, most of comminuting methods like jet mill and ball mill are not suitable and some others like sol-gel are useful for formulations. For energetic materials, a safe [21] and high performance size reduction method such as sonocrystallization is required. In this method, the size distribution and the shape of the crystals can be



*Figure 4: Particle size distribution of the sample prepared in the optimized situation.*



*Figure 5: TEM photograph of the sample prepared in the optimized situation.*

designed by control of the solvent concentration. In this study, HMX nanoparticles are successfully prepared by a simple ultrasonically reprecipitation method at the room temperature. By SEM photographs and utilizing softwares, the average particle size and PSD were surveyed. Preparation of low agglomerated and almost uniform spherical nanoparticles, confirmed that this method is safe and suitable for energetic materials size reduction.

Over the past several years, remarkable effort has been concentrated on the preparation of the organic microcrystals by reprecipitation. However, most of the reported organic microcrystals are limited to compounds and polymers. It is difficult to prepare microcrystals of compounds with polar groups by this method. Our result makes a contribution to this work by using organic and inorganic non-solvents. In the presence of ultrasonic irradiation, it also demonstrated the potential of preparing organic microcrystals with polar groups by reprecipitation method.

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