The Research and Development of Primary Explosives in Chinese Industrial Detonators

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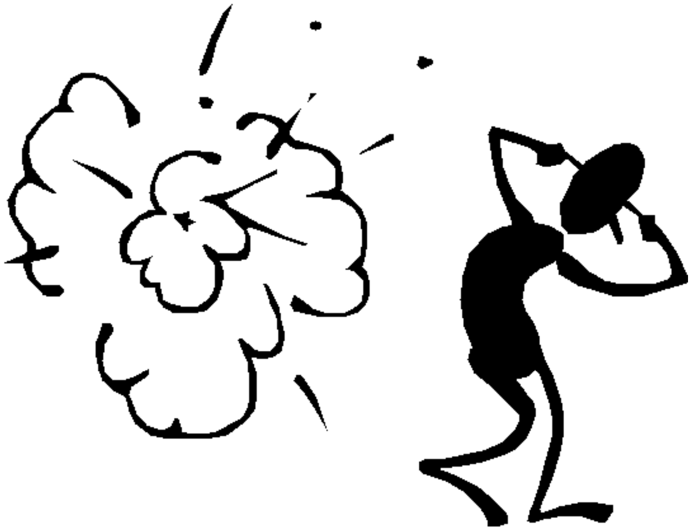
Contents

1 Introduction

- China is a rapidly developing country. Every year huge amounts of railways, highways and buildings are constructed and huge numbers of coal and ores are mined. All of these demand huge numbers of industrial explosives and industrial detonators. The amount consumed in 2009 is listed as below:
- Industrial explosive:
- 2.9 million tons
- Industrial detonator:
- 2.2 billion



- However the primary explosives are very sensitive and dangerous. Some accidents always occurred during the production of industrial detonator every year, which lead to irreparable damage. So a new safe and effective primary explosive is urgently needed in china.

2 The primary explosives in Chinese industrial detonators

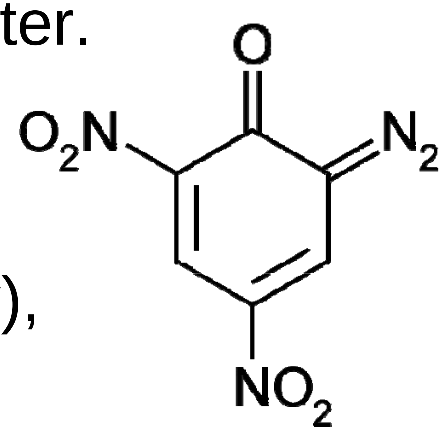
- Chinese industrial detonators can be divided into flame, electric and non-electric detonators, and the flame detonators has been eliminated.

electric blasting caps

non-electric blasting caps

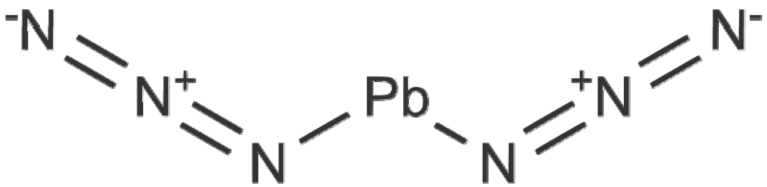
2.1 DDNP detonator

- The diazodinitrophenol (DDNP) was synthesized by Griess in 1858, it was fist used as dyestuff, and its explosion propriety was found in later.
- DDNP can directly initiate the RDX, it has good security (low impact and frication sensitivity), and it is widely applied in Chinese industrial detonators. But, in the producing process, a great deal of wastewater (200L/Kg) which pollute the environment will be produced, secondly, the pressure durability of DDNP is bad(<20Mp).



2.2 Lead azide (LA) detonator

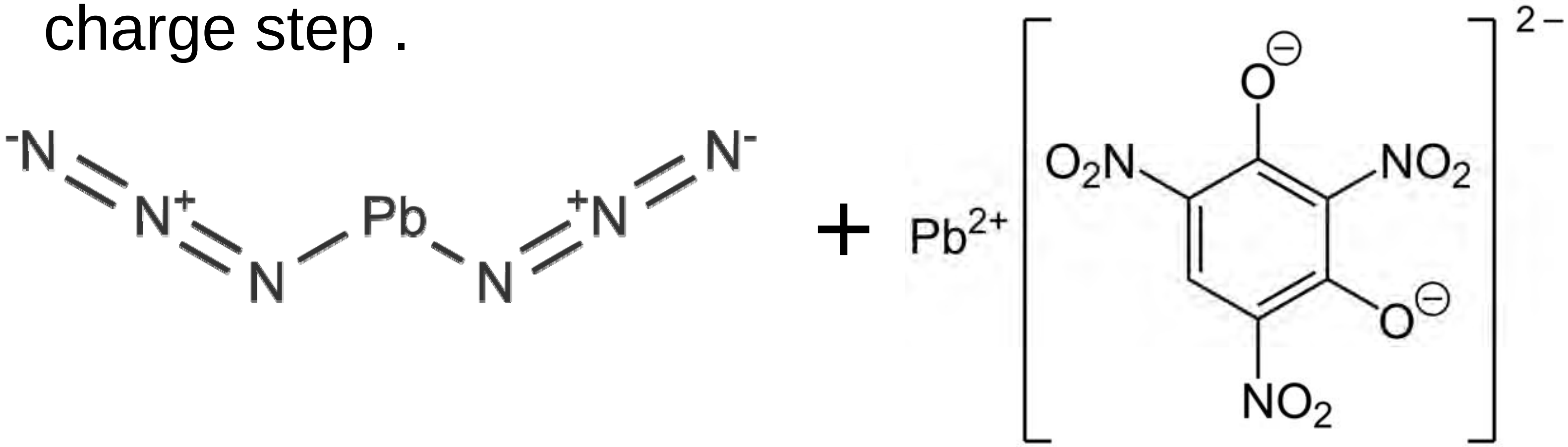
- Lead azide was firstly synthesized by Curtius in 1891. Its production was industrialized by French in 1907. It was widely applied on initiator and blasting elements during the First World War.
- It has many advantages: It is easy to be synthesized, has



a strong initiate ability and good pressure durability. But there are some shortcomings: the flame and stab sensitivity are lower; it has high mechanical sensitivity. It can be exploded in the water. So the security must be concerned in the process of production,transportation and application. Because the flame sensitivity is lower, lead styphnate （LTNR） is added in the detonator to improve the reliability of detonator’s ignition performance.

2.3 D·S co-precipitation detonator

- D·S Co-precipitation primary explosive is prepared by LA and LTNR in the co-precipitation method, it have the same detonation property as LA and the same flame sensitivity as LTNR. By applying it, the technique of detonator and the preparation of primary explosive are simplified. It has high mechanical sensitivity. Explosion is occurred during the process of detonator pressuring charge step .

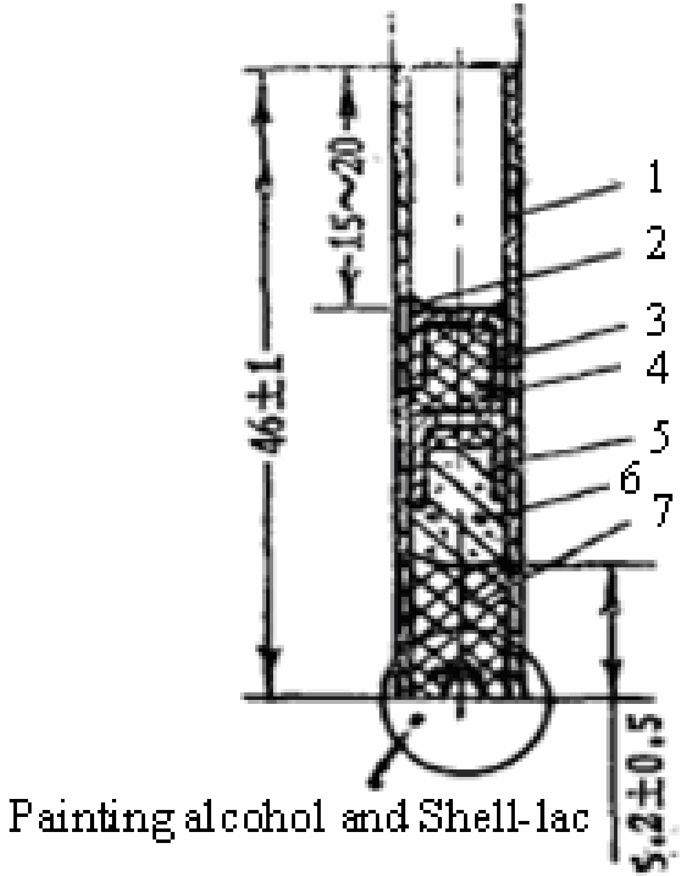


2.4 Double salt K·D detonator

- Double salt K·D is consistent of lead picrate and LA. It has good flame sensitivity as lead picrate and good initiating ability as LA, so it is used in the flame detonators. But it has high impact and frication sensitivity. Explosion is occurred during the process of detonator pressuring charge step.

2.5 K_1K ignition composition detonator

- K_1K ignition composition is mixed by potassium picrate and potassium perchlorate, it is yellow granules. It have a fast burning rate and have a good ignition sensitivity, in the certain conditions it can initiate the PETN explosive or composite explosives with oxidant which have high detonation sensitivity. It can be used as ignition composition in Non-primary detonator to initiate the explosives directly. But the preparation technique has strong influence to the detonator's reliability.

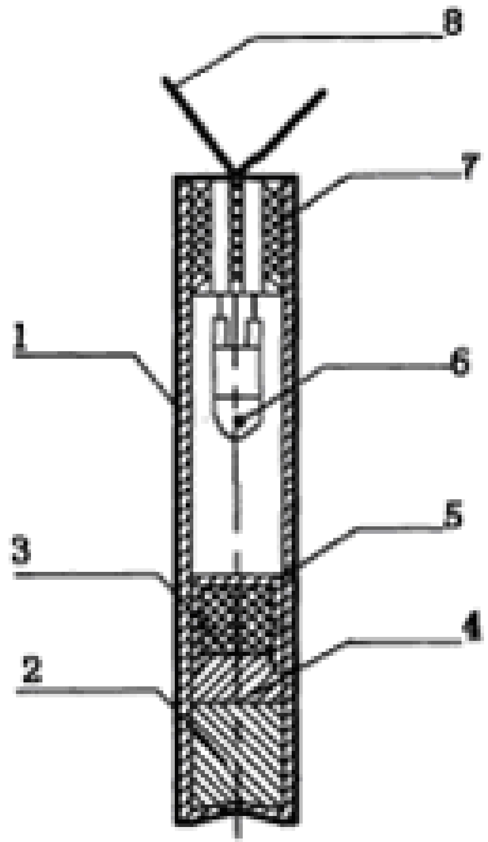


The structure of dual-cap detonator

1—shell; 2—painting; 3—strong cap; 4—primary charge(K_1K)
5—inner cap; 6—transition charge(PETN);
7—main charge(RDX)

2.6 NHN detonator

- Nickel hydrazing nitrate is rich-nitrogen compounds which have good burning and explosion performances. It is a primary explosive having the property of deflagration to detonation transition, can be used as the charge in the engineering detonators. It has high flame sensitivity and low impact and frication sensitivity and lead to little waste water in production process.

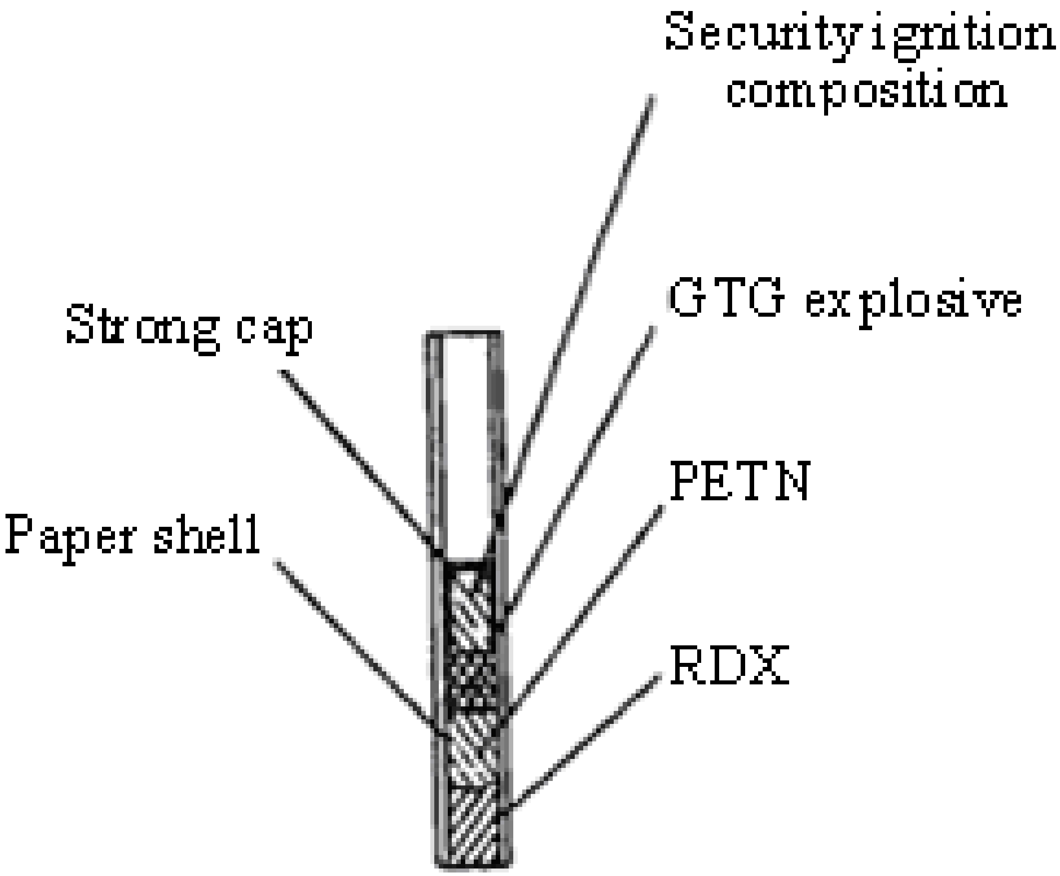


The structure of electric detonator with NHN

1—shell; 2—main charge(PETN); 3—NHN;
4—transition charge(PETN); 5—strong cap; 6—electric ignition;
7—plastic cork; 8—lead wire

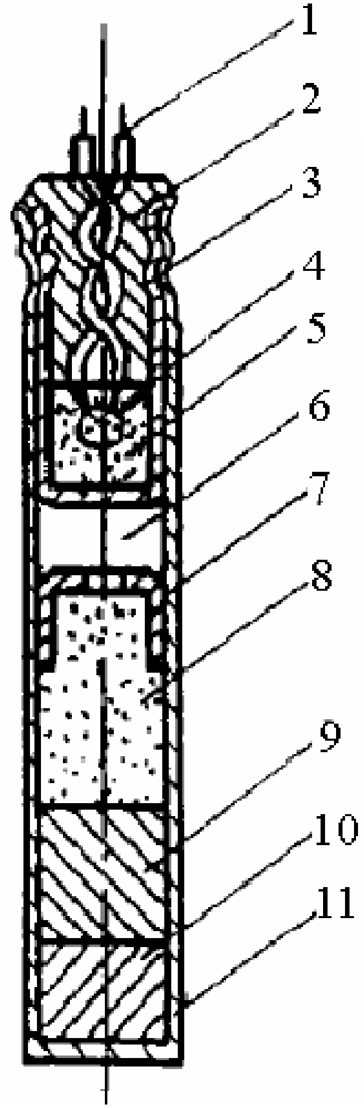
2.7 *GTG detonator*

- GTG is a typical explosive having the property of deflagration to detonation transition. When it is used as the primary explosive in the detonators, there are some special requirements on detonator's structure. In addition, this explosive has lower flame sensitivity, can not be used as charge loaded in the flame detonator.



The structure of flame detonator with GTG

2.8 The simple flying plate detonator



Drawing: The simple flying plate electric detonator without primary explosive

1-detonating fuse;
2-plastic cork;
3-big inner pipe;
4-ignition ball;
5-ignition composition(RDX);
6-hollow;
7-strong cap;
8-donor charge(RDX);
9-booster explosive(RDX);
10-main load powder(RDX);
11-the shell of detonator

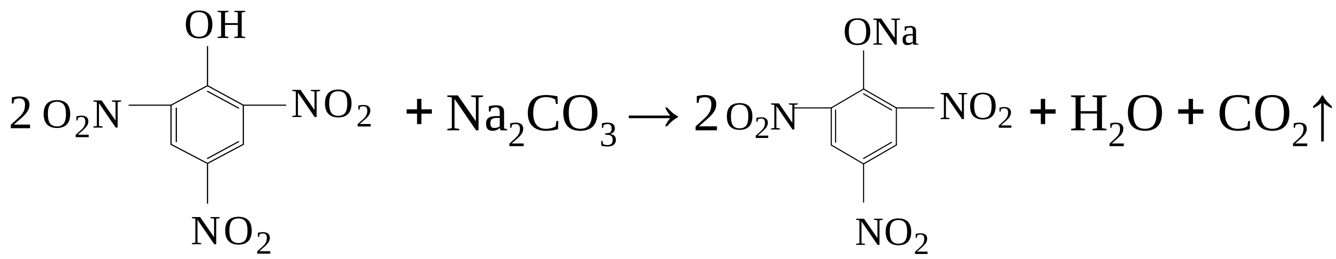
2.9 The characteristics of various detonators

Name	Date	Primary explosive	The structure of detonator	The type of detonator	Yield percentage /%
DDNP detonator	60	DDNP	Reinforce cap/6mm	flame、electric、non-electric detonator	70
LA detonator	50	LTNR + LA	Reinforce cap/6mm	flame、electric、non-electric detonator	4
D·S detonator	70	D·S	Reinforce cap/6mm	flame、electric、non-electric detonator	*
K·D detonator	80	K·D	Reinforce cap/6mm	flame、electric、non-electric detonator	8
K_1K detonator	89	K_1K	Dual Reinforce cap/6mm	flame、electric、non-electric detonator	*
NHN detonator	98	NHN	Reinforce cap/6mm	flame、electric、non-electric detonator	10
GTG detonator	99	K_1K + GTG	Reinforce cap/12mm	electric、non-electric detonator	4
The simple flying plate detonator	2002	Sensitized RDX	The flying plate	electric、non-electric detonator	4

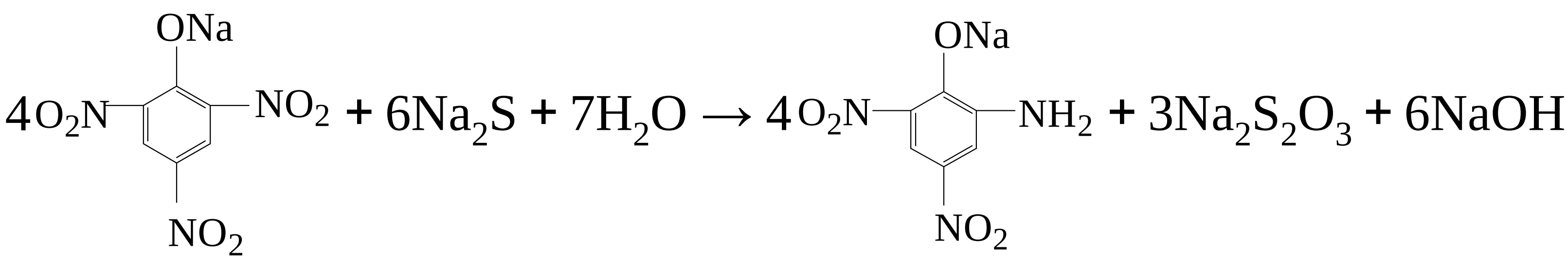
3 The synthesis of some primary explosives

- *3.1 The synthesis of the diazodinitrophenol* (DDNP)
- The pure DDNP is bright yellow needle-like crystallization, it's molecular formula is $C_6H_2(NO_2)_2N_2O$, and its molecular weight is 210.
- There are many kinds of methods to synthesize DDNP, and Clark's Law is adopted mainly in china: the picric acid is neutralized by the sodium carbonate and the sodium picrate is obtained. Reduce the sodium picrate amino sodium picrate can be obtained, then the DDNP is synthesized through diazotization method.

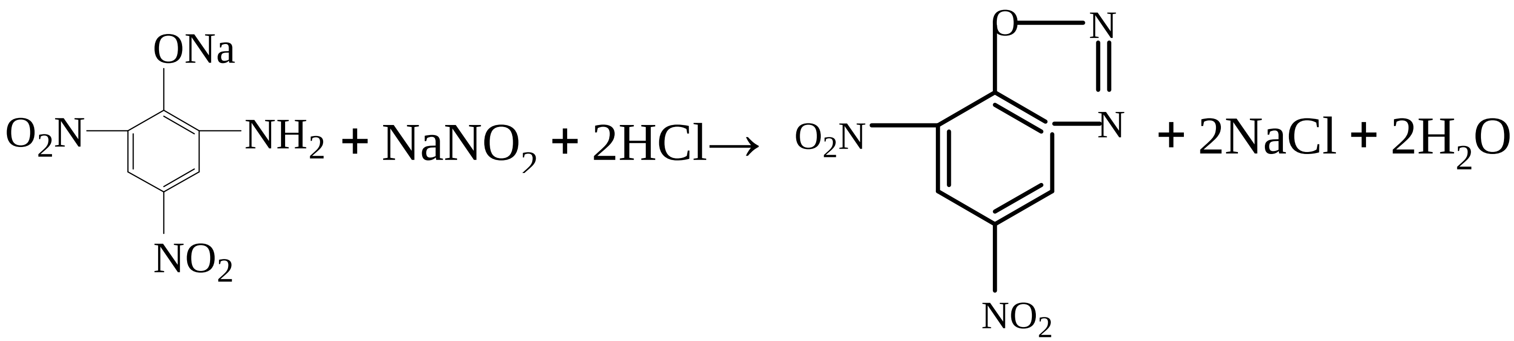
The neutralization reaction:



The reduction reaction



The diazotization reaction:



Because DDNP is safe in water, the production process of DDNP can be operated directly.

3.2 The synthesis of the azide lead

- Azide lead is white crystallization, it's molecular formula is $Pb(N_3)_2$, and it's molecular weight is 291.26.
- The synthesis of the azide lead is a simple metathetical reaction with quick reaction rate, and it's reaction equation is:

$$Pb(NO_3)_2 + NaN_3 \rightarrow Pb(N_3)_2 + NaNO_3$$

- Because violent explosive will happen even the azide lead is soaked in the water, so the production process of the azide lead should be operated isolated.

3.3 The synthesis of the D·S co-precipitation primary explosive

- The D·S co-precipitation primary explosive is prepared by the co-precipitation of sodium azide , lead nitrate and magnesium styphnate, and it’s reaction equations are:

$$2NaN_3 + Pb(NO_3)_2 \rightarrow Pb(N_3)_2 + 2NaNO_3$$

$$C_6H(NO_2)_3(OH)_2 + MgO \rightarrow C_6H(NO_2)_3O_2Mg + H_2O$$

$$C_6H(NO_2)_3O_2Mg + Pb(NO_3)_2 \rightarrow C_6H(NO_2)_3O_2Pb + Mg(NO_3)_2$$

3.4 The synthesis of the double salt K•D

- Double salt K•D is crystallization with color from yellow to red orange. Using the Sodium picrate and the Sodium azide in alkaline medium adopting lead nitrate as coprecipitator, we got the Double salt K•D primary explosive, and it's reaction equation is:

  $C_6H_2(NO_2)_3ONa+5NaN_3+2NaOH+4Pb(NO_3)_2$
  $\rightarrow C_6H_2(NO_2)_3OPb(OH)\cdot Pb(OH)N_3\cdot 2Pb(N_3)_2 + 8NaNO_3$

3.5 K_1K ignition composition

- Ignition composition K_1K is made by mixing the potassium picrate with the potassium perchlorate, and the proportion is potassium picrate(40～60%), potassium perchlorate(60～40%), the binder(3％). Nitrocellulose or polyvinyl butyral can choosed as binder.
- The reaction of potassium picrate is:
- $C_6H_2(NO_2)_3OH + KOH \rightarrow C_6H_2(NO_2)_3OK + H_2O$

3.6 Nickel hydrazine nitrate(NHN)

- Nickel hydrazine nitrate is rose granular polycrystalline, it's molecular formula is $[Ni(N_2H_4)_3](NO_3)_2$, and it's molecular weight is 278.8.
- it's reaction equation is:
- $3N_2H_4 \cdot H_2O + Ni(NO_3)_2 \rightarrow [Ni(N_2H_4)_3](NO_3)_2 + 3H_2O$
- The reaction occurred under weakly alkaline conditions.

3.7 Cadmium carbohydrazide perchlorate(II)（GTG）

- The scientific name of GTG is cadmium carbohydrazide perchlorate(Ⅱ), it's white polyhedron Crystal, it's molecular formula is: 〔$Cd(NH_2NHCONHNH_2)_3$〕$(ClO_4)_2$。
- Under specific composition, the cadmium carbohydrazide perchlorate(Ⅱ) is synthesized by mixing the water solution of carbohydrazide and the water solution of cadmium perchlorate, the main reaction equations are:
- $CdCO_3 + 2HClO_4 \rightarrow Cd(ClO_4)_2 + H_2O + CO_2$
- $Cd(ClO_4)_2 + 3CO(N_2H_3)_2 \rightarrow$ 〔$Cd(NH_2NHCONHNH_2)_3$〕$(ClO_4)_2$
- Usually, the pH value of carbohydrazide solution and perchloric acid solution is in 6~7, the reaction temperature is room temperature.

3.8 safety and wastewater of the some primary explosives during production

Name	Reaction steps	The dangerous process	Waste water
DDNP	3	drying	200L/Kg
LA	1	synthesis (can explode in water) 、 drying 、 pressing	Small scale
D·S	1	synthesis （ can explode in water ）、 drying 、 pressing	Small scale
K·D	1	synthesis （ can explode in water ）、 drying 、 pressing	Small scale
K_1K	2	granulation、 drying	circulating
NHN	1	drying	circulating
GTG	2	synthesis 、 drying	Small scale

- It can be concluded that:
- (1) LA and NHN are one step reactions, so they are easy to be synthesized.
- (2) DDNP will not explode in water, so they are safest. However, the LA will explode in water.
- (3) D·S and K·D will explode during the detonator pressing charge step usually.
- (4) The wastewater of DDNP is in significant quantity and the handling is hard too, so this is a huge difficulty in the detonator producing process in China. However, the wastewater produced during the producing process of K_1K and NHN are recyclable.

4 The sensitivity of various primary explosives

- In general, the ignition reliability of detonator is decided by the flame sensitivity of the primary explosive, the security of primary explosive is decided by its mechanical sensitivity.

Name	Flame sensitivity	Impact sensitivity	Friction sensitivity	Detonator temperature(℃)/5s
DDNP	>30cm	2.5	2.5	170
LA	>5cm	1	1	335
D·S	>30cm	1	1	255～316
K·D	>30cm	1	1	263
K_1K	>30cm	3	3	382
NHN	>30cm	2	2	283
GTG	>8cm	2	2	367
PETN	×	3	3	225

The sensitivity number is lower, The sensitivity is higher.

- (1) DDNP, D·S, K·D, K_1K and NHN have high flame sensitivity, they can be directly loaded in the detonator without adding the ignition compositions.
- (2) The mechanical sensitivity of LA and D·S and K·D are higher, in the production , application and transportation, it is dangerous. The K_1K , NHN and GTG have better security.

5 The detonator property of various primary explosives

- The another important technical index of primary explosive is its detonation performance which include the limiting charge and the main explosives and the constraint condition of detonator and pressure durability in general.

Name	explosive	Constraint condition	Limiting charge mg/explosive	Loading Pressure
DDNP detonator	RDX	Reinforce cap/6mm	<100/RDX	<20MP$_a$
LA detonator	RDX	Reinforce cap/6mm	<50/RDX	<150 MP$_a$
D·S detonator	RDX	Reinforce cap/6mm	50/RDX	<120 MP$_a$
K·D detonator	RDX	Reinforce cap/6mm	50/RDX	<120 MP$_a$
K$_1$K detonator	PETN	Dual Reinforce cap/6mm	<100/PETN	<30 MP$_a$
NHN detonator	RDX	Reinforce cap/6mm	160/ RDX	<70 MP$_a$
GTG detonator	PETN	Reinforce cap/12mm	70/PETN	<50M MP$_a$
The simple flying plate detonator	PETN	The flying plate	×	Loosing charge

The loading pressure is larger, it is safer for transport and usage. But for some primary explosives when the loading pressure is too large, the detonator will hardly be initiated.

6 Prospects

- (1) Propose a kind of primary explosive which is in sensitive and have a strong detonation and produce little waste water in production process;
- (2) Improve DDNP's synthesis route in order to reduce the production of waste water;
- (3) The cost for wastewater treatment of DDNP is high now. so a inexpensive and easy treatment method is urgently needed.
- (4) The optimization and popularization of NHN.

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Thank you!