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Synthesis and characterization of spherical 2-diazo-4,6-dinitrophenol (DDNP)

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ABSTRACT

Spherical 2-diazo-4,6-dinitrophenol (DDNP) with good flowability and controlled bulk density (0.65–0.95 g/cm^3) has been prepared at factory scale by the modified method using 4-methylphenol as crystal control ingredient. Results showed that the yield of product was increased by 5–10%, and the waste water was significantly decreased due to circulation use of waste water compared with traditional method. Synthesized spherical DDNP was characterized by IR, laser granularity measurement, SEM, HPLC and XRD. IR spectrum confirmed the structural features of spherical DDNP. The particle analysis revealed that the modified method could offer spherical DDNP with average particle size of 350 μm and high purity (>98.52%). The XRD peaks of spherical DDNP have similar diffraction angles as those of traditional DDNP. The DSC profile of spherical DDNP showed the exothermic decomposition in the temperature range of 161.2–188.5 °C. The product can be pressed at over 40 MPa without dead pressed phenomenon, and the minimum detonating charge of spherical DDNP was measured to be about 0.15 g. Furthermore, impact sensitivity test suggested that spherical DDNP is less sensitive than traditional DDNP.

1. Introduction

2-Diazo-4,6-dinitrophenol (DDNP) has been widely used in commercial and military detonators as an efficient primary explosive. It possesses nitro and diazo groups in a benzene ring, and its structure is shown in Fig. 1 [1]. DDNP has attracted substantial attention of researchers in energetic material field. DDNP is a green energetic compound without lead [2,3], and its good energy capability is comparable with that of high explosives such as HMX, RDX. Besides, DDNP has favorable ignition performance and chemical stability, and its ignition property is about twice greater than that of mercury fulminate. The impact and friction sensitivity of DDNP are lower than that of mercury fulminate and close to that of lead azide [4,5]. Moreover, DDNP can be prepared from readily available starting materials. Hence, among existing primary explosives, DDNP with good flowability and higher bulk density is a very promising initiator.

In views of the above, it is worth working on the synthesis of DDNP. DDNP was first synthesized by Griess in 1858, since then different synthetic methods of DDNP with different morphologies have been developed. Clark obtained DDNP by method A and method B in the form of granular powder and needle-like crystals, respectively [6]. In fact, DDNP produced by these two methods was poor flowability with low density. Tabular DDNP crystals with bulk density of about 0.55 g/cm^3 was prepared by Frederick by means of adding a nitrite to a mixture of picramic acid and an added acid in the presence of a triphenylmethane dye [7]. His significant contribution lay in the addition of additive as crystal growth control ingredient. However, the average dimension of tabular DDNP was only 60 μm. DDNP manufactured by adding hydrochloric acid and sodium nitrite into sodium picramate at the same time was poor compression resistance in the form of petal shaped glomerocrysts [5]. It seems that those traditional methods cannot provide DDNP with desirable properties. Moreover, preparation of DDNP by those traditional methods suffers from main drawbacks like, (a) producing a large amount of waste water, (b) difficulty of charge caused by poor flowability and low density, and (c) dead pressed phenomenon or occasion explosion caused by low compression resistance. Therefore, these disadvantages of DDNP limit its further application.

In order to solve these problems mentioned above, it is not strange to take an intensive study on the synthesis of DDNP. It is considered that sphericized technology should be a better choice. Moreover, crystal obtained by sphericized technology not only increases its flowability and density but also modifies its properties [8]. Reduced-sensitivity RDX with spherical morphology was obtained by sphericized technology [9,10]. Likewise, it implies that spherical DDNP may be prepared by this technology. However, detailed information about synthesis of spherical DDNP is not readily available in open literature. Therefore, we try our best to prepare spherical DDNP in order to obtain desirable DDNP.

In this work, spherical DDNP with average size of 350 μm was synthesized by modified method. The synthesis was carried out by treatment of picric acid with sodium sulfide solution to obtain sodium picramate followed by its diazotization with sodium nitrite,

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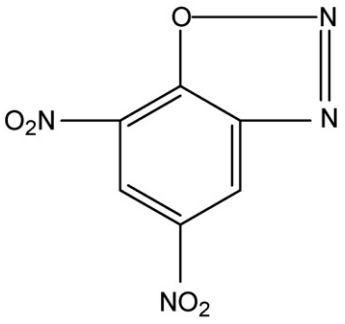

Fig. 1. Structure of DDNP.

hydrochloric acid and 4-methylphenol as crystal control ingredient. The spherical DDNP prepared by this process is desirable to have good flowability and higher bulk density as well as preferable performances. The paper also discusses characterization of spherical DDNP. In short, the highlights of this study are as follows: (a) using 4-methylphenol as additive, (b) adopting single feeding hydrochloric acid with multiholes, (c) recycling use of waste water, and (d) improving quality and properties of DDNP.

2. Experimental

2.1. Materials

4-Methylphenol (AR grade) was obtained from Nanjing long yan Chemical Industry Co., Ltd. The other chemicals and reagents used in the present study were purchased from trade without further purification.

2.2. Synthesis

2.2.1. Synthesis of traditional DDNP

Traditional DDNP with brown yellow color is synthesized by the reported method [5]. DDNP prepared by this process, having a bulk density of 0.45–0.60 g/cm^3 and an average particle size of 150 μm, is poor free flowing in the form of loose petal shaped glomerocryst. Further, the yield of DDNP obtained by this manufacture is about 60% (based on picric acid) together with 200–300 kg of waste water per kilogram DDNP. Moreover, its compression resistance is less than 25 MPa with dead pressed phenomenon or hazards of occasional explosions.

2.2.2. Synthesis of spherical DDNP

The synthesis of spherical DDNP involves two steps.

2.2.2.1. Synthesis of sodium picramate. 400 kg of water and 45 kg of picric acid (containing 20% water) were added to an 800 L steel neutralization reactor fitted with a stirrer, a thermometer and water condenser, then the suspension was stirred. After mixture was heated up to 60 °C, about 50–55 kg of 12.7% sodium sulfide solution was added to the suspension of picric acid by constant flow pump. During the addition, the temperature of reaction mixture was maintained at 60 °C. When the color of reaction solution changed from yellow to red and pH value of reaction solution was 8–9, addition was then stopped. The reaction mixture was filtered to remove foreign material such as sulfur, and the dark red solution of sodium picrate was obtained.

The solution of sodium picrate was added to reduction reactor, and agitator was started. The solution of sodium picrate was warmed up to 50 °C. 160–165 kg of 12.7% sodium sulfide solution was added with multiholes by constant flow pump within 35 min. The temperature was kept at about 50–55 °C during the reduction. After completion of addition of the sodium sulfide solution, agitation was continued for another 5 min at the same temperature. The reaction mixture was cooled to room temperature and filtered, and the precipitate was washed with water to get jujube red color and wedge shaped crystals of sodium picramate, in a yield of about 36 kg (dry basis). Finally, the basic mother liquor was equally divided into two portions, which can be used as a partial reaction liquid of next two batches for synthesizing sodium picramate again, respectively.

2.2.2.2. Synthesis of spherical DDNP. 11 kg of sodium nitrite was added to the stirred suspension of 36 kg of sodium picramate in 170 kg of water in the diazotization reactor. Immediately upon the dissolution of sodium nitrite, 60 g of 4-methylphenol dissolved in 200 g of 20% sodium hydroxide solution was also added into above reaction mixture. About 120 kg solution of 8.2% hydrochloric acid was added at a uniform rate through circular arc with lots of diameters of 3 mm multiholes by constant flow pump over a period of 60 min. During diazotization, the temperature was maintained at 30–33 °C. After completion of addition of hydrochloric acid, the reaction mixture was continuously stirred at 30–33 °C for 5 min. Agitation was then stopped, and the precipitate was allowed to settle. The precipitate was filtered off without further wash with water, and was dried to give 24 kg of desired spherical DDNP having good flowability and a bulk density of 0.86 g/cm^3 as well as a yield of 67% (based on picric acid). Moreover, acid waste water also can be used again as above. As a result, the amount of waste water for three batches with circulation use of waste water was equivalent to that of two batches without circulation use of waste water, and the total waste water of per kilogram DDNP was about 30–50 kg.

The compound has been manufactured in factory scale and applied to detonator charge. Spherical DDNP with controlled bulk density of 0.65–0.95 g/cm^3 was obtained in the yield of 65–70% by changing crystal control ingredients at the mass range of 60–126 g and altering feeding time in the time range of 60–85 min.

2.3. General methods

The crystal morphologies were examined by LE0438VP scanning electron microscope (SEM) instrument (Britain) at 12 kV and 10 μA. A laser sizer instrument (LS230, USA) was employed for particle size distribution study. The structural features of spherical DDNP were confirmed by 8400S (Japan) infra red spectrophotometer (IR), using KBr pellets. The purity of the DDNP was determined by LC3000 high performance liquid chromatography (HPLC) with C18 column, and mobile phase consists of methanol–water (50:50) at a flow rate of 1 μL/min with UV detector at 254 nm [11]. Bulk density of the DDNP was measured by following standard procedure: measuring of volume of given mass sample. The X-ray diffraction (XRD) analysis was carried out on Rigaku (Japan) diffractometer, using Cu Kα radiation at 40 kV and 100 μA. The compression resistance of spherical DDNP was tested by extent of damage on lead plate witness. Spherical DDNP was placed into detonator no. 8 (350 mg of RDX as main charge and 250 mg of RDX as secondary charge were pressed at 70 and 40 MPa, respectively.) and pressed at various pressures with dwell time of 45 s, then the detonator with spherical DDNP was held vertically on a 5 mm lead plate and initiated by fuse. The diameter of hole punched on the lead plate was measured to assess its compression resistance [12]. Minimum detonating charge of spherical DDNP was tested by similar method, and different masses of spherical DDNP samples were filled into detonator no. 8 and pressed at 10 MPa. The evaluation was carried out as above, and traditional DDNP was used as a reference. The differential scanning calorimeter (DSC) analysis was recorded on a Netzsch DSC 204 (Germany) instrument by heating 0.625 ± 0.005 mg of spherical DDNP sample at a rate of 5, 10, and 15 °C/min in nitrogen (50 mL/min) atmo-

Fig. 2. SEM images of sodium picramate samples. (a) Prepared by modified method and (b) prepared by traditional method.

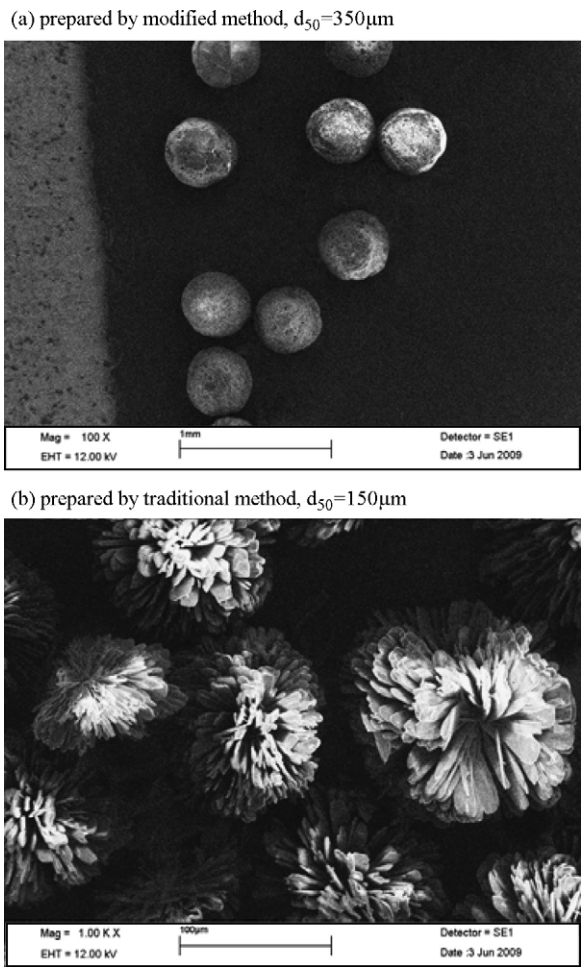

Fig. 3. SEM images of DDNP samples. (a) Prepared by modified method, d_{50} = 350 μm and (b) prepared by traditional method, d_{50} = 150 μm.

sphere. A CGY-1 impact instrument was used to test the impact sensitivity of DDNP, and each sample (20 mg) was tested 35 times to obtain a H_{50} (height for 50% probability of explosion) with 500 g drop weight [13].

3. Results and discussions

3.1. SEM of sodium picramate studies

The morphologies of two kinds of sodium picramate samples are shown in Fig. 2. The sodium picramate prepared by modified method (Fig. 2(a)) has cuneiform crystal morphology with smooth particle surfaces. SEM image of Fig. 2(b) shows that sodium picramate synthesized by traditional method yields fine needle shaped particles with loose agglomerates. As we know, sodium picramate is very important intermediate for preparing DDNP, and its morphology and particle size can directly affect the quality of DDNP. Further, lots of experiments indicated that cuneiform sodium picramate is more favorable to the diazotization than needle shaped sodium picramate. It can be explained that the latter dissolves faster in comparison with the former during diazotization reaction. As a result, the speed of reaction is difficult to be controlled.

3.2. Infra red spectrum studies

The IR spectrum of spherical DDNP showed absorption bands and other characteristics group frequencies. The band at 3103, 3068 and 1639 cm^{-1} correspond to –CH and C=C stretching frequencies. The characteristic strong absorption of diazo group (N=N) is observed at 2200 cm^{-1}. The two intense absorptions at 1558 and 1419 cm^{-1} reveal the characteristic frequencies for asymmetric and symmetric vibrations due to NO_2 groups [14]. The absorption assignable to benzene ring appears at range of 1700–1900 cm^{-1}. The other vibrations observed in IR spectrum at 1159, 908 and 775 cm^{-1} may attribute to diazo ring frequencies. Therefore, the structural features of spherical DDNP are confirmed by IR spectroscopy.

3.3. SEM of DDNP studies

The SEM images of spherical DDNP and traditional DDNP are shown in Fig. 3(a) and (b), respectively. The differences in morphology between the two kinds of DDNP samples are obvious. The DDNP synthesized by modified method has spherical type crystal morphology with smooth and integrated particle surfaces. Whereas the DDNP obtained by traditional method presents unregulated petal shaped glomerocryst microstructure with very coarse surfaces and exterior defects. The average particle sizes of spherical DDNP and traditional DDNP are 350 and 150 μm, respectively. During the work, it was found that the inner of spherical DDNP comprises a large number of fine petal shaped DDNP crystals, radiating distribution from inner to outer. It can be inferred that these fine petal shaped DDNP crystals are aggregated closely with newly formed fine DDNP minicrystals as particle crystal nucleus by the agglutination effect of 4-methylphenol, and they grow radially from inner

Table 1
Compression resistance data for spherical DDNP and traditional DDNP.

Samples	Bulk density (g/cm^3)	Pressure (MPa)	Number of initiation	Number of non-initiation	Probability of explosion (%)	Pore sizes of lead plate (mm)
Spherical DDNP	0.86	20	200	0	100.0	9.3–10.6
		30	200	0	100.0	9.4–10.8
		40	200	0	100.0	9.3–10.8
		50	200	50	75.0	9.2–10.6
Traditional DDNP	0.58	20	200	0	100.0	9.1–10.3
		30	200	48	76.0	9.2–10.5
		40	200	137	31.5	9.2–10.4
		50	200	200	0	0

Table 2
Minimum detonating charge results for spherical DDNP and traditional DDNP.

Samples	Bulk density (g/cm^3)	Charge mass (g)	Number of initiation	Number of non-initiation	Probability of explosion (%)	Pore sizes of lead plate (mm)
Spherical DDNP	0.86	0.10	200	60	70.0	9.4–10.2
		0.15	200	0	100.0	9.4–10.5
		0.20	200	0	100.0	9.5–10.7
Traditional DDNP	0.58	0.10	200	200	0	0
		0.15	200	105	47.5	9.2–9.8
		0.20	200	0	100.0	9.3–10.5

during diazotization. This trend corresponds with classical growth way of spherical particle [15,16]. Moreover, experiments also showed that spherical DDNP becomes more compact and rounder as 4-methylphenol increases, i.e. the bulk density and flowability of spherical DDNP increase with increasing 4-methylphenol, but the particle size decreases. In addition, 4-methylphenol can play as protective film to prevent foreign substance from entering spherical DDNP so as to increase purity.

3.4. X-ray studies

Fig. 4 reveals the peak intensity of XRD patterns for spherical DDNP and traditional DDNP as a function of the diffraction angle (2θ). It indicates that the peaks of spherical DDNP have the similar diffraction angles as those of traditional DDNP, implying that spherical DDNP has the same crystal phase (DDNP belongs to the orthorhombic space group [17]) as traditional DDNP. Further, the peak intensities of spherical DDNP are obviously stronger than those of traditional DDNP at the similar position, but the full widths at half maximum (FWHM) of peaks are slightly smaller than those of traditional DDNP at corresponding position. For example, the peak (2θ = 24.398) with FWHM of 0.212 in XRD pattern of spherical DDNP has an intensity of 23,516, while for traditional DDNP, the peak with FWHM of 0.276 has an intensity of only 16,474. On the one hand, traditional DDNP has coarse and unregulated crystal faces, making the probability of getting incident light equal, but spherical DDNP has smooth integrated surfaces, uniform particle distribution and compact texture, only certain crystal faces has higher probability for getting incident light [18]. On the other hand, traditional DDNP has many petal-like glomerocrysts and twinned crystals, and this polycrystalline structure leads to the divergence and extinction of incident light with the result that the peak intensity of XRD decreases with increasing FWHM of peaks [19,20]. Therefore, we can draw a conclusion that spherical DDNP has less crystal defects inside particles than traditional DDNP from the results of XRD patterns.

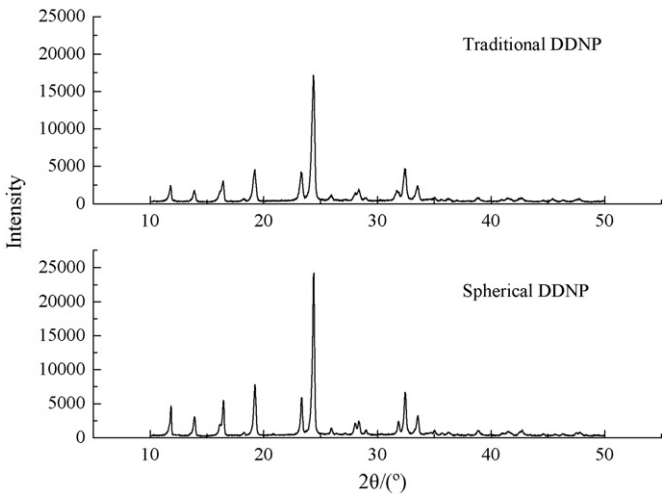

Fig. 4. XRD patterns of traditional DDNP and spherical DDNP.

3.5. Performance test studies

Spherical DDNP with bulk density of 0.86 g/cm^3 was pressed in detonator no. 8 to test its compression resistance by the diameter of hole punched on lead plate, and the results are shown in Table 1. The compression resistance of spherical DDNP can reach up to 40 MPa, while for traditional DDNP it is about 20 MPa. Further, there are no hazards of occasional explosions and dead pressed phenomena for spherical DDNP. The compression resistance of spherical DDNP is substantially increased by modified method. It can be explained that spherical DDNP with smooth surfaces and good flowability becomes very firm and elastic in contrast to traditional DDNP, avoiding dead pressed phenomenon.

Similarly, spherical DDNP with different masses was pressed in detonator no. 8 to test its minimum detonating charge. The results are presented in Table 2. The minimum detonating charges of spherical DDNP and traditional DDNP for RDX are 0.15 and 0.20 g, respectively. It indicated that the ability of spherical DDNP to initiate the detonation of RDX is stronger than that of traditional DDNP. Because spherical DDNP has high purity (>98.52%) and no dead pressed phenomenon. These advantageous factors can facilitate heat penetration into particles and shorten the time of detonation growth, finally detonator can be initiated thoroughly [21].

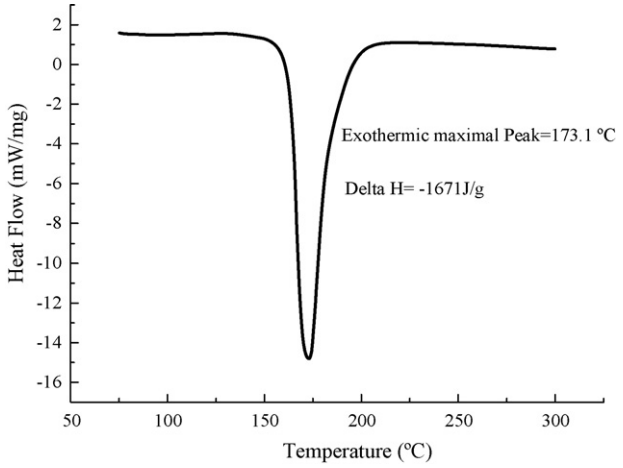

Fig. 5. DSC profile of spherical DDNP.

Table 3
Impact sensitivity data for spherical DDNP and traditional DDNP.

Samples	Impact sensitivity (H_{50}, cm)
Spherical DDNP	25.3
Traditional DDNP	18.6

3.6. DSC curve studies

The DSC curve of spherical DDNP is depicted in Fig. 5. In DSC, spherical DDNP only has a narrow and sharp exothermic peak, suggesting that it can directly decompose from solid to gas without melting. For spherical DDNP, the exothermic decomposing appears in the temperature range of 161.2–188.5 °C with peak decomposition temperature (T_{max}) at 173.1 °C and heat output of 1671 J/g at heating rate of 10 °C/min. Similarly, the T_{max} of spherical DDNP at heat rates of 5, 15 °C/min were 167.7 and 180.5 °C with heat output of 1597 and 1713 J/g, respectively. Moreover, the activation energy of spherical DDNP has been calculated by Kissinger method [22], and is found to be 179 kJ/mol. In a word, DDNP has a lower thermal decomposition temperature in contrast to lead styphnate, but it has an excellent thermal stability for long term storage at temperature below 60 °C [23].

3.7. Sensitivity test studies

Spherical DDNP and traditional DDNP were subjected to impact sensitivity test. The results of impact sensitivity test are given in Table 3. The impact sensitivity of spherical DDNP and traditional DDNP are 25.3 and 18.6 cm, respectively. It showed that spherical DDNP has lower impact sensitivity in contrast with traditional DDNP. According to the hot spot growth mechanism [24], spherical DDNP has smooth surfaces and few crystal defects, which can efficiently decrease the number of hot spots. Moreover, there are plenty of tiny air holes among the spherical DDNP particles, which can cushion a blow from the impact stimuli [25]. Hence, it is difficult for hot spots to grow owing to these unique characteristics, and spherical DDNP presents the lower impact sensitivity.

4. Conclusions

The modified method for the synthesis of spherical DDNP in good free flowing form with high bulk density has been established on factory scale by adopting 4-methylphenol as crystal growth control ingredient. Results showed that the modified method is an efficient preparation method for spherical DDNP. It not only increases the yield of spherical DDNP and improves the quality of spherical DDNP but also decreases waste water. The HPLC, SEM and XRD analysis indicated that spherical DDNP with high purity (>98.52%) and smooth surfaces has an average particle size of 350 μm and contact texture as well as few defects. Performance tests revealed that spherical DDNP has higher compression resistance (over 40 MPa) and higher initiating ability compared with traditional DDNP. DSC curve of spherical DDNP depicted exothermic decomposing at the temperature range of 161.2–188.5 °C (T_{max} = 173.1 °C). Impact sensitivity test also indicated that spherical DDNP is more insensitive to impact stimuli than traditional DDNP. In conclusion, those problems mentioned above are successfully solved by modified method for synthesizing desired spherical DDNP.

The advantages of the method used in this study in comparison to reported methods are such as (a) simple operation of preparation process and easy of reaction conditions control, (b) intermediate sodium picramate with desired morphology and particle size in favor of the diazotization, (c) product DDNP with spherical type crystal morphology and larger particle size but without dust of DDNP microcrystalline, which is particularly easy of charge, (d) remarkable increase in compression resistance of product without dead pressed phenomenon or occasion explosion, and (e) larger decrease in waste water due to circulation use of waste water, reducing the cost of effluent disposal.

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