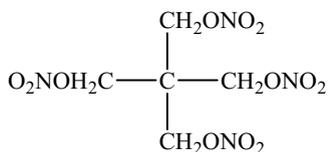# Chapter 7
# Pentaerythritol Tetranitrate

Pentaerythritol tetranitrate, also known as nitrated pentaerythritol, is abbreviated as PETN. PETN was first produced in 1891 by Tollens [1]. PETN is the most stable nitrate and more powerful than RDX. It is an explosive with a wide range of applications. After the World War I, the synthesis, production, and application range of pentaerythritol tetranitrate were extensively studied in many countries, and with successively widespread applications in the military. From the mid-1930s to 1940s, its annual production in the United States was more than 6000 tons, and the monthly production capacity in Germany was 1600 tons. From 1940s to 1950s, an annual production in the former Soviet Union had been up to 1 million tons. Because the raw materials to synthesize pentaerythritol, including formaldehyde and acetaldehyde, can be obtained from by-products of oil cleavage or carbohydrates, the synthesis of pentaerythritol tetranitrate has extensive material source and is easy to implement. Because the mechanical sensitivity, physical stability, chemical stability and service performance, and other properties of pentaerythritol tetranitrate are inferior to that of ammonium nitrate explosives, it is possible that pentaerythritol tetranitrate will be replaced by the second-generation explosives (RDX and HMX) or third-generation new ones (CL20, TKX-50).

## 7.1 Physicochemical Properties of Pentaerythritol Tetranitrate

PETN is a white crystalline with two crystal forms and belongs to the tetragonal crystal system. Its crystal shape varies with different solvents during the crystallization, including needle, bevel square, stable $\alpha$-cubic, and unstable $\beta$-cubic [2–4].

Chemical formula: $C_5H_8N_4O_{12}$;
Structure:

$$O_2NOH_2C \longrightarrow \overset{\displaystyle CH_2ONO_2}{\underset{\displaystyle CH_2ONO_2}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}} \longrightarrow CH_2ONO_2$$

Relatively molecular weight: 316.12;
Oxygen balance: −10.2% (according to the produced $CO_2$);
Oxygen content (%): 17.72;
Nitrogen content (%): 18.21;
Density (g/cm$^3$): 1.77;
Melting point (°C): 141.3; and
Moisture absorption: PETN cannot adsorb water.
Solubility: PETN is almost insoluble in water, but soluble in acetone, methyl acetate, and dimethyl. In alcohol, ether, and benzene carboxylic acid, it is insoluble.

### 7.1.1  Physical Properties of Pentaerythritol Tetranitrate

Pentaerythritol tetranitrate is a crystalline substance that is insoluble in water but with different degrees of dissolution in acid and polar reagents. PETN solubility in solvents are shown in Table 7.1.

As listed in Table 7.1, the solubility of pentaerythritol tetranitrate in acetone is the largest. With the change of water content in acetone, the solubility of PETN is different, which are shown in Fig. 7.1.

PETN has relatively good infiltration in liquid or melted aromatic nitro compounds, and eutectic is formed after the infiltration. The solubility of PETN in TNT and the melting point of its formed eutectic in aromatic nitro compounds are listed in Tables 7.2 and 7.3.

PETN and nitroglycerin can be miscible with each other to form NG eutectic, whose composition and freezing point are shown in Table 7.4.

In addition to the mentioned above, PETN can also form a ternary eutectic with some nitro compounds, whose composition and freezing point are shown in Table 7.5.

Pentaerythritol tetranitrate has four -$CH_2ONO_2$ groups, which are uniformly located around the central carbon atom to form a symmetrical structure, so PETN is quite stable and is more stable than other polyol nitrates. At 100 °C, the military PETN lost weight only 0.1% in 40 hours, the amount of gas released by the vacuum stability test under the same conditions was 0.5 ml/g.Unlike other liquid nitrates, it does not form colloidal solutions with nitrocellulose.

PETN is soluble in nitric acid and its solubility increases with increasing temperature. The solubility of PETN in nitric acid is shown in Fig. 7.2.

PETN's heat capacity is 1.67 J/(g °C), its burning heat is 8259.2 J/g, its melting enthalpy is 96.2–100.4 kJ/mol, and its enthalpy of sublimation is 151.9 kJ/mol. Its dipole moment in a dilute solution of benzene is 2.0 Debye, while it is 2.5 Debye in

**Table 7.1** Pentaerythritol tetranitrate solubility in organic solvents

| Solvent | Content | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | The PETN dissolution capability of solvent (100 mL) at different temperatures | | | | | | | | | |
| | 0 | 20 | 25 | 30 | 40 | 47 | 50 | 60 | 80 | 100 |
| Acetone | 14.37 | 24.95 | – | – | 30.56 | – | – | 42.68 | – | – |
| Benzene | 0.15 | 0.45 | – | – | 1.16 | – | – | 3.35 | – | – |
| β-ethoxylethyl acetate | – | 1.5 | – | 4.1 | 7.6 | – | 11.2 | 14.2 | – | – |
| Tetrachloromethane | – | 0.096 | – | 0.108 | 0.118 | – | 0.121 | – | – | – |
| Chloroform | – | 0.09 | – | – | – | – | – | – | – | – |
| Ethylene epoxide | – | 0.35 | – | 2.8 | 6.1 | – | 9.2 | 12.2 | – | – |
| Ethyl ether | 0.20 | 0.34 | – | – | – | 0.45 | – | – | – | – |
| Ethanol | 0.07 | 0.195 | – | – | 0.415 | – | – | 11.6 (61 °C) | – | – |
| Dichloroethane | – | 0.9 (10 °C) | – | 1.25 | 5.02 (43 °C) | – | 8.28 | 13.8 (65 °C) | – | – |
| Methanol | – | 0.46 | – | – | 1.15 | – | – | 2.60 | – | – |
| Ethyl formate | – | 13.0 | – | 17.0 | 22.0 | – | 31.0 | – | – | – |
| Ethyl acetate | – | 6.322 (19 °C) | – | – | – | – | 17.863 | – | – | – |
| 2-Methyl-1-propanol | – | 0.27 | – | 0.31 | 0.39 | – | 0.52 | – | – | – |
| Nitromethane | 3.36 | – | 8.89 | – | – | – | – | – | 8.89 | – |
| Tetrachloroethane | – | 0.18 | – | 0.27 | 0.40 | – | 0.58 | – | – | – |
| Toluene | 0.15 | 0.43 | – | – | 0.62 | – | – | 2.49 | – | 15.92 |
| Dimethyl Formamide | – | – | – | – | 40 | – | – | 50 | – | 70 |
| Pyridine | – | 5.436 (19 °C) | – | – | – | – | 8.567 | – | – | – |
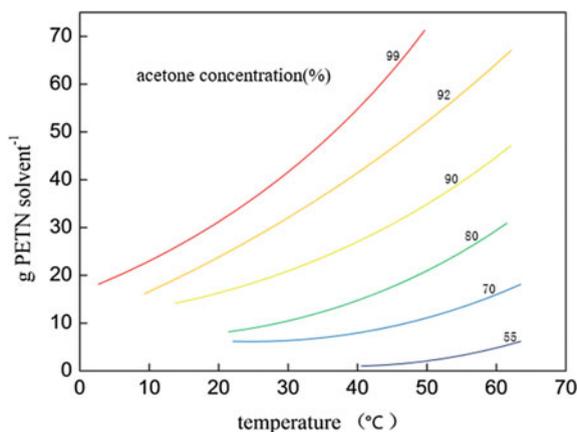
**Fig. 7.1**  The solubility of PETN in acetone with different concentrations

**Table 7.2**  The solubility of PETN in TNT at different temperatures (g • 100 g TNT-1)

| Temperature (°C) | 80 | 85 | 90 | 95 | 100 | 105 | 110 | 115 | 120 | 125 |
|---|---|---|---|---|---|---|---|---|---|---|
| Solubility | 19.3 | 25.0 | 32.1 | 39.5 | 48.6 | 58.2 | 70.0 | 87.8 | 115.0 | 161.0 |

**Table 7.3**  The eutectic formed from PETN and other aromatic substrates

| Content of aromatic nitro compound (%) | Content of PETN (%) | Melting point (°C) |
|---|---|---|
| m-Dinitrobenzene 80 | 20 | 82.4 |
| 2,4-Dinitrotoluene 90 | 10 | 67.3 |
| α-Trinitrotoluene 87 | 13 | 76.1 |
| Tetralite 70 | 30 | 111.3 |
| Nitromannite 80 | 20 | 101.3 |
| Diethyl diphenyl urea 88 | 12 | 68.0 |

**Table 7.4**  Composition of eutectic from PETN and NG

| Item (%) | Content (%) | Melting point (°C) |
|---|---|---|
| NG content in the eutectic | 98.5 | 98.9 |
| PETN content in the eutectic | 1.5 | 1.1 |

l,4-dioxocyclohexane. Ultraviolet absorption spectrum characteristic of PETN crystal is that it can entirely absorb ultraviolet light with wavelengths of below 280 nm. The absorption is shown in Fig. 7.3.

After the stability treatment and refining of PETN, it is stable at room temperature. In order to assess the thermal stability of PETN, the following experiment can be done to verify its stability. 0.5 g of PETN is placed in a tiny glass container under the helium protection. This container was heated up under vacuum to observe
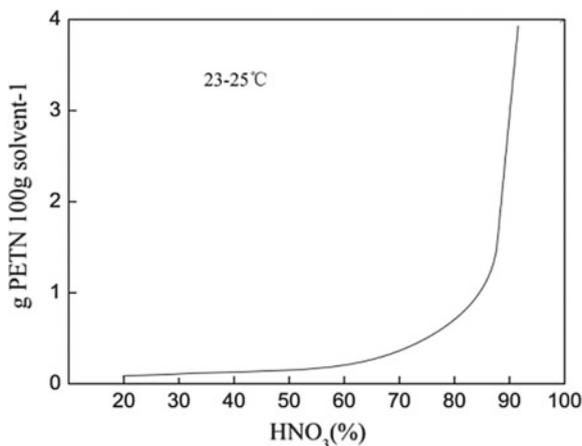
**Fig. 7.2**  Solubility of PETN in HNO$_3$ with different concentrations

**Table 7.5**  Freezing points of ternary eutectic of PETN with some nitro compounds

| Composition of ternary eutectic | Freezing points (°C) |
|---|---|
| PETN (16%), trinitro-m-xylene (8.5%), m-dinitrobenzene (75.5%) | 79.5 |
| PETN (12.5%), 1,8-dinitronaphthalene (16.5%), m-dinitrobenzene (71.0%) | 69 |

**Fig. 7.3**  Ultraviolet absorption spectra of PETN single crystal
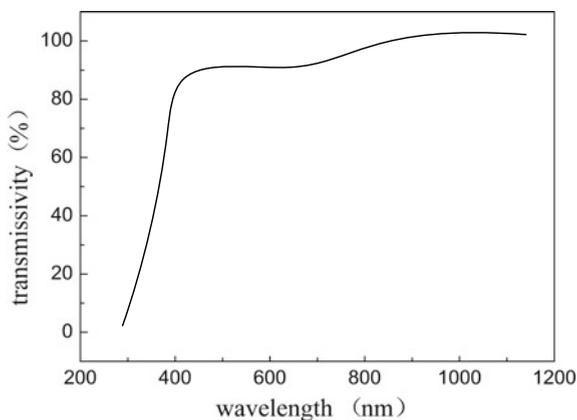


the decomposition of PETN under at temperatures. The relationship between PETN decomposing fraction and time at different temperatures is shown in Fig. 7.4.

Figure 7.4 shows that PETN has decomposed slightly at 60 °C, but with very long induction period. With the increase of temperature, its decomposition rate is increased and the decomposition rate is accelerated with the increase of liquefaction

**Fig. 7.4** The relationship
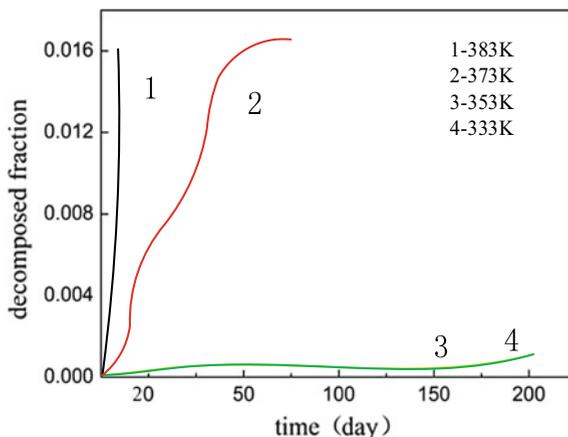between PETN decomposing
fraction and time [3]



**Table 7.6** $\Delta E$ and $A$ of the thermal decomposition of PETN

| Temperature (°C) | State | $\Delta E$ (KJ/mol) | $A$ (s$^{-1}$) |
|---|---|---|---|
| 108–120 | Solid | 212.97 | $10^{20.6}$ |
| 137–157 | Liquid (melting point) | 218.82 | $10^{23.1}$ |

degree, thus to significantly increase the decomposition acceleration. The effect of hydrolysis is also observed, in which the generated water is increased with the increase of the acid product from the decomposition.

PETN is decomposed to release nitric oxide at 140–145 °C, to release yellow smoke when it is heated to 175 °C, to decompose violently at 190 °C, and to explode violently at 202–205 °C. In the thermal decomposition rate constant equation, the relationship between A or $\Delta E$ and temperature is shown in Table 7.6 [5, 6].

Acetone, acid, and alkali all can accelerate the hydrolysis of PETN, and Fig. 7.5 shows the 2-h hydrolysis results of 10 g of PETN in 500 mL of medium.

As shown in Fig. 7.5, after PETN is heated in water at 100 °C for 2 h, it has almost no weight loss. But, when the temperature rises to 125 °C under pressure, PETN hydrolyzes very rapidly. When acetone is added, 0.1% of nitric acid or sodium hydroxide can increase the hydrolysis rate of PETN, in which sodium hydroxide affects PETN hydrolysis most [6]. Hydrolysis product in alkaline medium is mainly pentaerythritol dinitrate.
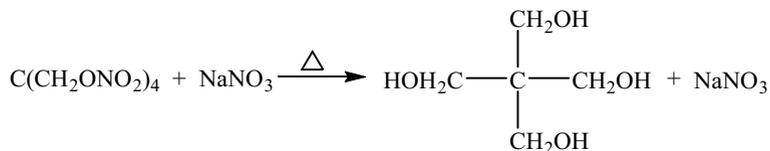
$$C(CH_2ONO_2)_4 + NaNO_3 \xrightarrow{\triangle} HOH_2C-\underset{\underset{CH_2OH}{|}}{\overset{\overset{CH_2OH}{|}}{C}}-CH_2OH + NaNO_3$$

**Fig. 7.5** The relationship of PETN weight loss with temperature in different media [3]
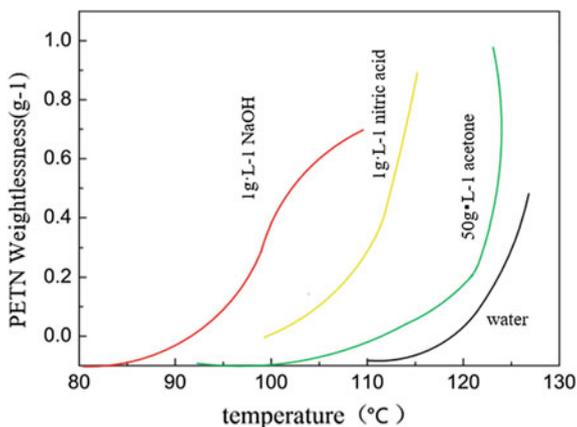


**Table 7.7** Hydrolysis products of PETN in the presence of hydrochloric acid (%)

| Chemical | After 4 h | After 5 h | After 6 h |
|---|---|---|---|
| Pentaerythritol | 0 | $7.7 \pm 1.1$ | $31.9 \pm 0.7$ |
| Pentaerythritol nitrate | 0 | $13.4 \pm 1.7$ | $25.6 \pm 1.9$ |
| Pentaerythritol dinitrate | $23.0 \pm 1.7$ | $34.7 \pm 0.8$ | $27.7 \pm 2.1$ |
| Pentaerythritol trinitrate | $38.9 \pm 0.9$ | $27.8 \pm 2.1$ | $11.1 \pm 1.4$ |
| PETN | $38.9 \pm 0.9$ | $14.8 \pm 1.9$ | $5.6 \pm 0.1$ |

The hydrolysis results of PETN in dioxocyclohexane solutions (3:1) with l N hydrochloric acid as catalyst. And the hydrolysis products formed are listed in Table 7.7.

The refined PETN crystals from aqueous acetone have remnant traces of water, which should be removed through drying because the PETN crystal with water has relatively low stability and is not easy to store. The crystal is crushed and dried to remove moisture and improve the stability of PETN.

## 7.1.2   Chemical Properties of Pentaerythritol Tetranitrate

Pentaerythritol tetranitrate has symmetrical structure and cannot react to many chemicals. Unlike most nitrates, pentaerythritol tetranitrate neither reduces Fehling's reagent, also form adducts with aromatic nitro compounds. When pentaerythritol tetranitrate is long-term treated in water at 100 °C, there is hydrolysis. When the water temperature rises to 125 °C and pressurized, the hydrolysis is very rapidly. Under this condition, if there is 0.1% nitric acid, the hydrolysis is

significantly accelerated. The hydrolysis rate of pentaerythritol tetranitrate with dilute NaOH is faster than that with acid. No matter what the hydrolysis conditions of pentaerythritol tetranitrate, the final product is pentaerythritol dinitrate in all cases.
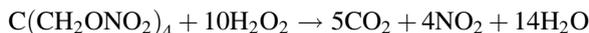
(1)  Oxidization of pentaerythritol tetranitrate

The oxygen balance of pentaerythritol tetranitrate is $-10.2\%$, and the oxygen content is $60.74\%/mol$; thus, pentaerythritol tetranitrate is nitrate with a negative oxygen balance. When it meets with strong oxidizing agents, such as hypochlorite, reaction can lead to the nitrogen–oxygen bond cleavage quickly on $-ONO_2$ group, thus to cause the explosion and violent reaction. However, perchlorate (AP) can chemically react with PETN. After ammonium perchlorate and PETN are mixed evenly according to a certain ratio, the total energy of PETN can be significantly improved. Due to the addition of ammonium perchlorate, PETN sensitivity has been increased as well.

When pentaerythritol tetranitrate reacts with hydrogen peroxide, the reaction is more violent than that with sodium hypochlorite, and its decomposition releases nitrogen oxide. When a few drops of hydrogen peroxide are added into pentaerythritol tetranitrate, gas bubbles are immediately popped up with the smell of nitrogen oxides. With large amounts of hydrogen peroxide, an explosion can be caused.

$$C(CH_2ONO_2)_4 + 6H_2O_2 \rightarrow 5CO_2 + 4NO + 10H_2O$$
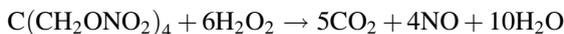
When PETN reacts with excess hydrogen peroxide, the final hydroxide from decomposition is mainly tetravalent nitrogen.

$$C(CH_2ONO_2)_4 + 10H_2O_2 \rightarrow 5CO_2 + 4NO_2 + 14H_2O$$

(2)  Reaction of pentaerythritol tetranitrate with reducing agent

Pentaerythritol tetranitrate usually do not react with hydrogen, but its $-ONO_2$ can be converted into $-NH_2$ and $H_2O$ when it is heated under pressure.

$$C(CH_2ONO_2)_4 \xrightarrow[\Delta]{catalyst,\ H_2} CH_2O + CH_3CHO + 2(NH_4)_2CO_3 + H_2O$$
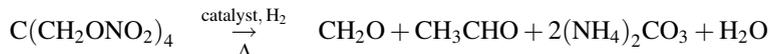
PETN is normally relatively stable with metal hydride, but it can be reduced and decomposed with released ammonia in the decomposition products when it is heated [7].

Sodium sulfide can slowly decompose PETN, but this decomposing is far less easy than other nitrates. In laboratories, this method can be sued to destruct a small amount of PETN.

In boiling ferrous chloride solution, PETN decomposes very quickly to release nitrogen oxide. So, this method can be used to determine nitrogen content in nitrate explosives.

(3)  Chemical stability of pentaerythritol tetranitrate

The high chemical stability of PETN is better than that of all other nitrates, and its Abel's test can be up to a few hours.

When PETN and TNT or other nitro compounds are mixed, it can also be accelerated to decompose at low temperature. At 110 °C, PETN and TNT mixture begin autocatalytic decomposition after a certain time of induction period, which is easier than pure PETN solid. Among mixture series and PETN with TNT, the mixture with 20% of TNT is the easiest one to decompose.

The stability of PETN is the key to directly relate to whether we can expand its applications. Therefore, how to improve the stability of PETN is important. American army had used polyvinylpyrrolidone with molecular weight of about 90,000 or phenolic resin with polymerization degree of 100 to cover PETN as mainly loaded explosive during a variety of fighting, leading to significant improvement of thermal stability of PETN explosives. At 120 °C, during the stability test under vacuum, the released gas volume within 20 h is about 1/10 of the untreated PETN under the same conditions. After nitrobenzene, dinitro, trinitrobenzene, and other nitroaromatics are added into PETN, its stability is decreased and the PETN mixtures can be heated at 120–135 °C. PETN stability modification results with some materials are listed in Table 7.8.

(4)  The toxicity of PETN

PETN has a lower toxicity than nitroglycerine [8] with a very low vapor pressure and very small solubility, and thus no one can be poisoned through inhalation of vapor. Even a small amount of PETN dust particles is inhaled, and it will not cause harmful effects. PETN is a long-term coronary drug to use to treat angina in medicine.

**Table 7.8** The stability of PETN modified with some mixtures

| Additive | pH of extracted water sample at 120 °C | | | |
|---|---|---|---|---|
|  | 1 h | 2 h | 3 h | 4 h |
| Pure PETN | 7.16 | 7.15 | 6.33 | 5.86 |
| p-Nitrotoluene (9.1%) | 5.34 | 3.50 | 3.19 | 1.92 |
| 2,4-Dinitrotoluene (9.1%) | 6.30 | 4.20 | 3.13 | 2.92 |
| $d_4^{20}$-Trinitrotoluene (9.1%) | 6.54 | 5.70 | 3.32 | 3.03 |
| Phenolic resin (2.0%) | 7.12 | 7.10 | 7.08 | 7.07 |

## 7.2   The Explosion Properties of Pentaerythritol Tetranitrate

The oxygen balance of PETN is −10.1% with a nitrogen of 17.72%, and its explosion decomposition products are different with different detonation methods. Its explosion decomposition reaction is done according to the following formula:

$$C_5H_8N_4O_{12} \rightarrow CO_2 + CO + 3C + NO_2 + 3NO + 4H_2O$$
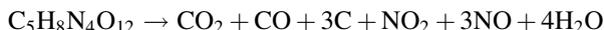
Different detonation methods have different PETN explosion reactions in different ways, and the percentage composition of collected gas is listed in Table 7.9.

PETN is hard to ignite. When it is mounted in the pipe with a diameter of 18 mm, it can be ignited only when it is warmed up to 95 °C and its burning is very low. Few of PETN or very thin layer of PETN can be ignited in air and burnt smoothly. When piles of PETN are ignited, especially when it exceeds 1000 g, PETN is burnt on its surface first, and this surface burning turns into detonation quickly. When PETN is ignited or overheated in the closed container, even a little of PETN turns into detonation [9, 10]. The detonation point of PETN is 202–205 °C.

PETN has a high impact sensitivity, and its limit fall of 2 kg drop weight is 17 cm. With 10 kg drop weight, its 25 cm high explosion ratio is 100%. The sensitivity of PETN is higher than that of RDX and HMX. Therefore, when PETN is charged as the main ammunition, it is needed to passivate before using. When passivating reagents are added into the PETN, it is inevitable to decrease the explosion property. Therefore, the main developing field of PETN is to find appropriate passivating reagents of PETN [11].

The friction sensitivity of PETN is relatively high, and its detonation sensitivity is very high. Its limit dose of 0.01 g of lead azide and that of tetryl is 0.025 g under the same conditions. The sand-loaded lead expansion value of PETN is 500 cm$^3$, and its water-filled lead expansion value is 560 cm$^3$, indicating that PETN is a good booster primer and can also be used as secondary charged drug and booster primer of detonator. Different from many other explosives, PETN does not lose its explosive power and its explosion rate is also increased after its intercrystal air is removed and PETN is used as nonexplosive liquid replacement. PETN explosive characteristics under different explosion conditions are shown in Table 7.10.

**Table 7.9**  Gas products of PETN explosive decomposition of (%)

| Detonation method | NO$_2$ | NO | N$_2$O | N$_2$ | CO$_2$ | CO | H$_2$ | O$_2$ |
|---|---|---|---|---|---|---|---|---|
| Detonator | – | 5.3 | – | 22.8 | 37.0 | 26.7 | 6.8 | 1.4 |
| Impact | – | 24.3 | 5.3 | 9.4 | 19.1 | 35.4 | 6.5 | – |
| Thermal decomposition at 210 °C | 12.0 | 47.6 | 9.5 | 1.6 | 6.3 | 21.0 | 2.0 | – |

**Table 7.10**  Conditions of PETN explosion rate test under

| Explosion rate when the loading density is $1.00$ g/cm$^{-3}$ (m/s) | | Explosion rate when the loading density is $1.40$ g/cm$^{-3}$ (m/s) | |
|---|---|---|---|
| Dry PETN | PETN with 10% water | Dry PETN | PETN with 20 gb glycerin |
| 7295 | 7445 | 7125 | 7825 |

PETN with 40% of water can still be detonated with 8# detonator, but TNT with 15% of water cannot be detonated, which is very different from that the slurry of nitroglycerine and water that is hard to detonate.

When PETN is heated to above its melting point (205–225 °C), it explodes. At 161 °C or above, PETN is slightly decomposed and the activation energy E = 196.65 J/mol and $\log_{10}B = 19.8$ at the first stage of decomposition. Typically, the normal decomposition of PETN is

$$C_{15.8}H_{25.3}O_{38.0}N_{12.7} \rightarrow 12.13CO + 3.38CO_2 + 10.35H_2O + 0.1CH_4 + 1.71H_2$$
$$+ 0.1C_2H_2 + 0.2NH_3 + 0.11HCN + 6.23N_2$$
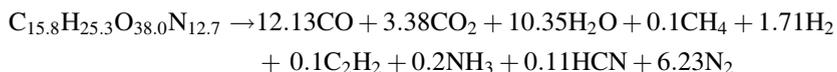
PETN is sensitive to shock. With 0.02 MPa kinetic energy impact on the surface of PETN, its risk of explosion is up to 50%. The friction sensitivity of PETN is not high although its explosive detonation sensitivity is extremely high. When the wax in PETN is 10%, it is still very easy to detonate. The electric spark sensitivity of PETN is very high. When capacitor discharges between 2000 and 12,000 V, PETN can be detonated.

Ultraviolet rays can detonate PETN. When PETN is strongly radiated for 1.2 ms with ultraviolet (900 J of energy), it rapidly decomposes with the same explosion decomposition under the heat. If the ultraviolet light with 480 J of energy, it can explode within 20 ms. γ rays can also make PETN to decompose.

The flame insensitivity of PETN is low, and it is difficult to ignite with a flame, which is significantly different from the straight-chain nitrate. When seamless steel tubes (Φ18 mm) are loaded with PETN, it cannot be ignited. The only way to ignite PETN is to heat the tube to above 95 °C, which can cause the fire while its burning rate is only 0.047 cm/s. When the pressure is increased, burning with a constant speed can be reached. The relationship between burning rate and pressure is $U = 0.02 + 0.018P$.

In addition to the abovementioned sensitivity of PETN, its detonation sensitivity is also associated with the crystal results and status [12]. Explosion rate of PETN under different loading densities is shown in Table 7.11.

**Table 7.11**  PETN explosion rate with different loading densities

| Loading density of PETN (g/cm$^{-3}$) | Explosion rate (m/s) |
|---|---|
| 0.85 | 5330 |
| 1.50 | 7600 |
| 1.70 | 8300 |
| 1.73 | 8500 |

**Table 7.12** Other characteristic data of PETN

| Item | Parameter |
|---|---|
| Explosion heat (J/g) | 6401.52 |
| Specific volume (ml/g) | 768 |
| Explosion temperature (°C) | 4230 |
| Brisance (mm) | The compression value of lead column with 25 g of dosage is 14–16 |
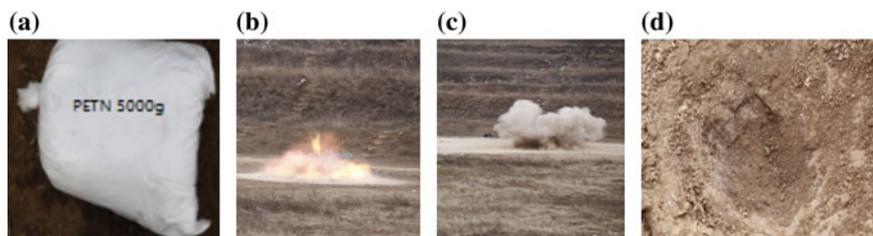


**Fig. 7.6** Scene of the explosion of 5000 g PETN

Explosion rate of PETN is high and its critical diameter is small (When the density is 1 g/cm$^3$, the critical diameter is 3 mm). Thus, explosion rate of detonating wire made of PETN is very small. Even it is bended, the change of explosion rate is within 0.8–1.0%, which is the reason it is widely used in detonating wire. Other characteristics of PETN are shown in Table 7.12.

When PETN is loosely loaded, its explosive power is less than that with loaded PETN with a certain charging pressure. Figure 7.6 shows the PETN explosion scene of 5000 g with a certain bulk density.

In Fig. 7.6a is 5000 g of PETN with random package, b is the light at the moment of an explosion, c is the instant smoke from the explosion, and d is the surface then after the explosion of PETN (5000 g).

The explosion performance of pressed PETN with a certain density is totally different from that of loose PETN. Figure 7.7 is the explosion effect of 1000 g PETN with a density of 1.75 g/cm$^3$ on the same ground of Fig. 7.6.

In Fig. 7.7a is 1000 g of PETN with a density of 1.75 g/cm$^3$, b is the instant smoke from the explosion, and c is the dent on the ground from the explosion.

As shown in Figs. 7.6 and 7.7, PETN has different explosion performances with different densities. After the explosion of 5000 g of PETN with regular packing density ($\rho = 0.42$ g/cm$^3$), the volume of explosion dent is 0.67 m$^3$ and the bottom of the dent is pressed to very tight, while the dent of only 1000 g of the latter PETN with a density of 1.75 g/cm$^3$ is 0.73 m$^3$. And the dent depth is 276 mm after the removal of loose soil, but the former dent depth is only 167 mm. Through this simple comparison test, it is shown that PETN explosive power is directly related to its loading density.
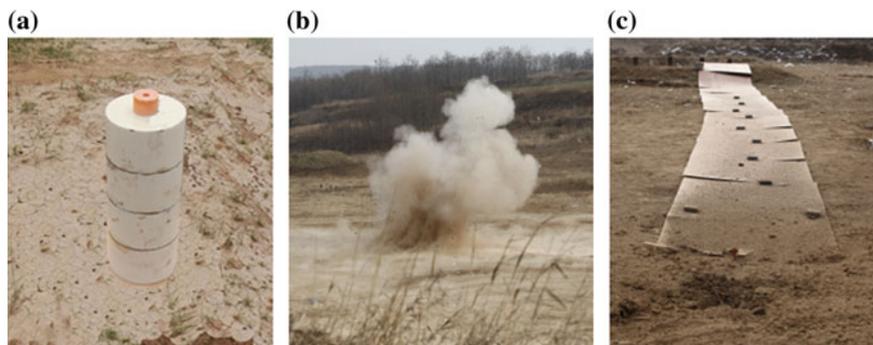
**Fig. 7.7** Scene of the explosion of 1000 g PETN with density of 1.75 g/cm$^3$

**Table 7.13** Sensitivity and power of passivated PETN

| Passivating reagents | The dropping limit of 2 kg drop hammer (cm) | Power (mL) | Passivating reagents | The dropping limit of 2 kg drop hammer (cm) | Power (mL) |
|---|---|---|---|---|---|
| Unpassivated PETN | 30 | 500 | Dinitrotoluene (5%) | – | 430 |
| Wax (5%) | 35 | 415 | Dinitrotoluene (10%) | 57 | 425 |
| Wax (10%) | 60 | 340 | Dinitrotoluene (15%) | – | 355 |

Passivating reagents of PETN include both nonexplosive substances and substances with low explosive power. Explosive properties of passivated PETN are still better than that of TNT and tetryl. Sensitivity and power of passivated PETN are shown in Table 7.13.

## 7.3   Production Technology of Pentaerythritol Tetranitrate

Whether industrially or in laboratory, pentaerythritol tetranitrate is usually synthesized through the direct nitration of pentaerythritol with nitric acid or the mixed acid from nitric acid and sulfuric acid, and the basic reaction is

$$C(CH_2OH)_4 + 4HNO_3 \rightarrow C(CH_2ONO_2)_4 + 4H_2O$$
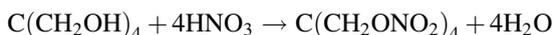
According to the difference in the operation and nitrating reagents, there are four methods to prepare pentaerythritol tetranitrate from pentaerythritol, and the four methods are the nitric–sulfuric mixed acid method, nitric acid–sulfuric acid method,

sulfuric acid–nitric acid method, and nitric acid method. However, in most indus-trial manufacturers, PETN is still prepared through the direct nitration of pen-taerythritol with concentrated nitric acid, and nitrated product of pentaerythritol and its purity depend on the purity of pentaerythritol. When concentrated nitric acid is used to nitrate pentaerythritol to prepare pentaerythritol tetranitrate with the pen-taerythritol purity of 98%, product is relatively easy to precipitate out once the concentration of wasted nitric acid is diluted to around 30% after the nitration. If the purity of pentaerythritol is 95%, the wasted acid is diluted to that with 50–60% of nitric acid concentration after the nitration. If pentaerythritol purity is below 95%, the product is directly filtrated after the nitration. When the concentration of waste acid is higher, nitric acid concentration is higher, and its solubility of impurities and PETN is larger. With a lower concentration of nitric acid after the dilution, the dissolved substances are less, and the yield of crude products is larger, and the wasted acid is relatively easier to deal with. According to the needs of environ-mental protection and green manufacturing, this section is focused on the prepa-ration process of pentaerythritol tetranitrate with nitric acid method [2, 3, 6, 7, 13–16].

## 7.3.1   Nitric Acid Methods to Prepare Pentaerythritol Tetranitrate

Environmentally friendly and green manufacturing process to prepare pentaery-thritol tetranitrate with nitric acid methods, and the process is shown in Fig. 7.8.

The process of nitric acid method to produce PETN has intermittent and con-tinuous processes. Now, continuous process is used to produce PETN in every country.
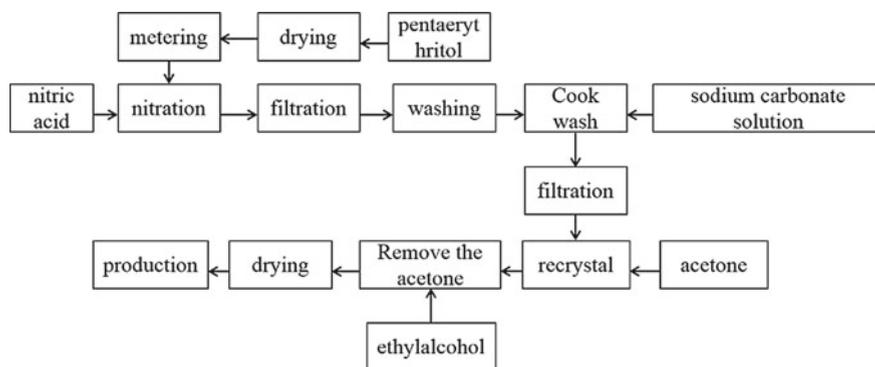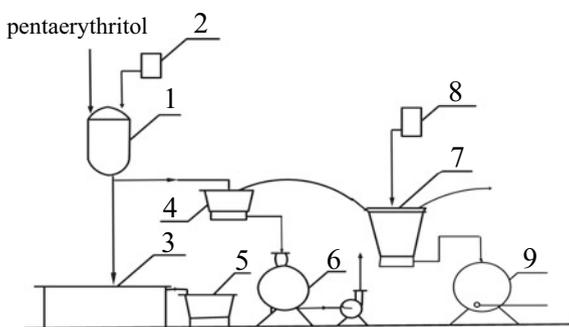


**Fig. 7.8**  Preparation process of pentaerythritol tetranitrate with nitric acid method

**Fig. 7.9** The process of intermittent nitric acid method to produce PETN [6]. 1. Nitration reactor, 2. nitric acid measurement tank, 3. safety pool, 4 and 5. vacuum filters, 6. vacuum collector of wasted acid, 7. washing tank, 8. sink, 9. vacuum collector of washing water

(1) Manufacturing process of intermittent method to produce PETN

Intermittent manufacturing process to directly prepare PETN with nitric acid is a general method with low production instrument investment, easy operation, simple technology, and relatively safe production process. During the production, water in pentaerythritol is removed first, then pentaerythritol is shattered into 200 mesh, and the material is loaded into the reactor. After the nitration, stability treatment is done following the vacuum filtration, and the raw product is recrystallized in acetone to obtain PETN. The process of intermittent nitric acid method to produce PETN is described in Fig. 7.9.

300 kilograms of nitric acid (93–95%) was added into the nitrating reactor. With constant stirring (120 RPM) and cooling, pentaerythritol (60 kg) is gradually added which is dried, crushed, and sieved in advance, in which the nitrator's temperature is kept below 20 °C. The temperature is kept for another 30 min after the chemicals feeding, PETN is crystallized out from wasted acid with a density of 1.43 g/cm$^3$. The nitrating reagent is added into the vacuum filter 4. The filtering period is 10–15 min to make the acid content in the filtered cake not more than 25%. The wasted acid concentration is 78% and added into the vacuum collector 6.

Acidic PETN is sent to antiacid steel washing tank 7, and the washing tank is equipped with blender and porous ceramic fake bottom (as the filtering board). The tank is filled with water with 6.5 times of PETN volume, PETN is added under the stirring. The stirring is continued for another 15 min after the addition of PETN is finished. Then, acidic water is filtered out with pumping. Water is used to wash again for three times, in which water is 1.5 times of PETN each time, to make acidity of rough products to fall down to around 1%. The obtained PETN is sent to boiling–washing tank with 1% sodium carbonate solution that is 8–10 times of PETN, which is neutralized for 1 h at 85–90 °C. The solution is always kept as alkaline to remove the acid among PETN crystals. The final acidity of PETN crystal is only 0.3–0.5. After the removal of water with vacuum filtration, recrystallization in acetone is done.

During the refining, 2.2 kg acetone per kg PETN is used to dissolve PETN at 58 °C. Carbonate ammonium that is 1 time of calculated volume is added to neutralize the residual acid. After 1 h of stabilization processing, the solution goes
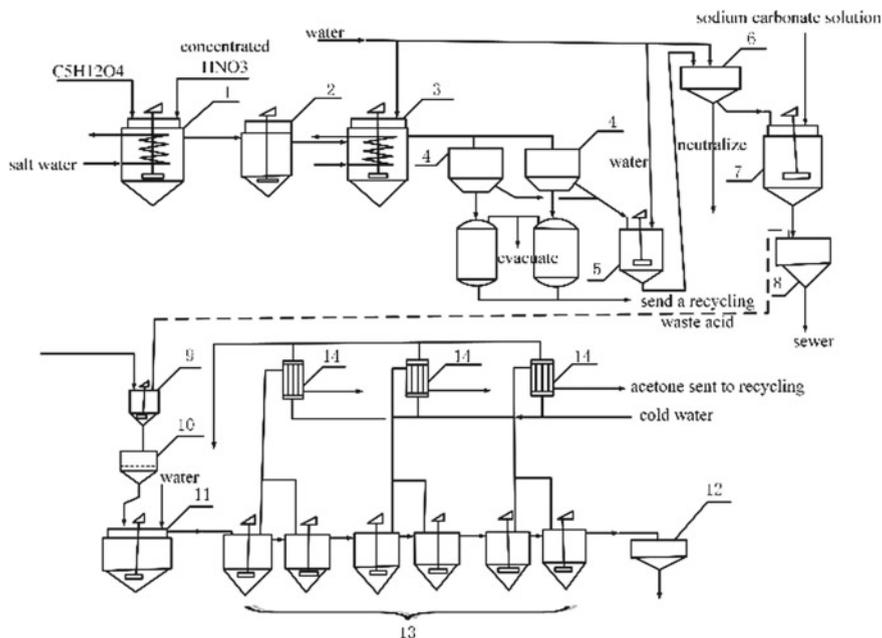
**Fig. 7.10** Process flow of continuous production of PETN with nitric acid method [3]. 1. nitrator, 2, 3. diluting tank, 4. filter, 5. washing tank, 6, 8, 10 and 12. filter, 7. filtering tank, 9. dissolution tank, 11. diluting tank, 13. distillation equipment, 14. steam condenser

through the filter that is preheat to 50–55 °C and enter into the crystallization reactor that is preheat to 50 °C to cool down and crystallize slowly, in which the initial cooling rate is 1 °C every 5 min followed by 2–2.5 °C/min. The whole crystallizing process needs 2 h. In this process, the hot acetone solution cannot be added into cold container or cooled down too fast; otherwise, PETN will be crystallized on the wall of crystallizing reactor and pipe to form a hard shell that affects the crystallization.

The purified PETN is separated from solvent acetone in the vacuum filter. After the separation, there is still 15–20% of acetone in PETN, which is then washed with a small amount of ethanol to remove the residual acetone. The PETN containing 15–20% ethanol is dried for 12 h at 40 °C in the drying box. After the discharge of product, PETN is sieved and loaded in cloth bags.

(2) Processes of continuous nitration, dilution crystallization method are shown in Fig. 7.10

This continuous nitration process is started with an intermittent nitration. The concentrated nitric acid (98–99%) is added into the nitrator 1, and pentaerythritol with 1/5 of nitric acid is added through a screwing conveyor within about 40 min. The temperature is maintained at 15–20 °C through cooling.

Then, the continuous nitration is begun. Concentrated nitric acid and pentaerythritol are added continuously according to their ratio, the nitration solution spills into the nitrator 2 and is cooled down to 10 °C, and the nitration solution with the suspension of this PETN crystal with 80% nitric acid flows into dilution tank 3. Water is added to dilute nitric acid concentration to 30% and the temperature is maintained at 15–20 °C. The solution flows into the vacuum filter 4, and these two filters are used alternatively. A filtered-out acid containing PETN is washed into the washer unit.

After the PETN was washed in the washing tank 5, it is sent to the filter 6. After the removal of the acidic washing water, PETN is sent into neutralizing tank 7, in which sodium carbonate at 60 °C is used to wash for 1.5 h. After the filtering through vacuum filters 8, filtrate should be alkaline.

After PETN washed with base, it is refined with continuous crystallization method. In dissolving tank 9, PETN with 10% water is dissolved in acetone at about 45 °C, and a small amount of sodium carbonate (500 L of acetone and 1.5 kg of sodium carbonate per 100 g pentaerythritol) is added. After the temperature is increased to 50 °C, the solution flows through the filter 10 and enters into diluting tank 11. At 60 °C, a certain amount of water is added to dilute the acetone concentration to 50–55%. This acetone with suspension containing PETN grains flows into distiller groups 13 with blenders and heaters, in which acetone is distilled out and the steam is condensed in the steam condenser 14. The temperature of the first distiller is kept at 85 °C, and its concentration of acetone is maintained at 12–15%. The temperature of the second distiller is kept at 90 °C, and its concentration of acetone is maintained at 3–5%. The temperature of distillers 3, 4, and 5 is kept at 100 °C, and only traces of acetone are left. When acetone is distilled out, PETN crystallizes and becomes its final shape, PETN crystals from this method are in large size and uniform, and it is sent to dry after water which is separated through the filter 12.

## 7.3.2 Purification of Pentaerythritol Tetranitrate

Acidic PETN is sent to antiacid steel washing tank, and the washing tank is equipped with blender and porous ceramic fake bottom (as the filtering board). The tank is filled with water with 6.5 times of PETN volume, and PETN is added under the stirring. The stirring is continued for another 15 min after the addition of PETN is finished. The obtained PETN is sent to boiling–washing tank with 1% sodium carbonate solution that is 8–10 times of PETN, which is neutralized for 1 h at 85–90 °C. The solution is always kept as alkaline to remove the acid among PETN crystals. The final acidity of PETN crystal is only 0.3–0.5. After the removal of water with vacuum filtration, recrystallization in acetone is done.

During the refining, 2.2 kg acetone per kg PETN is used to dissolve PETN at 58 °C. Carbonate ammonium that is 1 time of calculated volume is added to neutralize the residual acid. After 1 h of stabilization processing, the solution goes through the filter that is preheated to 50–55 °C and enters into the crystallization reactor that is preheated to 50 °C to cool down and crystallize slowly, in which the initial cooling rate is 1 °C every 5 min followed by 2–2.5 °C/min. The whole crystallizing process needs 2 h. In this process, the hot acetone solution cannot be added into cold container or cooled down too fast; otherwise, PETN will be crystallized on the wall of crystallizing reactor and pipe to form a hard shell that affects the crystallization.

The purified PETN is separated from solvent acetone in the vacuum filter. After the separation, there is still 15–20% of acetone in PETN, which is then washed with a small amount of ethanol to remove the residual acetone. The PETN containing 15–20% ethanol is dried for 12 h at 40 °C in the drying box. After the discharge of product, PETN is sieved and loaded in cloth bags.

After PETN washed with base, it is refined with continuous crystallization method. In the dissolving tank 9, PETN with 10% water is dissolved in acetone at about 45 °C, and a small amount of sodium carbonate (500 L of acetone and 1.5 kg of sodium carbonate per 100 g pentaerythritol) is added. After the temperature is increased to 50 °C, the solution flows through the filter 10 and enters into diluting tank 11. At 60 °C, a certain amount of water is added to dilute the acetone concentration to 50–55%. This acetone with suspension containing PETN grains flows into distiller groups 13 with blenders and heaters, in which acetone is distilled out and the steam is condensed in the steam condenser 14. The temperature of the first distiller is kept at 85 °C, and its concentration of acetone is maintained at 12–15%. The temperature of the second distiller is kept at 90 °C, and its concentration of acetone is maintained at 3–5%. The temperature of distillers 3, 4, and 5 is kept at 100 °C, and only traces of acetone are left. When acetone is distilled out, PETN crystallizes and becomes its final shape, and PETN crystals from this method are in large size and uniform. After PETN is separated with water in filter 1, it is sent to dry.

Now, the simple cooling crystallization method is used generally, whose mother liquid can be reused, but contents of water and PETN in the mother liquor change in a wide range to make the process difficult to control. Thus, diluting crystallization method is usually used. In the dilution crystallization method, solution is diluted to that with acetone content of 55%, cooled to around 30 °C, and filtered. After the dilution, acetone is removed before the filtration.

Product quality requirements are different according to the different applications. PETN made in the USA for various applications is divided into four categories. The first is used as a detonating wire, the second is used as the booster in the ammunition of small arms, the third is used in PETN/TNT, and the fourth is used to make a detonator. The specification of PETN made in the USA is shown in Tables 7.14 and 7.15.

**Table 7.14**  Indicators of PETN as explosive

| Item | Property indicator |
|---|---|
| Color | White crystal or powder |
| m.p. (°C) | $\geq 140.0$ |
| Nitrogen content (%) | $\geq 17.50$ |
| Compound insoluble in acetone (%) | $\leq 0.1$ |
| Insoluble particle (sieve number) | No particle left on 40# sieve |
| Acidity basicity (%) | $\leq 0.003$ |
| Vacuum stability (120 °C) | $\leq 5$ mL (20 h) |
| Particle size | Determined according to customer's requirements |

**Table 7.15**  Particle size of PETN made in USA

| USA standard sieve number | Percentage of going through | | | |
|---|---|---|---|---|
| | The first group | The second group | The third group | The fourth group |
| 30 | – | – | $95_{min}$ | |
| 80 | 100 | – | – | – |
| 100 | – | – | – | $20_{max}$ |
| 100 | $85_{min}$ | $95_{min}$ | – | $5_{min}$ |
| 140 | $85_{min}$ | – | – | – |
| 200 | $30_{max}$ | $80_{max}$ | $30_{max}$ | – |
| 200 | – | $65_{min}$ | – | – |

### 7.3.3   Passivation of Pentaerythritol Tetranitrate

Passivation of PETN is to cover the refined PETN with a layer of passivating reagent, such as wax oil yellow soluble, wax oil red soluble, to reduce the sensitivity of PETN. In the method, water is first added to round passivating machine equipped with jacket and stirring equipment. After stirring is started, refined PETN is added and heated up to 95 °C above, followed by the addition of 0.2% of SOAP flakes. Then, melted passivating reagents that are heated to 90 °C above are added, and kept for 20–60 min at 95–99 °C before the mixture is cooled down to 80 °C. Then, water is added to the machine to cool down at 45 °C or lower, and filter is added to remove passivated wastewater. After the wastewater removal and filtration, the as-obtained crude PRTN is sent to dry, and the drying temperature is the same as nonpassivated purified PETN, which is 55–70 °C.

### 7.3.4  Influence Factors in Nitric Acid Method to Prepare Pentaerythritol Tetranitrate

(1) Effects of nitric acid concentration and the loading ratio

Production practice of PETN has proved that the nitrating rate of pentaerythritol with nitric acid is very fast. When the nitric acid concentration exceeds 80%, esterification reaction can be carried out completely and the product is PETN. When the nitric acid concentration is 60–80%, violent oxidation reaction will occur. When nitric acid concentration is lower than 60%, PETN cannot be obtained. Therefore, concentrated nitric acid is used in esterification, and the nitric acid concentration should be not less than 80% after the nitration is completed.

When the melting point of pentaerythritol is 249.2 °C, the concentration of nitric acid is 96.71% ($N_2O_3$ content is 0.87%), and nitration temperature is 19–20 °C, effects of different feeding ratios on the melting point and yield of product are listed in Table 7.16.

As listed in Table 7.16, nitric acid feeding ratio is more than 5; reaction results, products quality, and the yield are relatively good. When the feeding ratio falls down to 4.2:1, nitration reaction is still stable, product yield and its melting point begin to decrease significantly, the nitration smoke is increased, and its oxidation is enhanced. When the feeding ratio continues to decrease, the abovementioned phenomenon is further increased, the yield falls to 90%, the product is light green, white viscous material is found in the waste acid, the product is very unstable and can quickly decompose with large amount of smoke, and its color turns from yellow

**Table 7.16** Relationship between material feeding ratio and the yield and quality of PETN in pentaerythritol nitration

| Feeding ratio of nitric acid over pentaerythritol | Nitric acid (%) | Product yield (%) | m.p. (°C) | Waste acid component (HNO$_3$ %) |
|---|---|---|---|---|
| 4.97 | 159 | 98.3 | 136.8–140.7 | 78.77 |
| 5.0 | 159 | 97.5 | 137.1–140.2 | 80.78 |
| 4.52 | 136 | 97.8 | 137.2–140.2 | 79.43 |
| 4.49 | 134 | 97.4 | 138.5–140.2 | 78.08 |
| 4.19 | 119 | 97.4 | 137.1–139.9 | 76.87 |
| 4.18 | 119 | 97.7 | 138.1–140.1 | 75.06 |
| 4.21 | 119 | 98.0 | 137.3–140.8 | 76.64 |
| 3.93 | 106 | 93.6 | 135.5–139.8 | 71.63 |
| 3.93 | 106 | 94.8 | 136.5–139.9 | – |
| 3.93 | 106 | 93.9 | 135.9–139.6 | – |
| 3.73 | 95 | 89.3 | 135.5–139.9 | 66.60 |
| 3.75 | 95 | 89.5 | 136.1–139.4 | 67.82 |
| 3.71 | 95 | 89.2 | 136.3–139.9 | 65.34 |

**Table 7.17**  $NO_2$ content in nitrating reagent on the yield of PETN

| $NO_2$ content in nitric acid (%) | PETN yield (%) | $NO_2$ content in waste acid (%) |
|---|---|---|
| 0.2 | 97.2 | 0.7 |
| 1 | 97.3 | 2 |
| 2 | 94.2 | 4 |
| 3 | 88.2 | 8.8 |
| 4 | 88.2 | 12.1 |

to green. Therefore, when feeding ratio is not less than 4.2, in order to ensure smooth production, pentaerythritol:concentrated nitric acid of 1:4.5–6 generally is used. The usually used ratio is l:5, with about 140–220% of excessive nitric acid and above 78% of nitric acid concentration in waste acid (usually 78–86%).

The concentration of nitric acid used is 98.7%, chlorine dioxide content is 0.2%, there are 50 g of pentaerythritol and 250 g of nitric acid, and feeding temperature is 18–20 °C. Feeding time is 30 min, and the stirring is continued for 30 min at 20 °C after the feeding. When $NO_2$ content in nitric acid is less than 1%, there is no effect on the yield and stability of product. When $NO_2$ content in nitric acid is greater than 1%, there is an impact on the yield but without effect on its stability. Table 7.17 lists the effect of nitrogen oxides on the nitration results.

(2)  Effect of nitration temperature

When pentaerythritol is nitrated with 97.7% of nitric acid, pentaerythritol melting point at 225–245 °C, feed ratio of 1:5, and results with various nitration temperatures are shown in Table 7.18.

As listed in Table 7.18, at −1 to +l °C, the yield is the highest and product quality is also relatively good, but the temperature control is strict. When pentaerythritol quality is relatively high, the nitration temperature can be increased accordingly. Experiments show that, when pentaerythritol with melting point of 250 °C is used, nitric acid concentration is 97%, feeding ratio is controlled at 1:6, and nitration temperature is controlled at 25–41 °C, the yield of PETN can still reach to 96–97%, and the melting point of raw PETN is above 138.5 °C. Under the same conditions, when reaction temperature is controlled at 19–20 °C, the yield is 97% and the melting point of raw product is over 137 °C. When the nitration temperature of pentaerythritol is over 20 °C, although its effect on the yield of PETN and the quality is very limited, more smoke will produce at a higher nitration reaction temperature during the nitration. At 20 °C, a certain amount of smoke is

**Table 7.18**  Effect of temperature in pentaerythritol nitration on the yield of PETN

| Temperature (°C) | Yield (%) | PETN m.p. (°C) |
|---|---|---|
| −10 to −7 | 71.6 | 119–137.2 |
| −1 to +1 | 98.3 | 126.5–138.5 |
| 12–15 | 96.1 | 126–138.5 |
| 28–31 | 95.7 | 126–138.5 |

released only after the feeding. In order to control nitration reaction to release smoke to air, nitration temperature of PETN production is controlled within 10–22 °C in most countries.

(3)  Effect of pentaerythrit-2-ol content

Pentaerythrit-2-ol is the pentaerythritol impurity that generates hexanitropentaerythrit-2-ol with nitric acid, which affects the thermal stability and explosive performance of PETN. Thus, its content should be controlled strictly, which requires the control on the melting point of pentaerythritol. Production practice proves that, when 5 g of mixture from pentaerythritol with purity of above 99.9% and pentaerythrit-2-ol is nitrated with 97.7% of nitric acid at −1 to 2 °C and nitric acid feeding ratio of 1:9.8, more white stick rubber-like material in the product is generated from mixture with more pentaerythrit-2-ol after the water dilution when the reaction is completed. The white stick resin-like material can be dissolved in concentrated nitric acid. The experiment results are listed in Table 7.19.

With the increase of pentaerythrit-2-ol, the product yield is decreased and the melting point declines. However, some data in literature shows that a small amount of pentaerythrit-2-ol in the raw material (about 2–3%) can improve the crystal size and fluidity of PETN without large effect on the explosion performance. Therefore, less than 5% of pentaerythrit-2-ol hexanitrate in PETN explosive used in industry are allowed generally. The melting point of pentaerythritol raw material is over 240 °C (above 245 °C in most cases). Under the conditions described above, product with melting point at 137–140 °C can be obtained with the crude PETN yield of over 97%. This crude product can meet specifications after the refining.

(4)  Acid remover and crystallizing method in the refining

In order to improve product quality and stability, crude PETN is recrystallized in solvent after washing. The used solvent is usually acetone. The PETN is dissolved in hot acetone, then antacids is added to neutralize the acid remained, and the acid removing reagent can be sodium carbonate, ammonium carbonate, sodium bicarbonate, or ammonium bicarbonate.

However, under heating, ammonium carbonate or bicarbonate can be decomposed into ammonia and carbon dioxide, which go in the reflux condenser along with acetone vapor and then cooled down to generate ammonium carbonate to block the pipe, and then to affect the performance of ventilation equipment.

**Table 7.19**  Effect of pentaerythrit-2-ol content on the yield and mass of raw PETN

| Pentaerythrit-2-ol content (%) | Mass of product (g) | m.p. (°C) |
| --- | --- | --- |
| 0 | 11.5 | 129–139 |
| 10 | 11.4 | 123–138 |
| 20 | 11.1 | 104–135 |
| 30 | 10.8 | 95–133 |

In addition, it can also cause the condensation of acetone as follows:



The produced methyl isobutenyl ketone is very active to react with the generated ammonia from decomposition, then to generate a yellow 4-amino-methyl-pentaketone-2.



This yellow residue in PETN affects the quality and appearance of PETN. Thus, sodium carbonate or bicarbonate is usually used as an acid remover. In addition, aniline, sodium hydroxide, and ammonium hydroxide are also used as acid removers.

## 7.3.5 Waste Acid Treatment in the Production of PETN

Composition of waste acid generated from the nitration of pentaerythritol with concentrated nitric acid to produce PETN varies with different technology methods. The components in the isolated waste acid directly after the separation of PETN were 80–82% of $HNO_3$, 0.5–0.7% of $N_2O_3$, and 1.0–1.5% of nitrates. After PETN was diluted and crystallized out from nitration solution, in the waste acid nitric acid concentration was 45–60% with less than 0.55% of nitrate and a small quantity of nitric oxide. Its treatment methods were also not the same.

If the concentration of waste acid was high, the concentration of PETN, incomplete nitrates, and condensed pentaerythritol nitrate included was high, and the direct enrichment was not safe. Thus, it was needed to stabilize first, and then enrich. Stabilization treatment was to precipitate waste acid in the aluminum tank for more than 24 h in order to chromium nitrate content was decreased to below 0.75%. Then the waste acid flowed over five continuous towers, whose jackets were flushed with steam to heat these tower to 90–100 °C. The suitable amount of water was added into the third tower to let waste acid decompose large amounts of nitrogen oxides. The strong oxidation causes the complete decomposition of a small amount of nitrate that was not completely decomposed, in the waste acid in the first

or second towers. After this treatment, the waste acid concentration was 65–70% almost without nitrate, and it could be sent to concentrate.

Because the diluted acid concentration after the nitration is low and contents of PETN and impurities are low, the treatment of waste acid is relatively simple and safe, in which the waste acid can be concentrated safely after it is only needed to store at room temperature for 3–5 days or is kept at relatively high temperature for a few minutes. The generally used method is to precipitate the waste acid first for a certain period of time. Then, the waste acid was sent into ferrosilicon casing thermal decomposition device to heat to around 90–100 °C, in which its flow is controlled to make waste acid to stay in thermal decomposition device for about 20–30 min before its entering into ferrosilicon casing cooling device. After it is cooled down to 25–30 °C, it flows in the storage tank. Because the ester content in waste acid after this treatment is less than 0.1%, the waste acid can be pumped into nitric acid concentrating workshop to concentrate separately or with diluted nitric acid and the RDX waste acid.

During the thermal stability treatment, waste acid produces nitric acid vapor and nitrogen oxide gases, which are separated through vapor–liquid separator before entering to the sieve plate absorption tower with the nitric acid smoke from nitrating machine, maturing machine, diluting machine, and filter. After the water absorption, diluted nitric acid with more than 40% concentration is produced and then concentrated.

## 7.3.6  Solvent Recovery

Recycling method is determined according to the refining process of PETN. If it is mother acetone liquor from direct cooling crystallization method, it can be reused after it is mixed with a proper proportion of refresh acetone. According to the reported results, after it can be used for three times, the remained is distilled and recovered. While the mother liquor from direct dilution crystallization method is mixed and reused with the washing water from the purification, the acid is distilled until its concentration is 94–98% to reuse in the PETN purification.

The distillation method in detail is the waste acetone mother liquor, and washing water from purification are mixed together after a certain period of precipitation to obtain a mixture with about 20–40% of acetone, which is preheated to 60–85 °C in the slot preheating tank before entering into the distillation tower whose temperature at the bottom is kept at 95 °C above. The steam enters into the distillation column, whose temperature is kept at 50–57 °C on the top, and the acetone gas distilled out from the tower is condensed into liquid, whose density is determined in order to control its concentration above 94%. If temperature on the top of tower is over the regulated value, acetone density is not qualified, and all acetone should be refluxed until it is qualified to discharge. According to the quality control, the refluxing ratio is controlled accordingly in order to maintain the normal operation.

Acetone from PETN refining processes can be recovered through adsorption, in which the gas goes through the adsorption tower at room temperature, and then is adsorbed with activated carbon at 45 °C, and directly heated to 130 °C with steam after the adsorption is saturated. Then, the obtained desorption liquid is distilled with mother acetone liquid together to concentrate. After desorption, the adsorption tank is dried at about 120 °C with hot air first, then cooled down to 35 °C, and reused in the following.

## 7.4   Other Preparation Technologies of Pentaerythritol Tetranitrate [17–19]

### 7.4.1   Nitric–Sulfuric Mixed Acid Process to Produce PETN

Nitric–sulfuric mixed acid process to nitrate alcohol to produce the corresponding nitrate is a common reaction as shown in Fig. 7.11.
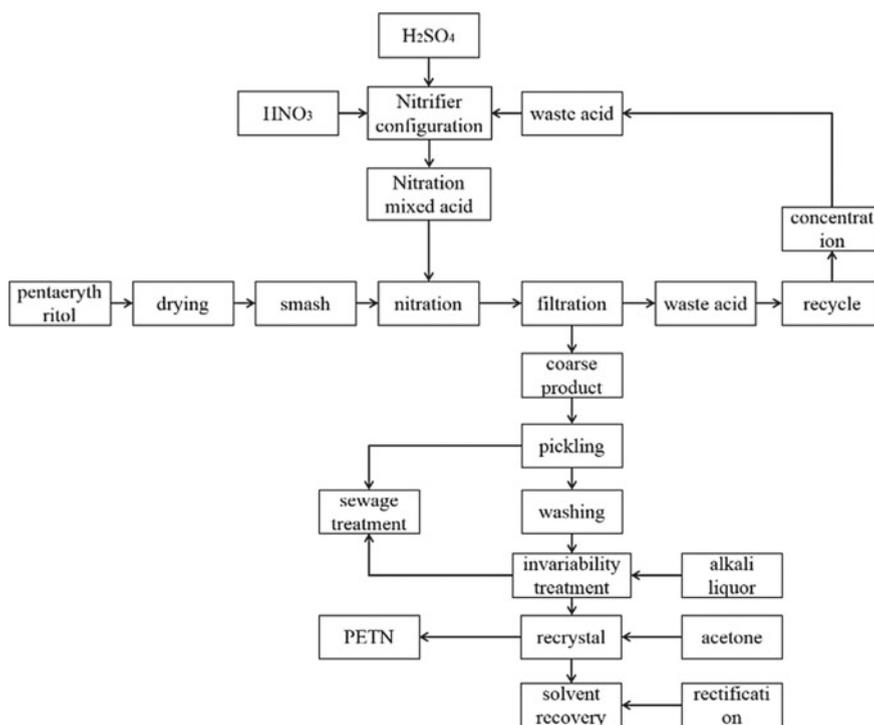


Fig. 7.11  Process of nitric–sulfuric mixed acid method to prepare pentaerythritol tetranitrate

With pentaerythritol as raw materials, it is nitrated with nitric–sulfuric mixed acid and after it is dried and crushed. After the filtration, water washing, and stability treatment, the crude product is obtained. After the recrystallization and purification, the white crystal is pentaerythritol tetranitrate with a final yield of 80%. Preparation of pentaerythritol tetranitrate prepared with this method is not easy to passivate and its stability is poor.

## 7.4.2   Other Preparation Technologies to Prepare Pentaerythritol Tetranitrate

(1)  Sulfuric acid precipitation method

Concentrated nitric acid with 6 times of pentaerythritol quality at 55 °C is used to nitrate pentaerythritol, and then concentrated sulfuric acid with 6–7 times of pentaerythritol quality is added to precipitate PETN completely.

(2)  Sulfonation nitration method

Pentaerythritol is dissolved into the concentrated sulfuric acid first to sulfonate, where pentaerythritol bisulfonate is formed.

$$C(CH_2OH)_4 + 2H_2SO_4 \rightarrow C(CH_2OSO_3H)_2(CH_2OH)_2 + 2H_2O$$

After the sulfonation, a certain amount of concentrated nitric acid is added to nitrate pentaerythritol to produce PETN.

$$C(CH_2OSO_3H)_2(CH_2OH)_2 + 4HNO_3 \rightarrow C(CH_2ONO_2)_4 + 2H_2SO_4 + 2H_2O$$
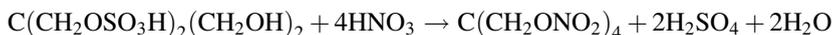
Due to the presence of sulfuric acid, the above reaction is conducted in two steps and the reaction heat is released in two times; thus, the nitration can occur at a relatively high temperature (50–60 °C) because the cooling and refrigerating equipment is not required. This reaction is suitable for pentaerythritol with a relatively low quality (such as that with a melting point of 190–195 °C). Particle size of the obtained crude products from this reaction is too thin to filter. And impurities in the crude product are the mixture of nitrate sulfate with poor stability. Therefore, impurities are removed completely during the safety treatment.

(3)  nitration with nitric/sulfuric mixed acid

At 30 °C, the mixed acid is used to nitrate pentaerythritol having a melting point of 257–258 °C, and the amount of nitric acid in the mixed acids is 6 times of that pentaerythritol. After the nitration, the waste acid is diluted to that with total acidity

**Fig. 7.12** Region with the highest yield of PETN in the mixed acid nitration
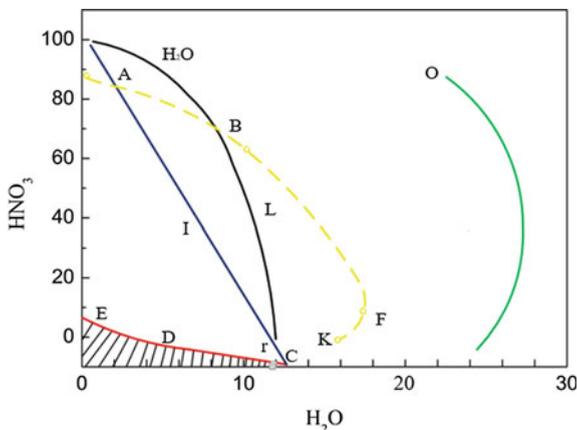
(in terms of sulfuric acid) of 20–30%, and the yield of PETN is up to 97.5%. The mixed acid component to get the highest yield is shown in Fig. 7.12.

As shown in Fig. 7.12, mixed acid between BF and OK can generate the highest yield (BF represents the mixed acid component, and OK represents the waste acid component). Curve ALC is the spectrum-measurable limit line of nitryl ion, and shadow under the EDC is the region where all nitric acid is ionized into nitryl ions. In order to get the highest yield, the mixed acid should have a certain amount of water, and this water content is related to the content of nitric acid in the mixed acids. If nitric acid in mixed acids is 10%, the optimum water content is 13–21%. In addition, an appropriate ratio between nitric acid and sulfuric acid should be kept. Otherwise, an ester mixture or sulfate will be produced.

Because six equivalents of nitric acid are needed to nitrate every pentaerythritol and mixed acid consumption is very large, therefore, this method has no practical value.
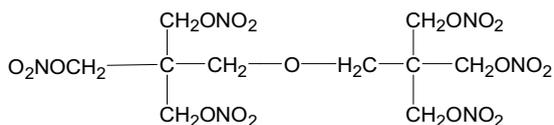
## 7.5 Other Methods to Prepare Pentaerythritol Nitrate [17–19]

### 7.5.1 Pentaerythritol Hexanitrate

Pentaerythrit-2-ol hexanitrate is an extremely strong explosive, and many of its chemical properties are similar to those of PETN. And its code is DPEHN.

Chemical formula: $C_{10}H_{16}N_6O_{19}$;
Structural formula:

$$O_2NOCH_2 \underset{\underset{CH_2ONO_2}{|}}{\overset{\overset{CH_2ONO_2}{|}}{C}} CH_2 \underset{}{} O \underset{}{} H_2C \underset{\underset{CH_2ONO_2}{|}}{\overset{\overset{CH_2ONO_2}{|}}{C}} CH_2ONO_2$$

Relative molecular weight: 523.8;

Oxygen balance: −27.49% (calculated according to $CO_2$);

Nitrogen content: 16.04%; and

Density: 1.63 g/cm$^3$.

Crystalline and melting point: The pentaerythrit-2-ol hexanitrate is white crystal with two crystal forms. The melting point of its stable form is 75 °C, which belongs to long cubic system with a sheet shape. Its unstable form has a melting point of 72.5 °C.

Solubility: The solubility of pentaerythrit-2-ol hexanitrate in acetone is larger than that of PETN, which can be used to separate these two nitrates. Its solubility in concentrated nitric acid is also larger than that of PETN (Table 7.20), which can be used to control the purity of crude PETN during the manufacture of PETN through controlling the concentration of waste acid.

The explosion performance of pentaerythrit-2-ol hexanitrate is worse than that of PETN, and its stability is also worse than that of PETN, but its mechanical sensitivity is higher than that of PETN. According to explosion properties and stability of PETN, it is harmful impurities of PETN. However, when acetone is used as a solvent to purify PETN, a small amount of pentaerythrit-2-ol hexanitrate can improve the shape and fluidity of PETN crystal, but it shall not exceed 5% in PETN.

Because industrial pentaerythritol contains pentaerythrit-2-ol, pentaerythrit-2-ol hexanitrate is the by-product during the manufacture of PETN. After the nitration of pentaerythritol, the content of pentaerythrit-2-ol hexanitrate in the crude products filtered out depends on the concentration of waste acid. The contents of pentaerythrit-2-ol hexanitrate in PETN with different treatment methods are listed in Table 7.21.

Crude PETN is added into an equal amount of acetone to dissolve. After a certain time, the undissolved PETN was filtered out. In the solution, pentaerythrit-2-ol hexanitrate content is more than that of PETN. Water is slowly added to this solution to separate the solution into two layers, in which the upper is a diluted acetone and the lower is pentaerythrit-2-ol hexanitrate solution with water

**Table 7.20** The solubility of DPEHN in nitric acid (25 °C, g/100 g solvent)

| Concentration of nitric acid (%) | PETN | DPEHN |
| --- | --- | --- |
| 97.7 | 2.17 | – |
| 91.8 | 1.28 | – |
| 81.7 | 0.81 | 4.70 |
| 72.8 | 0.55 | 1.60 |
| 60.5 | 0.14 | 0.72 |

**Table 7.21** DPEHN contents in PETN with different treatment methods

| Purity of pentaerythritol (%) | Treatment method | Yield (%) | m.p. (°C) | DPEHN content (%) | The final PETN content (%) |
|---|---|---|---|---|---|
| 86.3 | Nitrating solution is diluted | 93.9 | 117 | 15.9 | 84.1 |
| 86.3 | Nitrating solution is not diluted, and product is washed with water | 90.5 | 126–140 | 10.6 | 89.4 |
| 86.3 | Nitrating solution is not diluted, and product is washed with 97% nitric acid | 80.2 | 131–138.5 | 1.0 | 99 |

and acetone. After the separation of the two layers, the upper layer is treated with alcohol and the pentaerythrit-2-ol hexanitrate is precipitated out.

Another method is the direct nitration of pentaerythritol with concentrated nitric acid.

Because of the high mechanical sensitivity and relatively strong explosive power of pentaerythrit-2-ol hexanitrate, it can be used as a component of primer or igniter.
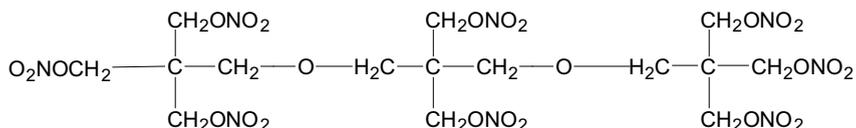
## 7.5.2   Pentaerythrit-3-ol Octanitrate

Pentaerythrit-3-ol octanitrate is a high nitrogen-containing derivative of pentaery-thritol and a white crystal with four crystal forms. Its code is TPEON.

(1)  Properties of pentaerythrit-3-ol octanitrate

Formula: $C_{15}H_{24}N_8O_{26}$;
Structural formula:



Relatively molecular weight: 732;
Oxygen balance: −34.97 (calculated according to $CO_2$); and
Nitrogen content: 15.31%.
Melting point: Melting points of TPEON with different crystalline morphologies are shown in Table 7.22.
Solubility: Pentaerythrit-3-ol octanitrate cannot be dissolved in water, but is soluble in ethanol and chloroform, and easily soluble in hot benzene and acetone.

Crystal I is stable with a crystalline density of 1.58 g/cm$^3$.

**Table 7.22** Melting points of TPEON with different crystal types (°C)

| I | II | III | IV |
|---|---|---|---|
| 83 | 76–77 | 68–70 | 64–65 |
| 83.3 | 74.6 | 72.1 | 69.0 |

**Table 7.23** Melting point of DPEHN-TPEON

| TPEON (%) | 100 | 95 | 90 | 50 | 20 | 10 | 0 |
|---|---|---|---|---|---|---|---|
| DPEHN (%) | 0 | 5 | 20 | 50 | 80 | 90 | 100 |
| m.p. (°C) | 83 | 68 | 73 | 60 eutectic mixture | 63 | 69 | 73 |

The melting point of the mixture of pentaerythrit-2-ol hexanitrate with pentaerythrit-3-ol octanitrate is listed in Table 7.23.

The explosion properties of pentaerythrit-3-ol octanitrate are listed in Table 7.24.

(2) Preparation of pentaerythrit-3-ol octanitrate

With stirring and cooling, 220 g of pentaerythrit-3-ol (its purity is over 99%) is added to 1760 g of 99% nitric acid, in which the amount of nitric acid is 6.3 times of the theoretical amount. The material feeding temperature is −25 to 0 °C, and the material is continuously stirred to react for 1 h at 0–5 °C. The reaction mixture is poured into crushed ice with the volume of no less than 8 times that of the reaction mixture. After left overnight, the product in the water is crushed, then filtered, washed with water, and then stirred with 1% ammonium carbonate with a solution having the amount of 5 times. After the filtration, it is washed with water again until

**Table 7.24** Explosion properties of PETN, DPEHN, and TPEON

| Property | PETN | DPEHN | TPEON |
|---|---|---|---|
| Oxygen balance (%) | −10 | −25 | −35 |
| Impact sensitivity, falling height of 2 kg drop hammer (the lower limit) (cm) | 17 | 14 | – |
| Picatinny Arsenal, falling height of 2 kg drop hammer (the lower limit) (cm) | 15 | 10 | 23 |
| Explosion point (5 s of delay) (°C) | 225 | 255 | 225 |
| Vacuum stability test (ml g$^{-1}$ 40 h$^{-1}$) 100 °C 120 °C | 0.5 11 | 3.7 11 | 2.45 specifically purified product 1.94 |
| Explosion heat (kcal kg$^{-1}$) | 1385 | 1092 | 1085 |
| Power (lead expansion, TNT is 100) | 173 | 17328 | – |
| Explosion rate (m s$^{-1}$) | ($\rho$ = 1.70) 8300 | ($\rho$ = 1.59) 7410 | ($\rho$ = 1.56) 7650 |

the solution is neutral (determined with litmus). The product is dried in air to obtain 422.3 g of pentaerythrit-3-ol octanitrate with a yield of 97.5% and melting point of 73–74 °C, which can be recrystallized with chloroform.

Because the low melting point of pentaerythrit-3-ol octanitrate is low, it can be used as the coating reagent of ammonium nitrate and PETN, or plasticizer of nitrocellulose.
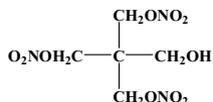
### 7.5.3   Nitrates of Pentaerythritol Derivatives

(1)  Pentaerythritol trinitrate

Its code is Petrin.
Molecular formula: $C_5H_7N_3O_{10}$;
Relatively molecular weight: 271;
Structural formula:

$$O_2NOH_2C - \overset{\overset{\displaystyle CH_2ONO_2}{|}}{\underset{\underset{\displaystyle CH_2ONO_2}{|}}{C}} - CH_2OH$$

Oxygen balance: −27% (calculated according to $CO_2$ generated);
Nitrogen content: 15.5%;
Melting point: 26–28 °C (white solid with low melting);
Density: 1.54 g/cm;
Impact sensitivity: lower than that of PETN;
100 °C vacuum stability test: the amount of gas released is 2.54–5.69 ml/g 40 h;
Explosion heat: 5037.54 kJ/g; and
Usage: It can be used as explosive, propellant or low melting point components in gunpowder.

The earliest method to prepare pentaerythritol trinitrate is to add pentaerythritol to 80% nitric acid, followed by dropwise addition of 80% sulfuric acid, in which the temperature is kept at 0–5 °C. After the temperature is kept for 2.5 h, the reaction mixture is poured into cold water, and the product is filtered out that contains PETN. Filter cake is dissolved in acetone and neutralized with added ammonium carbonate, and then water is added to precipitate PETN. Pentaerythritol trinitrate is remained in the filtrate. After the removal of solvent under vacuum, the average yield of trinitrate is 40%, and this is called Method A.

In another method, the reaction mixture is diluted with water after the reaction followed by dichloromethane extraction. The organic phase is separated, and the waste acid is neutralized with sodium bicarbonate solution. After the removal of solvent under vacuum, pentaerythritol trinitrate is directly obtained with a yield of about 50%. And the quality of product is much better than the Method A. This method is known as Method B.

Now, Method C is generally used to manufacture such products. Method C is similar to the above method except that methylene chloride (equal to the sum of reactants) is added before sulfuric acid. After the reaction, solvent is separated, and then dichloromethane is used to extract for one or several times. The extract liquids are merged together to neutralize and then concentrate. Because of the large amount of solvent, PETN in the concentrated solution should be crystallized and filtered out, and finally the solvent is vapored. The yield of pentaerythritol trinitrate is 65–67%.

(2)  Trinitroxypentaerythritol acrylate (Petrin Acrylate)

Molecular formula: $C_8H_{11}N_3O_{11}$;
Relatively molecular weight: 324.9;
Structural formula:

$$H_2C{=}HC{-}O_2CH_2C{-}\underset{\underset{CH_2ONO_2}{|}}{\overset{\overset{CH_2ONO_2}{|}}{C}}{-}CH_2ONO_2$$
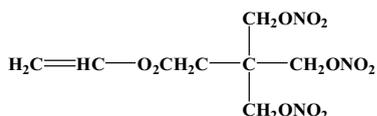
Oxygen balance: −51.7% (calculated according to $CO_2$ generated);
Nitrogen content: 12.9%;
Density of the white solid: 1.562 ($d_4^{20}$);
Melting point: 78–79 °C;
Formation enthalpy: −52231.75 J/g;
Explosion heat: 2971.5 J/g;
Explosion point: 168 °C with the heating rate of 5 °C/min;
Impact sensitivity: relatively low, its 5000 g hammer falling height is 43 cm;
Thermal stability: 35 min (1.3 g sample) in Abel test at 82 °C with good thermal stability;
Specific impulse: the specific impulse of a single base propellant from it is 214 s;
Burning rate: 5 mm/s. With the addition of oxidants, the specific impulse and the burning rate can be increased; and
Solubility: easily soluble in acetone and ethyl acetate, soluble in ethanol, diethyl ether and benzene, and insoluble in water.

As listed in Table 7.25, when trinitroxypentaerythritol acrylate is used in propellants and the propellant density is 1.3 g/cm$^3$, its specific impulse is 238 s.

**Table 7.25**  Trinitroxypentaerythritol acrylate

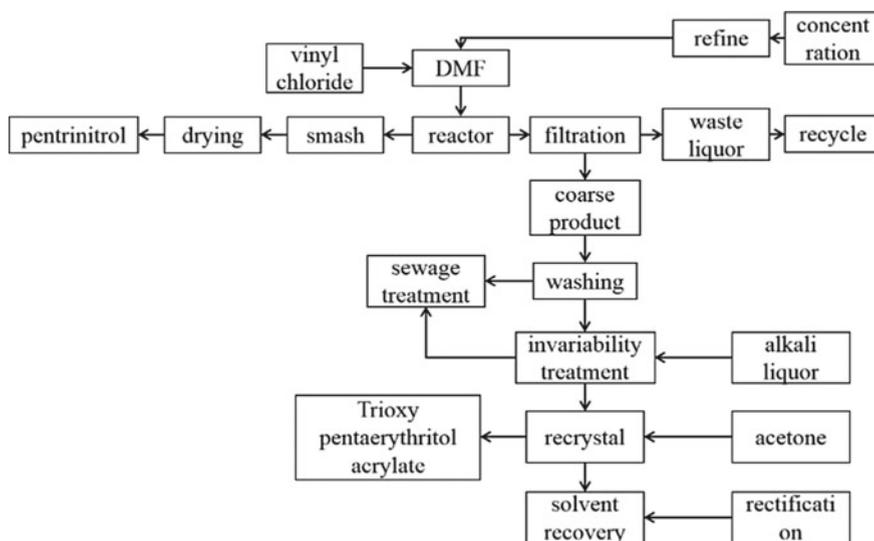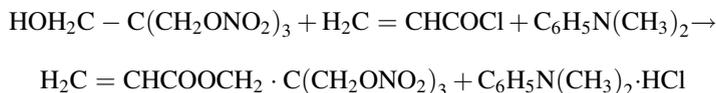| Component | Component content (%) |
|---|---|
| Petrin Acrylate (purity > 97%) (adhesive reagent) | 34.3 |
| Triethylene glycol dinitrate (plasticizer) | 11.8 |
| Ethylene glycol diacrylate (crosslinker) | 3.9 |
| Ammonium perchlorate (oxidant) | 51.0 |
| Hydroquinone (inhibitor) | 0.014 |

**Fig. 7.13**  The preparation process of trinitroxypentaerythritol acrylate

Trinitroxypentaerythritol acrylate can be polymerized into the polymer with a specific density of $d_4^{20}$ 1.492 g/cm$^3$, which is insoluble in all solvents, but can be swollen in acetone and ethyl acetate.

The main reaction to prepare trinitroxypentaerythritol acrylate is

$$HOH_2C - C(CH_2ONO_2)_3 + H_2C = CHCOCl + C_6H_5N(CH_3)_2 \rightarrow$$

$$H_2C = CHCOOCH_2 \cdot C(CH_2ONO_2)_3 + C_6H_5N(CH_3)_2 \cdot HCl$$

In this reaction, there is white smoke released when vinyl chloride is used. The process to prepare pentaerythritol acrylate from the reaction between pentaerythritol trinitrate and vinyl chloride is shown in Fig. 7.13.

(3)  Nitrates of other pentaerythritol derivatives

Other mixed nitrates of pentaerythritol are listed in Table 7.26, and most of them are explosive.

**Table 7.26** Pentaerythritol derivatives

| Compound | m.p. (°C) |
| --- | --- |
| Trinitroxypentaerythritol formate | 62–63 |
| Trinitroxypentaerythritol acetate | 87–88 |
| Trinitroxypentaerythritol propionate | 39–40 |
| Trinitroxypentaerythritol pentanoate | – |
| Trinitroxypentaerythritol caproate | – |
| Trinitroxypentaerythritol chloroacetate | 52–63 |
| Trinitroxypentaerythritol oxalate | 97–100 |
| Trinitroxypentaerythritol pentanedioate | 87–88 |
| Trinitroxypentaerythritol butyrate | 88–90 |
| Trinitroxypentaerythritol dimethylpentanedioate | 71.5–72.0 |
| Trinitroxypentaerythritol oxalate | 82–83 |
| Trinitroxypentaerythritol benzoate | 89–90 |
| Trinitroxypentaerythritol phthalate | 125.0–125.5 |
| Trinitroxypentaerythritol o-nitrobenzoate | 94–95 |
| Trinitroxypentaerythritol m-nitrobenzoate | 102–103 |
| Trinitroxypentaerythritol p-nitrobenzoate | 106–108 |
| Trinitroxypentaerythritol 3,5-dinitrobenzoate | 109–110 |
| Trinitroxypentaerythritol 4-chloro-3-nitrobenzoate | 112–113 |
| Trinitroxypentaerythritol benzenesulfonate | 116–117 |
| Trinitroxypentaerythritol p-methylbenzenesulfonate | 97–100 |
| Trinitroxypentaerythritol hydrochloric acid ester | 65–66 |
| Trinitroxypentaerythritol hydrobromic acid ester | 89–90 |
| Trinitroxypentaerythritol hydrogen iodide ester | 108.5–110.5 |
| Dinitroxypentaerythritol hydrochloric acid ester | – |
| Dinitroxypentaerythritol monohydrobromic acid ester | – |
| Dinitroxypentaerythritol bihydrobromic acid ester | 75 |
| Nitroxypentaerythritol trihydrobromic acid ester | 58–60 |

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