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Experimental Study on Charging Conditions of a Single Component DDT Detonator Using Nickel Hydrazine Nitrate

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Abstract

As a salt of a coordination compound of nickel, nickel hydrazine nitrate (NHN) is an energetic substance with characteristics halfway between those of primary and secondary explosives. It is less sensitive to friction and mechanical impact than other primary explosives, although it is highly sensitive to flames. NHN is not very dangerous to handle, but it explodes readily when exposed to flame. This property makes it possible to fabricate safety detonators with high detonation reliability and detonation capacity. NHN was synthesized by reacting solution of $Ni(NO_3)_2 \cdot 6H_2O$ *and* $N_2H_4 \cdot H_2O$ *and structural analyses performed by Fourier-transform infrared spectroscopy. Single component-detonator using NHN consists of detonator body, reinforcing plug, secondary charge, and primary charge. A rational way to avoid the deformation and destruction of the paper tube from moisture is to use a low-cost and moisture proof tube, so detonator body was made of polyethylene tube. Both primary and secondary charges are prepared using only NHN, which can cause accidents in charging process. The stability of the charging process can be ensured by NHN whose moisture is about 10%, and which is treated with 3% PVA solution. The effect of charging density and charging quantity on the primary and secondary charges in the optimum detonator structure determined through several experiments was investigated. The charging conditions of DDT detonator (deflagration to detonation transition detonator) using nickel nitrate hydrazine were determined. The priming ability of DDT detonator was evaluated by the penetration test using 5 mm lead plate.*

Keywords: Nickel hydrazine nitrate, detonator, deflagration to detonation transition, polyethylene, lead plate

INTRODUCTION

The age of lead-based primary explosives began in the early 1900s when lead azide (LA) and lead styphnate (LS) were found to be effective alternatives to mercury fulminate (MF), which was discovered in 1628 [1–3].

Due to their relative affordability, dependability, and effectiveness, lead-based primary explosives – lead styphnate and lead azide – remain the most utilized in industrial initiating explosive devices (IEDs) such as primers and detonators.

Azide is widely utilized in demolition charges and missile warheads for both military and civilian uses since it always burns to detonation, unless there are extremely rare circumstances.

However, lead has a cumulative effect on both the environment and humans, and azides are more hazardous than cyanide.

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Therefore, the search for new lead-free primary explosives for use in rockets, satellites, weaponry, mining, and tunneling is fueled by increased worries about lead pollution [4].

Furthermore, synthesis, processing, storage, and transportation of lead-based initiators are exceedingly dangerous due to their susceptibility to detonation from a variety of unintentional inputs. Nickel hydrazine nitrate (chemical formula: $[Ni(N_2H_4)_3]\ (NO_3)_2$) have attracted great attention because some properties of NHN are much better than that of lead azid [5–9].

Although NHN is relatively dull to an impact, friction and electrostatic sensitivity compared to other primary explosives, flame sensitivity is equivalent to lead styphnate and is more environmentally friendly.

Secondary explosives are relatively insensitive to external stimulus such as flame, heat, impact, friction, electric spark, etc.

However, when a little quantity of a main explosive (such as MF, LA, LS, SA (silver azide), and tetrazene) meets it, it can produce an explosive shock that causes them to burst with more force.

Therefore, a detonator and often a booster are needed for secondary high explosives, and industrial detonators typically include both primary and secondary explosives. While shock waves cause secondary explosives to detonate, burning causes primary explosives to do so.

One significant distinction between main and secondary explosives is this. Nickel Hydrazine Nitrate is a high-energy coordination compound explosive, and the sensitivity and explosive performance takes in the middle of primary and secondary explosives.

Usually compounds which easily explode when ignited are also mechanically sensitive to detonation, but NHN is that it is supposedly somewhat less sensitive to mechanical impact than RDX.

In particular, RDX only burns when ignited, while NHN will undergo the DDT (Deflagration to Detonation Transition) in a metal shell. In contrast, NHN still readily explodes when ignited with flames.

In combustion theory, the process by which a high-speed deflagration turns into a detonation (known as the Deflagration to Detonation Transition, or DDT) is still a very challenging issue.

Deflagrations, shocks and shock reflections, boundary layers, and all their interactions with one another make up the unsolved problem of DDT [10–12].

Experiments have not yet revealed the precise mechanism of DDT, but NHN in a steel cylindrical capsule can travel through the process faster and farther than RDX.

Therefore, NHN is regarded as most powerful energetic coordination compound, which can replace primary explosive, such as lead azide, and keep the output of secondary explosive such as RDX.

RDX may generate a high amount of waste acid due to the use of concentrated nitric acid during manufacture, so the waste acid treatment process is costly and involves serious environmental pollution problems.

Due to this fact, NHN is a relatively safe, reliable and environmentally friendly explosive capable of manufacturing an industrial detonator without using any other high-energy materials.

In this article, a report is presented on the structure of DDT detonator using NHN as a single component and the results of testing charging condition–charging quantity and density.

EXPERIMENTAL

Materials

Nickel hydrazine nitrate can be synthesized by reacting nickel (II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) and hydrazine monohydrate ($N_2H_4 \cdot H_2O$).

All chemicals used in this experiment were reagent grade, these purchased from Shanghai Chemical Reagent Company and deionized water was used.

NHN was obtained in 95% yield under certain conditions, i.e., reaction temperature, agitation rate, addition mode, etc., and were fully dried in a constant temperature drying oven (202-00AB) prior to use.

IR spectra were recorded in absorbance mode by using a Nicolet 6700 Fourier-transform infrared (FTIR) spectrophotometer.

The Fourier transform infrared (FTIR) spectrum of NHN is shown in Figure 1, were obtained with 32 scan summations at 4cm^{-1} resolution.

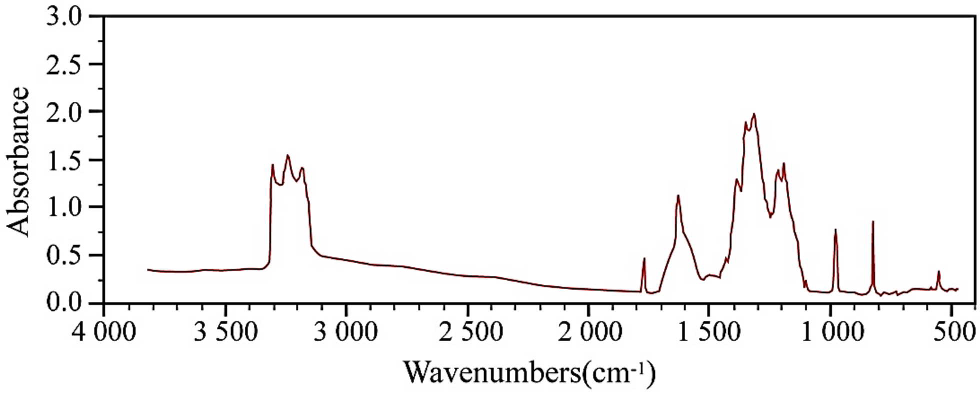


Figure 1. IR spectra of NHN.

The IR peaks in the range of 3 320~3 100 cm^{-1} and a band at 1 626 cm^{-1} was attributed to the stretching vibration and degenerate distortion of N–H group, respectively.

The bands at 1356 cm^{-1} and 1321 cm^{-1} can be attributed to the strong stretching vibrations of intercalated anions (NO_3^-).

A band at 976 cm^{-1} can be assigned to the stretching vibrational mode of hydrazine ligands. The absorption peak at 550 cm^{-1} is ascribed to the Ni–N stretching modes.

The Fourier transform infrared (FTIR) spectrum result indicates that the product mainly consists of NHN.

And then, the characteristic peak at about 1763 cm^{-1} is due to the absorption of water molecules.

Moisture content in NHN product was estimated as mass loss after drying it at 333 K in an OHAUS MB45 humidity analyzer and a measurement result of 0.41% was obtained.

The crystal density of NHN was measured by specific gravity method using absolute alcohol and result of the crystal density measurement is 2.12 g/cm^3.

The apparent density was measured in the following experimental apparatus (Figure 2).

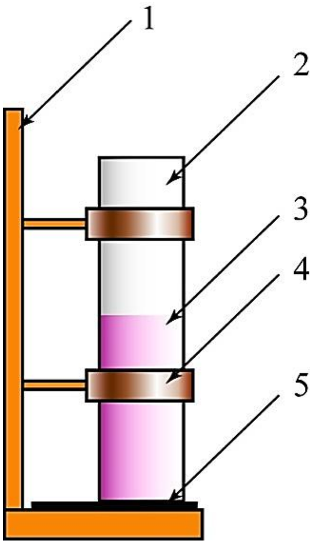


Figure 2. Apparent density measurement apparatus.

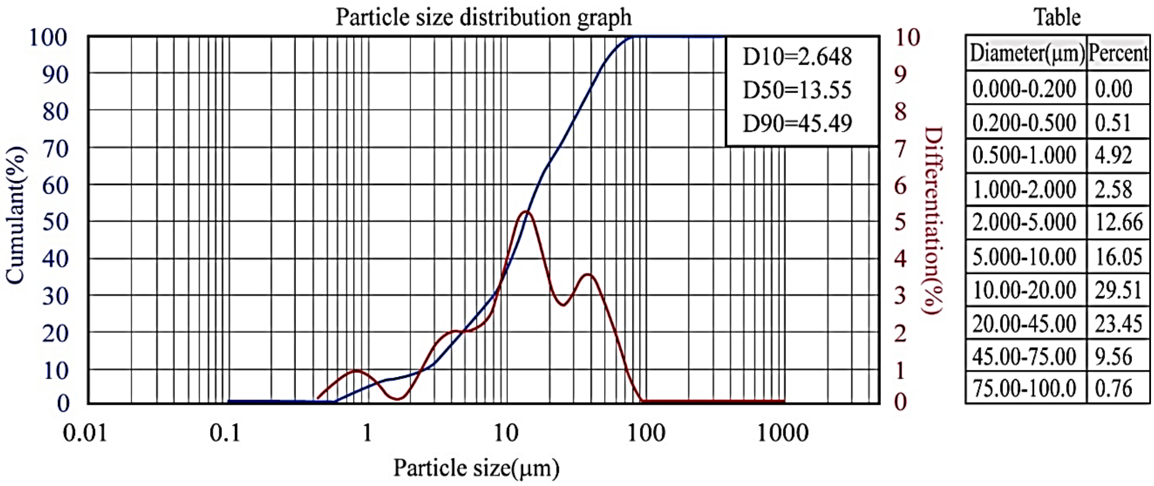
(1-Supporting rod, 2-Test tube, 3-Sample, 4-Supporting ring, 5-Rubber plate)

Put the sample in a test tube of known weight and weigh 10 g with accuracy of 0.0002 g. The test tube was installed in the measurement apparatus and dropped 30 times at 10 mm height.

The height of the sample in the test tube was indicated, and sample was taken out from the test tube. And then filled with distilled water to the marked mark, and weighed with an accuracy of 0.0002 g.

The density of the sample measured using the volume of water and weight of sample was 0.92 g/cm^3.

Particle size was measured using Laser Particle Size Analyzer (Bettersizer SE) and Bettersizer SE particle size analysis report is given in Figure 3.



Diameter(μm)	Percent
0.000-0.200	0.00
0.200-0.500	0.51
0.500-1.000	4.92
1.000-2.000	2.58
2.000-5.000	12.66
5.000-10.00	16.05
10.00-20.00	29.51
20.00-45.00	23.45
45.00-75.00	9.56
75.00-100.0	0.76

Figure 3. Particle size analysis report.

Safety issues of detonators are all raised in the process of manufacturing, storage and handling of primers, but the highest incidence is in the charging process.

External stimuli are delivered to the detonator and the charge since the priming process includes the compression of the charge and the assembling of the components.

With a far lower sensitivity to shock and friction (16.0 N) than LA (0.1 N), NHN is a rather safe explosive to operate with. This makes it an ideal fuel to charge NHN to the detonator.

In particular, when NHN has a certain quantity of moisture, its impact sensitivity is low. NHN is described as “hydrolytically stable”, which means that it is not vulnerable to moisture.

Hence, NHN is safer if it contains about 10% moisture, thus using NHN containing about 10% moisture in the charging process. From the thermal data, safety and explosion characteristic data, it is clear that NHN is sensitive to heat, forms large volumes of high-pressure gas, and can cause detonation under sealed conditions.

The detonation velocity and detonation pressure of NHN can reach the level of RDX charged to the detonator when the charging density is adjusted.

Because of this characteristic, NHN can be used solely in detonators to replace lead azide as a primary, RDX as a secondary explosive.

Deflagration to detonation transition occurs at a certain amount of NHN in the compressed charging section and detonation amplification also occurs in the NHN charge part loaded at a certain density.

The evaluation of detonator’s reliability is carried out by lead plate penetration test. The single component DDT-detonator using NHN is of great value because of its simplicity in composition and manufacturing method, its environment friendly and relatively high safety.

STRUCTURE AND MANUFACTURING METHOD

The optimum structural parameters of the detonator were determined through a number of experiments that considered the influence of factors on the priming ability of detonator and convenience of manufacturing process.

The influence factors affecting on priming ability of detonator are thickness and internal diameter of the detonator body, the strength and length of the reinforcing plug, the diameter of the hole, the charging density, and the charging quantity, etc.

The detonator body increases the utilization of chemical reaction energy by preventing the interference of lateral rarefaction waves.

The relatively thin thickness of detonator body will result in a long growth length of the DDT (deflagration to detonation transition), and an incomplete detonation.

As the strength of the detonator body increases, the strength of the reflected shock wave at the detonator body wall increases and the action of the rarefaction wave decreases, so that the detonation velocity increases due to the increased detonation energy transferred to the unreacted zone.

With the increase of the thickness of the detonator body made of polyethylene cylindrical tube, the detonation velocity gradually increases to the maximum detonation velocity, and does not increase significantly above 0.5 mm thickness of the detonator body.

The internal diameter of the detonator body should be determined considering the critical diameter and the limiting diameter of NHN.

When the internal diameter of the detonator body increases from the critical diameter to the limiting diameter, the detonation velocity increases gradually, and when the diameter of the detonator body exceeds the limiting diameter, the detonation velocity no longer increases and reaches the maximum detonation velocity.

By full experiments, it was concluded that the limiting diameter of NHN was between 6 and 7 mm.

The thickness of the detonator body and internal diameter was determined 1 mm and 7 mm respectively in consideration of the strength and cost of the detonator body.

The reinforcing plug reduces the impact sensitivity of the detonator, accelerates the detonation growth rate of the detonator, reduces the limiting charging quantity, and prevents the NHN from leaking when the detonator is subjected to vibration.

The length of the reinforcing plug is important to accelerate the DDT and to ensure the strength of the detonation wave.

The reinforcing plug was made of 0.7 mm thick steel sheet in consideration of cost, and the lead plate penetration diameter increased with increasing the length of the reinforcing plug, but no further increase was observed above 13 mm.

Thus, the length of the reinforcing plug above 13 mm indicates that the DDT is fully completed and the condition for steady detonation is sufficient.

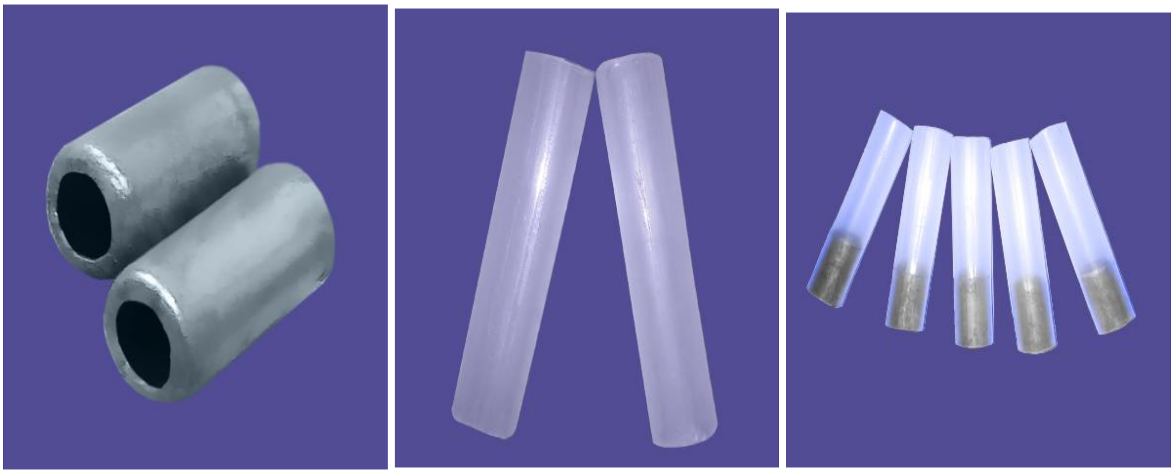
Hence, the length of the reinforcing plug was determined 13 mm.

The increase of inlet diameter in the reinforcing plug leads to decrease in priming ability due to the loss of the combustion products and combustion pressure.

However, if the inlet diameter is too small, the flame transmission by the blasting fuse may be poor.

When the inlet diameter is greater than 3.5 mm, the lead plate penetration diameter begins to decrease, so the inlet diameter was chosen 3.5 mm.

The reinforcing plug, detonator body, assembled detonator body is shown in the following Figure 4.



a) b) c)

Figure 4. Particle size analysis report (a) Reinforcing plug, (b) Detonator body, (c) Assembled detonator body.

The structure of a single component DDT-detonator using NHN is shown in Figure 5.

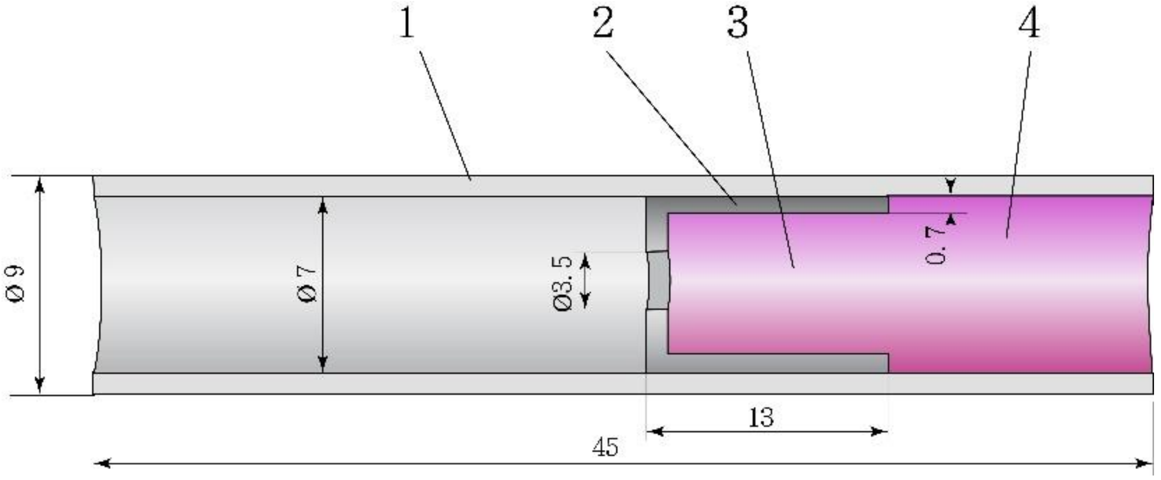


Figure 5. The structure of a single component DDT detonator using NHN (1-Detonator body, 2-Reinforcing plug, 3-Secondary charge, 4-Primary charge).

The single component DDT-detonator using NHN is largely composed of reinforcing plug, detonator body, primary charge and secondary charge.

The manufacturing process of detonator consists of preparation of charge, preparation of detonator body, charging process, drying process, examining process and packing process.

Preparation of Charge

NHN was treated with 3% PVA solution and NHN contained about 10% moisture in this case.

Preparation of Detonator Body

A reinforcing plug was assembled to the tube body.

Charging Process

The charging process is divided into two stages. First, the NHN treated with PVA was pressed to a given density and then, NHN and the reinforcing plug put into the detonator body and pressed to a given density.

Drying Process

The prepared detonator shall be dried sufficiently at 50–60°C for over 3 hours.

Examining Process

Priming ability of DDT-detonator is checked by lead plate penetration test (Figure 6).

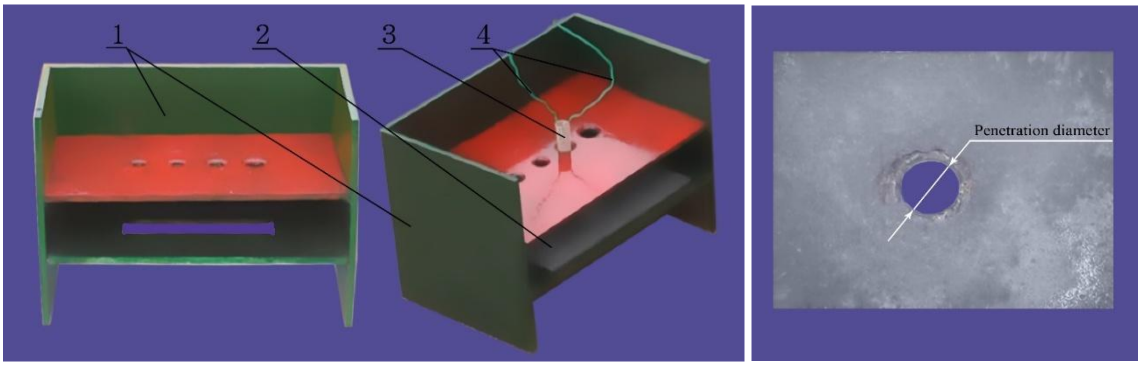


Figure 6. Lead plate penetration test (1-Lead plate penetration test tool, 2-Lead plate, 3-detonator, 4-Electric igniter).

DDT occurs in the secondary charge portion of NHN, where the detonation waves formed detonates the primary charge.

Thickness of lead plates made of electric lead is 5 mm, and the penetration diameter shall be more than the diameter of detonator.

RESULTS AND DISCUSSIONS

Effect of Primary Charge Parameters

In the test, NHN was pressed and charged in place of hexogen, an explosive, in the industrial detonator, which is currently in use, and penetration tests were carried out to determine the optimal NHN charge parameters.

Effect of Charging Density (Charging Quantity 1 g)

A higher charging density, the higher priming ability, but the charging condition becomes difficult, so the charging density must be properly.

Considering the practical condition that it is difficult to maintain the charging density of more than 1.5 g/cm^3 by using manual compression method, the charging density was determined below 1.5 g/cm^3.

The effect of the charging density of the primary charge on the penetration diameter of the lead plate is shown in Figure 7.

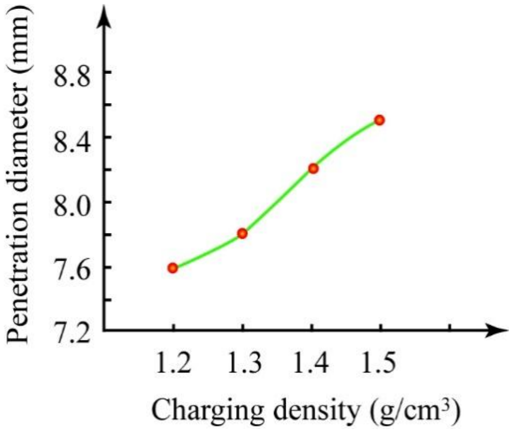


Figure 7. Penetration diameter depends on charging density of the primary charge.

The huge number of experimental and theoretical studies were performed about deflagration to detonation transition (DDT) [13–17], and DDT studies are essential to manufacture of DDT detonator.

Detonation velocity is defined as the velocity at which the chemical reaction zone propagates through a given explosive and is considered as one of the most important physical detonation parameters.

The detonation velocity is 7000 m/s under the condition of 1.7g/cm^3 charging density, and the higher the charging density, the higher the detonation velocity.

The detonation velocity increases as the charging density increases, and as a result the priming ability of DDT-detonator increases.

However, the sensitivity of charge decreases with increasing charging density, but the primary charge is sufficiently detonated by a strong shock wave.

In other words, the primary charge does not exhibit incomplete detonation even under high charge density conditions, and the higher the charging density, the larger the lead plate penetration diameter.

As shown in Figure 7, as the charging density increases, the penetration diameter also increases because the detonation velocity increases with increasing charging density.

As a consequence, it can be seen that the primary charge satisfies the characteristics of NHN as a secondary explosive in the detonator if the charging density of NHN is above 1.4 g/cm^3.

EFFECT OF CHARGING QUANTITY (CHARGING DENSITY 1.4 G/cm^3)

The lead plate penetration diameter according to the charging of the primary charge is shown in Figure 8.

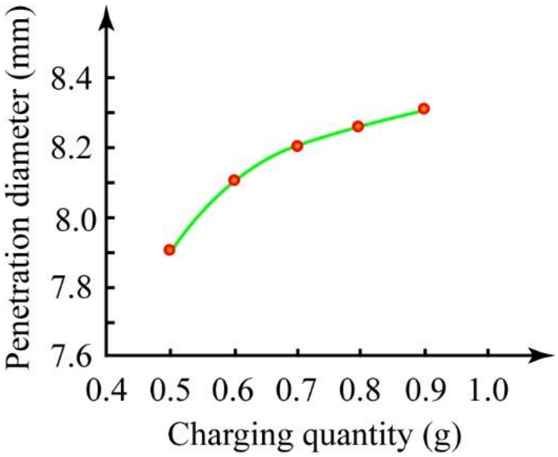


Figure 8. Penetration diameter depends on charging quantity of the primary charge.

As the charging quantity increases, the energy released from the primary charge increases gradually, and the lead plate penetration diameter increases gradually.

However, the DDT is sufficient under certain charging quantity conditions, and higher charging quantity has no significant effect on the lead plate penetration diameter.

Therefore, with the increase of charging quantity, the lead plate penetration diameter tends to a certain threshold value.

As shown in Figure 8, the lead plate penetration test is satisfactory when the charge is above 0.6 g. Therefore, the primary charge was 0.6 ± 0.02 g and the charging density was 1.4 ± 0.05 g/cm^3.

INFLUENCE OF SECONDARY CHARGE PARAMETERS

Under the given conditions, it is the effect of charge diameter and envelope that influence the minimum charge amount at which the deflagration to detonation transition occurs, and the charging density also has a decisive effect.

Depending on the charging density, the deflagration to detonation transition behavior is expressed quadratically, i.e., when the charging density increases to a certain value, the induced detonation distance decreases and then the induced detonation distance tends to increase again when the charging density increases further.

In the test, NHN is pressed (charging density 1.4 g/cm^3 and amount 0.6 g) for a primary charge. Also, NHN is charged for primary with reinforcing plug and penetrating test of lead plate is performed to determine the charge parameters.

EFFECT OF CHARGING DENSITY (CHARGING QUANTITY 0.5 G)

The variation of the lead plate penetration diameter with the charging density of the secondary charge is shown in Figure 9.

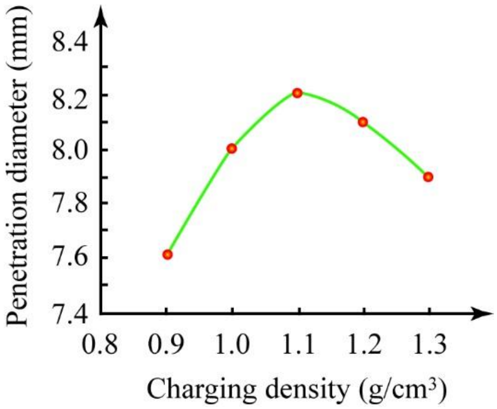


Figure 9. Penetration diameter depends on charging density of the secondary charge.

A major difference between primary charge and secondary charge arises from the fact that secondary charge is initiated to detonate by burning whereas primary charge is initiated to detonate by shock waves.

Therefore, the most important property of a secondary charge is its ability to undergo a fast deflagration to detonation transition (DDT). All other parameters are equal, the faster the DDT, the better the primary charges.

For DDT to occur, a certain degree of porosity must be provided in deflagrating material which means a large surface area of exposure.

When the charging density is increased to a certain extent, the energy separation is more than the energy loss, which is beneficial for DDT, but above a certain charging density, the porosity in which the flame can propagate decreases, and rather the high charging density negatively affects DDT.

Especially, if the charging density is too high, the detonation will not propagate.

As shown in Figure 9, with increasing charging density, the penetration diameter also increases and reduces again above 1.1 g/cm^3, which is related to the declining deflagration to detonation transition behavior with decreasing gas flow channel with increasing charging density.

Therefore, the optimum charging density of the secondary charge was 1.1 g/cm^3.

Effect of Charging Quantity (Charging Density 1.1 g/cm^3)

The variation of the lead plate penetration diameter with the quantity of the secondary charge is shown in Figure 10.

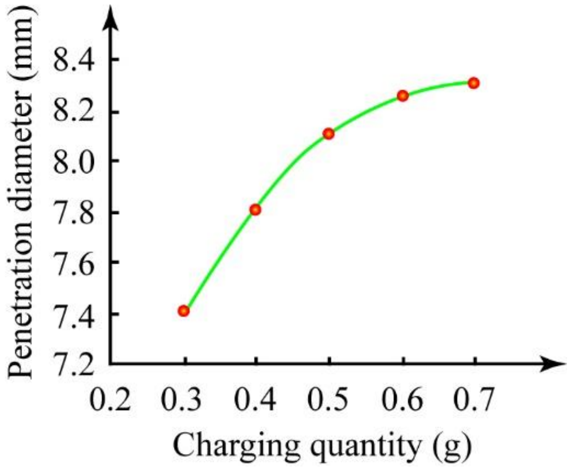


Figure 10. Penetration diameter depends on charging quantity of the secondary charge.

Primary charge is exploded with greater violence when set off by an explosion shock obtained by detonating a small amount of a secondary charge in contact with it.

As the charging quantity increases, a large amount of energy releases, which means that it sustains a steady-state detonation more easily.

Thus, penetration diameter depends on charging quantity of the secondary charge, and the secondary charge produces strong detonation with increasing charging quantity.

As shown in Figure 10, it can be seen that the lead plate penetration test is satisfactory when the charge is above 0.5 g.

Therefore, the second charge was 0.5 ± 0.02 g and the charging density was 1.1 ± 0.05 g/cm^3. This detonator is now widely used in many coal and ore mines for industrial blasting.

Its application prospects are increasing with each passing day due to its advantages such as low cost, easy and safe of manufacturing process, environmental protection, waterproofing and high operating reliability.

CONCLUSIONS

It was analyzed the influence of factors affecting the lead plate penetration diameter and determined the optimum manufacturing conditions, thus solving the key problem in the manufacturing of a single component DDT-Detonator for industrial blasting.

Research on thickness and internal diameter of the detonator body, the strength and length of the reinforcing plug, the diameter of the hole, etc. are regarded as the key factors in the optimization of charging density and charging quantity.

One of the important conditions for DDT to occur is a high degree of confinement experienced by the deflagrating material.

Therefore, the material and thickness of the reinforcing plug and detonator body were determined to have sufficient strength for DDT.

The material of the reinforcing plug and detonator body is steel and polyethylene, respectively, and the thickness is 0.7mm and 1.0mm, respectively. The length of the reinforcing plug and detonator body was determined to able ensure sufficient DDT length under the above mentioned conditions.

The length of the reinforcing plug and detonator body is 13 mm and 45 mm, respectively.

The diameter of the hole in the reinforcing plug has a very significant effect on the energy loss and confinement degree in the secondary charge.

The diameter of the hole was determined as 3.5 mm and diameter of detonator body is 7mm.

It is also characteristic that NHN was treated with 3% PVA solution and contained about 10% moisture in the preparation of charge.

The detonator proposed in this paper can achieve sufficient priming ability by using NHN as a single component without using primary and secondary explosive separately.

- Primary charge: 0.6 ± 0.02 g of charge and 1.4 ± 0.05 g/cm^3 of charging density.
- Secondary charge: 0.5 ± 0.02 g of charge and 1.1 ± 0.05 g/cm^3 of charging density.

From the test results, it can be seen that a single-component DDT-detonator prepared with the above-mentioned charging conditions using a polyethylene tube and a steel reinforcing plug can fully replace a LA-RDX industrial detonator.

Additionally, this would speed up the adoption and acceptance of the LA-RDX system detonator by requiring just minor changes to the manufacturing process.

Therefore, the charging process may be automated, the manufacturing process is straightforward, and the manufacturing cost is significantly decreased. In addition, it has the great advantage of environmental protection in that there is no lead in the composition.

Acknowledgments

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