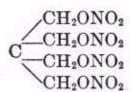
# NITROPENTAERYTHRITE (PENTAERYTHRITE TETRANITRATE)



Of the solid esters of nitric acid, nitropentaerythrite has the most promise of practical use because in contrast to its closely related homologues, erythrite tetranitrate and nitromannite, it has a high chemical stability and is not too sensitive to mechanical influences.

It has been proposed as an addition to smokeless powders<sup>33</sup> to raise their flammability -and ease of combustion, and as a filler for blasting caps in place of or in mixture with tetranitromethyl aniline (tetryl) or trinitrotoluene,<sup>34</sup> where on account of its energy content which is higher than that of the aromatic nitrocompounds it would exert a greater initiating effect. Its disadvantage in this connection has been up to the present time a too great sensitiveness on pressing.

Furthermore, according to Jean Harle, Rouen, German patent 336280 (1914), it may serve as a filler for cordeau detonant, either alone or mixed with fusible aromatic nitrocompounds.

For general use as an explosive or explosive component, for example in place of nitroglycerine for improving the ease of detonation, the relatively high price has been a disadvantage up to the present time, because both the synthesis of the raw material and the conversion into the ester are not sufficiently developed.

# PENTAERYTHRITE, C(CH<sub>2</sub>OH)<sub>4</sub>

This is a quadrivalent alcohol formed by the condensation of 1 molecule of acetaldehyde with 4 molecules of formaldehyde in the presence of slaked lime, forming formic acid as a by-product, in dilute aqueous solution:

$$8CH_2O + 2CH_3CHO + Ca(OH)_2 = 2C(CH_2OH)_4 + Ca(HCOO)_2$$

the synthesis was first described by Tollens and Wigand in 1891, and Rave and Tollens<sup>36</sup> in 1893. Stettbacher<sup>37</sup> described it, at length. Theoretically 100 parts of acetaldehyde give 309 parts of pentaerythrite and 104 parts of formic acid with 273 parts of formaldehyde and 40 parts of water.

According to Stettbacher about 65 per cent of theory was obtained in preparing the crude product.

The process is as follows: 1940 grams of formadehyde, or 4.85 kg. of a 40 per cent solution, and 600 grams of acetaldehyde (1 kg. of 60 per cent) commercial aldehyde) are dissolved in 90 liters of water containing 1600 grams of slaked lime in suspension. The solution is in a wooden cask which can be closed, since no pressure changes are encountered in the reaction. The cask is rolled about several times a day in order to bring the lime into sufficient contact with the solution. After about three weeks the reaction is complete. The solution is syphoned or filtered off and the calcium formate precipitated by oxalic acid, the alkaline reaction changing to acid and the brown color changing to yellow. The oxalate is allowed to settle, and the water is driven off under diminished pressure. The crystals obtained on cooling are centri-fuged or drained from the syrupy mother liquor. A mixture like the above gives about 1200 grams of crude pentaerythrite having a melting point of 235 to 240°C. For further purification the brown, crude product is stirred with a little alcohol and sucked dry on a filter, leaving the pentaerythrite perfectly white, and after several recrystallizations from water an absolutely pure product is obtained. For nitration this recrystallization is not necessary. Pure pentaerythrite forms tetragonal crystals melting at 253°C. It dissolves in 18 parts of water at 15°C. An improvement in the production of pentaerythrite is disclosed in German patent 298932 (1914), issued to the Rhein.-Westf. Sprengstoff A.-G., in which the precipitation of the calcium formate by oxalic acid or sulphuric acid, with the subsequent difficult recovery of the free formic acid, is avoided, and instead the calcium formate, whose solubility changes very little with change of temperature as compared to the pentaerythrite, is thrown out by the proper hot concentration and so obtained as a by-product, filtered hot, and then on cooling the pentaerythrite is separated by crystallization.

For the similar synthesis of enneaheptite from acetone and formaldehyde by water and slaked lime see Tollens; *Ann.* 289, page 47.<sup>18</sup>

## *Nitropentaerythrite*

Preparation.<sup>39</sup> Mixed acid is not suitable for the nitration of this compound. On adding the latter to mixed acid the finely divided tetranitrate is not obtained, but instead a tough product difficult to purify and of low stability. On the other hand, pentaerythrite dis-solves in a large excess of concentrated nitric acid, with partial esterification, which is completed by the gradual addition of concentrated sulphuric acid. One hundred grams of 94 per cent nitric acid at 25 to 30°C. dissolves only about 4 to 5 grams of pentaerythrite to a clear solution.

If more is added, or if the acid is too cold the ester precipitates out as crystals. If the temperature is allowed to rise too high, in order to get more into solution, the charge takes fire very easily. It is best to operate as follows:

One hundred grams of finely powdered pentaerythrite is gradually dissolved in 400 cc. of nitric acid of a specific gravity of 1.52, with good cooling to 25 to 30°C. Theoretically 185.3 grams of HNO3 is required, so that the above is a triple excess. Toward the end of the nitration the difficultly soluble nitrate partly separates. By the gradual addition of 400 cc. of concentrated sulphuric acid of a specific gravity of 1.84 and cooling, it is completely precipitated. It is allowed to stand for an hour and sucked dry on a filter, the acid being displaced first with a 50 per cent sulphuric acid and then with water. The last traces of free acid are removed by washing with a dilute soda solution. The theoretical yield is 232.5 grams. The yield of crude product amounts to 85 to 90 per cent of theory, according to the degree of purity of the pentaerythrite used. The crude product is not sufficiently stable chemically, since it still encloses traces of acid which cannot be separated by heating with water, even when alkalies are added. The iodine test is only a few minutes. For complete purification it is dissolved in a little hot acetone, some ammonium carbonate added, and the solution filtered through a hot water filter into twice its volume of 90 per cent alcohol, precipitating absolutely pure nitropentaerythrite in fine needles. The yield of the pure product is about 90 per cent of the crude used, and about 85 per cent of theory.

*Properties*. Pure nitropentaerythrite melts at 138.5°0. according to Will,<sup>40</sup> forms well defined crystals, and has an extraordinary chemical stability. It is insoluble in water, slightly soluble in alcohol and ether, and readily soluble in acetone. It withstands the iodine test at 80°C. for hours and can be stored at temperatures of 50 to 100°C. for a long time without decomposition.

As regards its chemical stability it exceeds its homologs, nitro-erythrite and nitromannite, considerably, as well as nitroglycerine and nitrocellulose, probably due to its peculiar molecular structure. In the polyvalent, aliphatic nitric esters having a chain structure of the carbon atoms, the chemical stability as a rule diminishes with the length of the carbon chain. Thus nitroglycerine is less stable than nitroglycol, and nitroerythrite and nitromannite less stable than nitroglycerine, while the still higher molecular nitrocellulose assumes a special position in which it must be remembered that it is not a pure ester and that not all of its hydroxyl groups can be esteri-fied by nitric acid. The highest nitrated nitrocellulose is a mixture of hexa- and pentanitrocellulose, with about 13.5 per cent nitrogen, containing 5 to 6 nitric acid radicals to a chain of 12 carbon atoms, while with nitroglycerine containing 18.50 per cent nitrogen and nitromannite with 18.58 per cent there is a nitric acid radical to each carbon atom. The lower stability of nitroglycerine, and particularly nitromannite, as compared to nitrocelluose, can therefore be explained by the greater accumulation of nitric radicals attached to the carbon chain.

A peculiar position is assumed by nitropentaerythrite as regards stability. It contains 4 nitric acid radicals to 5 carbon atoms, and 17.74 per cent nitrogen. Stettbacher<sup>41</sup> not improperly attributed this phenomenon to the peculiar position of the 4 methoxyl groups about the central quaternary carbon atom.

Above the melting point decomposition sets in. A small amount of nitrogenous gases begins to split off after one-half an hour at 140 to 145°C. In a bath of Wood's metal 0.2 gram of nitropentaerythrite at 175°C. and above gives off light yellow vapors, from 190°C. and up red fumes, and at about 205°C. there is a weak deflagration.

Flammability. Nitropentaerythrite is difficult to ignite. It does not take fire

from the spit of a fuse or the flame of a match. If ignited by a greater heat than this it bums quietly when in small quantities.

Stability on heating. Pure nitropentaerythrite can be stored in covered weighing bottles at 75°C. for weeks without decomposition. Even after several days at 90°C. there is no acid reaction, and the loss in weight is only 0.1 per cent.

Sensitiveness to mechanical effects. Nitropentaerythrite is relatively insensitive to friction. On rubbing in a rough porcelain mortar there is a loud crackling but no real detonation. On the other hand, the sensitiveness to shock is relatively high, although less than that of nitroglycerine and guhr dynamite. Under the 2 kg. weight nitropentaerythrite detonates at 20 cm. fairly regularly with a loud report, but only occasional detonations occur at 15 cm. and 10 cm.

Explosive character and strength. In view of the small oxygen deficiency of 10.1 per cent and the probable decomposition according to the following equation:

$$C(CH2ONO2)4 = 3CO2 + 2CO + 4H2O + 2N2$$

a fairly high explosive strength would be expected. The calculated heat of explosion of nitropentaerythrite, based upon a heat of formation of 131.2 Calories, is 1522.5 Calories per kilogram with water liquid, and 1403.2 Calories per kilogram with water gaseous, or 95 per cent of that of nitroglycerine. In the lead block 10 grams under sand tamping gave an expansion of about 500 cc. Nitropentaerythrite thus belongs to the strong explosives.

- 10 grams liquid nitroglycerine under water tamping...... about 600

The expansions are about as 93.3:100. Their relation therefore agrees rather well with their energy contents, or 1403.2:1485 as 94.5:100.

Moreover the sensitiveness to initial impulse is extremely high, higher than that of the highly nitrated aromatic nitrocompounds like tetryl (tetranitromethylaniline), so that nitropentaerythrite has been considered as a charge of blasting caps in place of aromatic nitrocompounds. For example, tetryl requires more than 20 mg. of lead azide to ensure its detonation, while 1 mg. of lead azide suffices for nitropentaerythrite.

The very high sensitiveness of nitropentaerythrite toward initial impulse is also shown by the fact that the weakest blasting cap, a No. 1, gives almost the same expansion in the lead block with this explosive as does the usual No. 8 cap. (See table 18.)

*Lead crusher test.* Nitropentaerythrite gives an extraordinary crushing effect on the lead cylinder. One hundred grams of it compresses the cylinder 22 mm. and deforms it considerably.

*Velocity of detonation.* The velocity of detonation is also very high. The author found, in an iron pipe 25 mm. internal diameter, at a density of 0.85, i.e., slight compression of the nitropentaerythrite, a velocity of 5330 meters per second.

**TABLE 18**Comparison of expansion by different blasting caps

	WITH NO. 8 CAP	WITH NO. 1 cap
	cc.	cc.
Net expansion	500	460
Deduction for the cap	30	5
	470	455

On the other hand Kast found with highly compressed material of a density 1.62 more than 8000 meters per second, or a velocity of detonation of the highest order.<sup>42</sup>

- <sup>32</sup> German patent 294755 and Swiss patent 74333, on the preparation of nitromethane from NaNOa and sodium methylsulphate.
- <sup>33</sup> German patent 81664 (1894), *Rhein.-Westf. Sprengstoff A..-G.*
- <sup>34</sup> German patent 265025 (1912); English patent 11809 (1913); French patent 451925 (1912), see also *Jahresber. d. Mil.-Vers. Amis, 3,* 13 (1896). <sup>86</sup> *Ann.* 265, p. 318. " *Ann.* 276, p. 58. " *Z. Schiess- u. Sprengstoffw.* (1916), p. 182
- $^{38}$  German patent 286527 (1913), to E. v. Herz, on the use of anhydroenneaheptite pentanitrate as a blasting cap charge.
- <sup>39</sup> Vignon, Gerin, *C. R.*, 133, p. 590; also Stettbacher, *loc. cit.*, and German patent 265025 (1912).
- <sup>4(1</sup> The author found the melting point to be 140 to 141 °C. <sup>41</sup> **Z.** *Schiess- u. Sprengstoffw.* (1916), p. 112.

Verified efficient method of preparing PETN from diluted HNO3

use
32,7 ml of 70% HNO3 (75% excess)
18,9 ml of 96% H2SO4
10,0 g of Pentaerythrite
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or
34,0 ml of 65% HNO3 (66% excess)
24,8 ml of 96% H2SO4
10,0 g of Pentaerythrite
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or
34,8 ml of 58% HNO3 (48% excess)
36,3 ml of 96% H2SO4
10,0 g of Pentaerythrite

#### Nitration:

- 1. Cool nitration mixture during mixing of acids, thus minimalize even minimal decomposition of HNO3. Nitration mixture must be cooled before nitration process to temperature of 10°C.
- 2. While stiring, add pentaerythritee in small portions (1-2g) to nitration mixture, always after previous batch is dissolved. Nitration mixture gradually thicken as PETN forming in solution.
- 3. Constantly monitor reaction temperature and maintain it in 10-15°C range. Interval of adding pentaerytritol conform to reaction temperature, must not rise over 15°C, leave beaker in cold water.
- 4. Stir with mixture for next 5 minutes after all pentaerythrite is added and dissolved. Mixture is now thick, but stirring is going well. During nitration process must not be developed any brown fumes of NOx!
- 5. Now put beaker with mixture into water bath and maintain temperature at 50°C, continuously stir with mixture. During 20 minutes at this temperature, all of possible sulfoesters come into PETN for maximal yield of nitration.
- 6. While maintaining mixture at higher temperature, mixture must be monitored for developing of NOx fumes. Only light brown colour can be in shrouded beaker. Raised development of NOx pointing to higher temperatures used (even during previous nitration) or insufficient chmemicals purity and further heating may end up in uncontrolled reaction and oxidation of formed PETN. In this case it is better to do not heat at all and end just after nitration (if brown fumes appears during nitration), the yield will be lower. In case of accidentally runaway reaction during heating, immedialtely pour mixture into cold water, don't try stop reaction by cooling beaker, it will not help.
- 7. When heating after 20 minutes pass off, pour reaction mixture into cold water and follow standart procedure of filtration, neutralization and purifying of PETN.

Yield was 22,1g of PETN from 10g of pentaerythrite, ~95% of theoretical yield (with 65% HNO3 used).

This procedure is result of my research of most effective method preparing PETN

from diluted HNO3. Acid ratios are precisely calculated on data from PETN nitration graph published by T. Urbanski in his book vol. IV. Generaly said, PETN is forming to maximum 30% of water portion in nitration mixture. But, when also H2SO4 is contained in nitration mixture, minimum ammount of water must be keep, or oxidation with small yields occur. With this acid ratios 20% of H2O is minimum. So, this nitration mixture has 20% of water on nitration start and 30% at the end, area for most effective nitration, but again only with this ratios. For other acid ratios must be all recalculated. Excess of HNO3 is used to controll ammount of reaction water. Only ammount of nitration mixture can be extended for lower mixture thickness, but it lower utilization of acids and overall efficiency. But it isn't necessary.

# **Concealing PETN**

[ Agent Orange \* (c) 1993 cTs ]

This text is a short complement to the file "Improvised PETN", which served as an introduction to the organic explosive PETN, pentaerythritol tetranitrate. Also included was a section detailing one of the proven methods for the manufacture of high-grade PETN.

#### Warning

There may be certain federal, state or local laws which prohibit the possesion or manufacture of certain substances mentioned herein. Severe penalities may be prescribed for violation of such laws. Be warned! The procedures to be followed in this manual and the resulting endproduct are extremly dangerous. Whenever dealing with high explosives, special precautions should be followed in accordance with industry standards for experimentation and production of high explosives. Failure to strictly such industry standards may result in harm to life or limb.

Therefore, the author disclaim any liability from any damages or injuries of any type that a reader or user of information contained within this manual may encounter from the use of said information. Use this manual and any endproduct or by-product at your own risk.

### **Plastic Bonded Explosives**

The plastic bonded explosive (PBX) is relatively new class of explosive that is composed of about 85 to 95 percent PETN and 5 to 15 percent plastic polymer, such as polystyrene or polyester. These explosives have high mechanical strength, excellent explosive properties, and are extremly stable and insensitive to shock. PBXs average detonation velocity is more than 7.800 meters per second.

Most PBXs are produced as powders for press loading, but they also can be made as slurries for casting or injection molding. Following are directions for a simplified version of PBX-1, composed of 90 percent PETN and 10 percent polystyrene plastic.

- 1. Weigh the required amount of ploystyrene foam (e.g., 100 grams of PBX consist of 10 grams polystyrene and 90 grams PETN) and place it in the mixing vessel.
- 2. Splash a little acetone over the foam and allow it to dissolve (this does not take long). When it has melted, add a little more acetone if necessary so the plastic has a layer of solvent over its surface that is about 1/4 to 1/2 inch thick.
- 3. Weigh the required amount of sifted PETN crystals. Pour these into the mixing vessel and stir with a spatula until a smooth, even, lump-free mix is obtained. Add a little more acetone if necessary.
- 4. Heat the mixing vessel in a hot-water bath to evaporate the excess solvent. Be sure you have adequate ventilation because acetone and its fumes are flammable and can be explosive. When the consistency of the mixture resembles that of thick oatmeal, the PBX may be pressed into molds and placed in a warm, well-ventilated area to cure.

The resulting is a strong, hard, plastic material that is extremly shock-resistant. It is, however, flammable, and even though it is hard to light, it will burn fiercly once lit. Just keep it away from open flames.

RDX can be substituted for the PETN, in the same proportions, yielding an explosive that is just as powerful, but a little harder to detonate. However, if PETN is used, do not drill the cap wells. PETN is much more sensitive than RDX, so form the cap wells before the material hardens completely.

#### **Plastic Explosives**

These are the most widely explosives used today. It is pound-for-pound the most powerful explosive in common use. Its power, stability, and versatility are unequalled.

One note of caution should be mentioned. The user of the plastic explosive, should avoid mashing it when loading it into special devices or preparing charges. The sectional density of an explosive has a direct bearing on its power and velocity. This is not to say that they will not explode when used in this manner, but they will not utilize their full explosive potential. Plastic explosives are composed of 85 to 90 percent PETN and 15 percent plasticizer. Following are the directions for a simple version of plastic explosive, composed of 85 percent PETN, 10 percent wax and 5 percent vaseline (by weight).

- 1. Weigh the required amount of PETN (e.g., 100 grams of plastic explosive consist of 85 grams PETN, 10 grams of wax and 5 grams of vaseline) and place it in the mixing vessel.
- 2. Weigh the required amount of wax and vaseline and place it in the mixing vessel.

- 3. Knead this mixture (using rubber gloves) to a uniform consistency.
- Shape into desired size, and place it in a suitable container of any kind (preferably in one of glass or plastic).

The resulting product is a soft plastic explosive, which limits are only the users imagination. RDX can be substituted for the PETN, in the same proportions, yielding an explosive that is just as powerful, but a little harder to detonate. Store this explosive in a relatively cool and dry place.

#### **Sheet Explosives**

Sheet explosives are one of the most powerful and versatile explosives available today. During World War II, the Germans used Nipolit, an early form of sheet explosive, but it wasn't until the early 1960s when Du Pont perfected Detasheet, the first reliable sheet explosive, that sheet explosives came into

wide use. Various forms of this product are used commercially for boosters, cutting steel, or explosive welding. This explosive is very powerful, though, oddly, the military version is less so than its civilian counterpart. The military form contains 63 percent PETN, while the civilian variant contains 85 percent PETN. The U.S. military versions of Detasheet are the M-118 and M-186 sheet explosives. The M-118 measures 1/4 inch thick by 3 inches wide by 12 inches long. The M-186 has the same width and thickness, but comes in a 50-foot roll. They are olive green, while the commercial types are usually orange or white. Because of their size and form, sheet explosives lend themselves to concealment in any number of places. They have been found in envelopes, suitcase linings, electronic equipment, and other concealed places. About the only limits are the user's imagination.