

2,4,6-TRINITROTOLUENE: REVIEW OF PRODUCTION METHODS AND APPLICATIONS

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Abstract

The article presents the current state and old aspects of TNT production, along with modifications that have appeared over the years in order to improve the detonation parameters and the physical properties of the material, as well as modern improvements in the production of TNT as a crushing explosive that can be cast. The aspects of applications in the context of historical outline and their changes over the years shall also be discussed in the following paper.

1. Introduction

2,4,6-trinitrotoluene, popularly known as TNT, is a chemical aromatic nitro compound that is used as one of the most common military blasting explosives. It melts at 80.2 °C, releasing sooty, black, toxic smoke while burning. Explosive decomposition occurs above 240 °C. The difference between these temperatures provides an adequate safety margin in the event of local overheating of the melt. TNT was invented in 1863 by the German chemist Wilbrand, but it was used as an explosive 30 years later, with its commercial production in Germany occurred in 1901. During World War I, however, it was not as widely used as picric acid (2,4,6-trinitrophenol), which was related to its low sensitivity to mechanical stimuli and a relatively large critical diameter of detonation. It is obtained by three-stage nitration of toluene with a mixture of sulfuric and nitric acids. As an explosive, it is characterized by durability, low sensitivity to stroke and friction and high temperature to initiate an explosion. Thanks to these properties, it is safe in the context of usage and storage, not to say that strong detonators must be used to cause ignition. It is non-hygroscopic.

The reactivity of TNT is the sum of the possible reactions that the functional groups can enter in the molecule. These are a methyl group, nitro groups in the 2, 4 and 6 positions as well as hydrogen atoms in positions 3 and 5. Reaction on each of the TNT functional groups (oxidation or reduction) leads to the formation of compounds with a higher reaction potential than TNT alone.

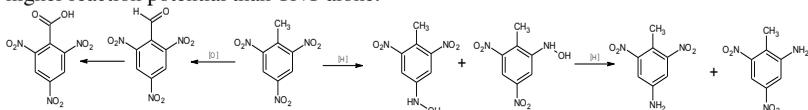


Fig. 1. Most important pathways of TNT oxidation and reduction.

Protons at positions 3 and 5 on the ring can be substituted under conditions of nucleophilic substitution (VNS), which is possible when a nucleophilic factor attaches to an electron-deficient aromatic ring contains a leaving group, located at the reaction center.

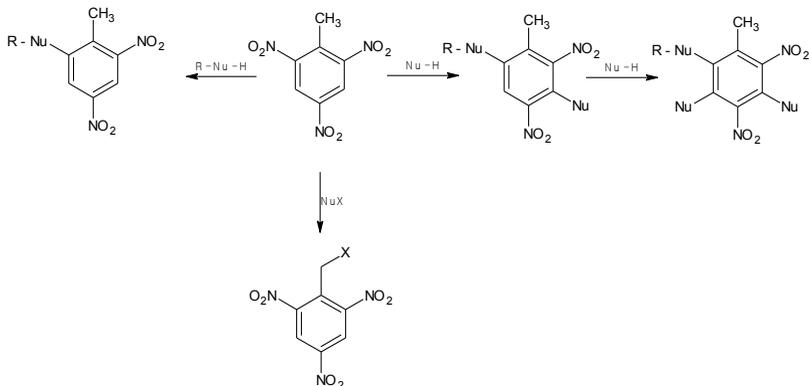


Fig.2. Most important pathways of nucleophilic substitution in TNT.

When describing the energy of very strong explosions, the parameter that can be commonly seen is the so-called TNT equivalent α_T . It is a basic characterization factor of nuclear weapons and is also used to describe the strength of other events, such as meteor strikes. It determines the mass of TNT that will release an equivalent amount of energy during an explosion as in the explosion of a given material. So it is often referred to as the power of the explosion. According to Sachs' law, a blast wave with the same characteristics is created by two charges with the same burst energies. Therefore, assuming the energy of the material of a given explosive as Q_X and Q_{TNT} , it is possible to determine what mass of this material m_X is equivalent to a given mass of TNT m_{TNT} according to the equation:

$$m_X Q_X = m_{TNT} Q_{TNT},$$

hence:

$$\alpha_T = \frac{m_{TNT}}{m_X} = \frac{Q_X}{Q_{TNT}}.$$

TNT makes it possible to compare the so-called blast ability various explosives. The higher the values of TNT equivalents of a given material, the higher the parameters of the blast wave generated after its outbreak.

Various forms of TNT are available on the market. One of them - TNT cast, has different characteristics than pressed because it does not detonate while exposed to a flame. Conventional cast explosives are based on TNT, or mixtures with hexogen (RDX) or octogen (HMX). This form can be used interchangeably with compressed TNT for filling bullets and mines. TNT produced in Polish chemical plants in Bydgoszcz and Tarnów is widely available on the defense markets. To this day, America remains the largest recipient of Polish TNT. The international brand of Polish Nitro-Chem has dominated the countries of Europe, including the countries of Africa, among others due to its extraordinary chemical purity. For example, in recent years in Bydgoszcz, the annual sales of TNT reached approximately 6,000 tons of TNT at a low unit price of approximately an estimated 20 PLN/ kg.

In the context of past applications, the significant impact of TNT on World War II cannot be overlooked. In the years 1920-1940, the production of TNT was an important branch of the armaments industry of the USSR, which contributed to the requirement of significant increase of oil production in the country, due to the fact that petroleum

products were the basic synthesis substrate. However, this did not happen, and therefore there was a sharp decline in the efficiency of the USSR's activities, resolved in 1944-1945 by supplies distributed from the United States.

2. Industrial production of TNT

2.1. Nitration of toluene

Currently used industrially, the TNT production method consists of two stages. The first is nitrating toluene to nitrotoluene with a mix of nitric and sulfuric acid. Due to the reaction, except the main product (2,4,6-TNT), unsymmetric TNT isomers (4-4.5%), tetranitromethane (0,05-0,1%), dinitrotoluene (0,05-0,5%). The qualitative criterium under which the TNT is assessed is its temperature of solidification, which is dependent on the undesirable impurities- it is required not to exceed 80.2 ° C. In the nitration of the pure TNT, the solidification temperature of 77-78 ° C is obtained, therefore it is required to introduce a second step of the process- purification from those undesirable content.

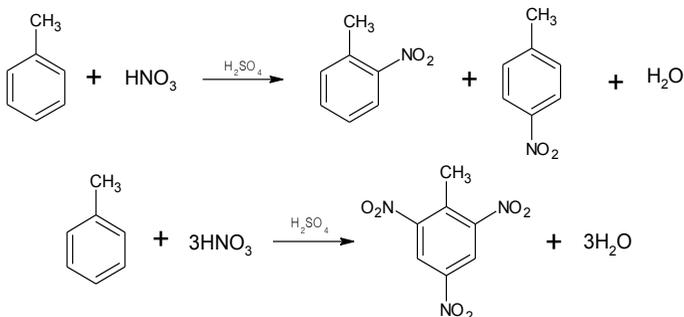


Fig.3. Reactions of the synthesis of TNT (2,5,6-trinitrotoluene) obtained by three-stage nitration with a mixture of sulphuric and nitric acids representing the main products ie TNT and the unsymmetrical o- and p-nitrotoluene isomers (without taking into account the impurities).

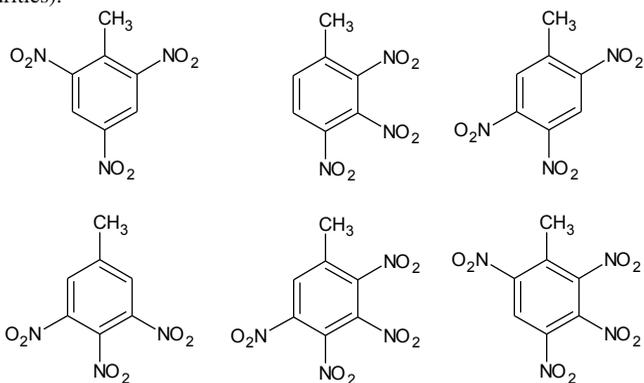


Fig.4. Possible isomers of TNT.

In order to obtain TNT with a high content of the desired isomer, the method of toluene nitration followed by purification of the product containing about 4-4.5% of unsymmetrical isomers can be used. An alternative process is the nitration of o-toluene or the nitration of a crude mixture of dinitrotoluenes, from which isomers derived from m-toluene have been removed so that the obtained product has about 1% of unsymmetrical isomers, which makes the purification much simpler and cheaper.

2.2. Purification of TNT

Purification of TNT can be done by chemical and crystallization methods. Chemical purification of crude TNT involves the usage of alkaline compounds in aqueous or alcoholic solutions. As a result of such purification, some of the nitro groups in the unsymmetrical isomers form the water-soluble salts of the corresponding sulfone derivatives. TNT also reacts with these compounds, albeit at a significantly slower rate, so that slight losses of the main product can be expected. In industrial practice, the most common purification process is cheap and simple sulphitization of raw TNT, which consists of the use of sodium sulfate. The impurities in crude TNT, so-called the "red waters", form water-soluble salts and are thus effectively removed. Other contaminants also react in this process to produce water-soluble organic products. An important pollutant is a tetranitromethane, which is formed in the last phase of trinitration because it increases the sensitivity of TNT to mechanical stimuli. The drawback of this type of treatment is the very good solubility of the aromatic salts formed in water, which makes them difficult and expensive to remove from post-production sewage. For this purpose, biological methods are used, since other methods have not found practical application.

Crystallization purification is not used in industry due to the fact that the usage of flammable and/or toxic solvents, such as ethanol, benzene, xylene, toluene, or phenol, is required, which causes considerable problems in industrial practice. There are also possible methods of purifying TNT with the use of other substances such as nitric acid, crystallization from a water emulsion by fractional crystallization, or distillation with steam or hot air blowing, but they are not used on an industrial scale.

2.3. Environmentally-friendly TNT production methods

Currently, experiments are being carried out to reduce the formation of undesirable sewage, which is more environmentally friendly. Attempts are made to nitrate o-nitrotoluene, and to purify the TNT formed by crystallization from selected solvents or by washing impurities from crude TNT, so that they accumulate on the surface of the crystals. These methods do not rely on chemical reactions that produce problematic wastewater. As a replacement, steam distillation of the raw products has been used, which proved to be effective. The solvents used for crystallization should be characterized by a high-temperature gradient, i.e. high solubility of the crystallized compound at high temperature and low solubility at low temperature. In this method, trichloroethene was considered the most appropriate, the only disadvantage of which was decomposition with the release of chloride acid causing corrosion of the equipment. The products obtained through these tests were of good quality, relatively high efficiency (approx. 87%), and easy to filter.

The washing purification method is made possible by the accumulation of impurities on the surface of the crystals, which becomes more noticeable, the slower the crystallization process is. In this method, the key is to properly prepare TNT crystals by melting them, placing water in the reactor heated to approx. 80 ° C, and then, after stabilizing the temperature, starting slow, gradually cooling to 50 ° C, filtering and drying the obtained suspension. High efficiencies of approx. 99.5% can be then

achieved. The choice of solvents is justified by the solubility of TNT and the safety of their use.

Based on the above experiments, it is possible to obtain a satisfactory quality of TNT without the sulfonation process.

3. Applications of TNT

3.1. Explosive formulations involving TNT

Initially, TNT was used on its own, but now it is commonly occurring as a component of popular explosive mixtures (including oktol, torpex, H-6, or HTA) which have reduced sensitivity to unintentional stimulation. Octole is a mixture of 70-75% octogen and 25-30% TNT, which, due to its high detonation speed, is mainly used to build warheads of cumulative missiles. The Torpedo Explosive, commonly known as the torpex, was developed during the II World War. It has about half the explosive power of pure TNT, which is included in the mixture (40%) except from the hexogen (50%) and aluminum (10%). An analogous mixture that differs only in the proportions of ingredients is HTA, which consists of 40% hexogen, 40% TNT and 20% aluminum. Another well-known mixture is Composition H-6, originally produced in the United States for use in naval weapons such as deep-sea torpedoes, sea mines, and bombs. The content of the composition differs from the country of production. The sample percentage is 30% of TNT, 45% of hexogen, 20% of aluminum, 0.5% of calcium chloride, and 5% of wax. However, TNT explosives have disadvantages as well- one of the most important ones is a significant increase in density after the mixture solidifies, which makes it possible to detach the solidifying charge from the wall of the projectile, as well as the formation of cracks or voids, the so-called caverns inside the casting. Considerable stresses, susceptibility to cracking and lack of structural homogeneity increase the sensitivity of the explosive in the context of cyclical thermal or mechanical interactions. Therefore, an accidental shock to a warhead containing such material, e.g. by a fragment or exposure to a shock wave, results in a full combat reaction or setting the material on fire.

3.2. Functional additives to TNT

With TNT-containing explosives at high temperatures, exudation of low-melting components, including TNT itself, can be observed. This is a highly disadvantageous occurrence, but it can be limited by the addition of cellulosic materials or nitrocellulose, which has a positive effect on the thermal resistance and mechanical strength of the casts, provided that the density of the composition is sufficiently low during pouring. TNT explosives are effective and cheap, but too sensitive for modern requirements.

Aluminum (Al) powder additives are also used in the case where the aim is to achieve an increase in detonation performance. The addition of aluminum significantly increases the heat of the explosion while reducing the detonation parameters, the larger the aluminum particles, the less significant is the decrease in the explosion.

The use of waxes (usually natural) is aimed at improving the flexibility of the casting and preventing cracking at low temperatures or under tensions occurring at a stroke. The preparation of such a composition consists of mixing at hot temperatures (82-84 ° C) the waxes with a plasticizer, after which the rest of the ingredients is introduced into the solution. Mixing takes place under reduced pressure and the resulting melt is poured directly into the molds. The cast is placed in incubators (70 ° C) and then gradually cooled down to room temperature (in about 10 h).

3.3. Effects of TNT on the environment

When it comes to BHP and safety, human exposure to high doses of TNT causes an increase in the tendency to develop anemia and liver dysfunction. There are also negative effects in the form of, among other, skin irritations. One should also pay attention to the significant environmental harm and the risk of explosion during production. The formation of post-production wastewater containing unsymmetrical TNT isomers characterized by a higher melting point called "red waters" is currently the subject of research into disposal methods.

4. New trends and alternatives to TNT

When it comes to fusible crushing materials in modern compositions, it is worth to notice, that the TNT has been replaced with 2,4-dinitroanisole (DNAN compositions), and hexogen or octogen substitutes are 3-nitro-1,2,4-triazole-5-one (TNTO compositions), nitroguanidine, and/or ammonium chlorate (VII). There are also compositions in which non-explosive substances, such as paraffin waxes or various types of chemo-setting or thermoplastic polymers, were used as the low-melting component (matrix). Compositions that contain energetic, thermoplastic elastomers as well as high-energy explosive compounds which have the crystal lattice with the minimal possible number of defects, are characterized by a greater degree of sophistication.

Such substitutes are characterized by different parameters. Blends incompatible with TNT such as the ones containing ammonium chlorate (VII) exhibit a decreased chemical stability of TNT. Another composition is DNAN which is a less sensitive TNT substitute. In the molten form, it shows several times greater solubility of RDX, which is responsible for reducing the viscosity of the suspensions and for obtaining more pourable compositions, even if a large contribution of non-melting components is used. It has also been shown many times that when using this material, the influence of random stimuli on the stability of the material was reduced. The disadvantages of DNAN include lower density, poorer detonation parameters compared to TNT, lower availability, and higher price.

Table 1. Fundamental properties of DNAN and TNT.

	DNAN	TNT
Molecular Formula	$C_7H_6N_2O_5$	$C_7H_5N_3O_6$
Formula weight	198,133	227,131
Composition (%)	C (42,43) H (3,05) N (14,14) O (40,38)	C (37,02) H (2,22) N (18,50) O (42,26)
Density (gcm^{-3})	1,336	1,654
Melting Point ($^{\circ}C$)	94,5	80,5
Physical Form	Needles (ethanol or H_2O), monoclinic	Orthorhombic (ethanol)
Solubility	<i>sl</i> (H_2O), <i>s</i> (ethanol, ether, acetone, benzene), <i>vs</i> (pyridine)	<i>i</i> (H_2O), <i>sl</i> (ethanol), <i>s</i> (ether), <i>vs</i> (acetone, benzene)

The methodology of producing TNT-based hot melt compositions is based on mixing the components (85-90 $^{\circ}C$) and introducing the waxes by attaching them to RDX or HMX particles or by introducing them into liquid TNT together with an emulsifier. In the next stages, the obtained suspension is poured into previously heated forms, e.g. missiles or bombs, and then gradually cooled down to obtain a homogeneous material. The inner surfaces of the molds are coated with varnishes or other substances to

consolidate the bonding of the explosive to the mold surface. It is also possible to solidify it in the form of granules, which can then be charged into explosive material by forcing or pressing.

5. Summary and conclusions

TNT has found its use, between others, in detonating fuses, and modern explosives, that are still being developed on its basis, in which it is desirable to minimize the amount of hydrogen and maximize the amount of nitrogen due to the increase in the enthalpy of formation and the increase in the volume of gaseous explosion products.

The low unit price of TNT makes it an intensively researched substrate for the production of many energetic compounds. The oldest explosive (1883) obtained from TNT is symmetrical trinitrobenzene (TNB), characterized by detonation parameters slightly higher than pure TNT, and its melting point is too high for cast explosives. Another material that can be obtained from TNT is cyano-2,4,6-trinitrobenzene, which has a better oxygen balance than pure TNT but has a significant hydrolytic susceptibility to the nitrile group, which is why it did not attract the attention of researchers. The methylation of TNT produces trinitroxylylene (TNX), i.e. 1,3-dimethyl-2,4,6-trinitrobenzene, which over time has begun to be synthesized by direct nitration of xylene to meet the needs of the petroleum industry. TNX is significantly less toxic than TNT, so it has been used extensively as a replacement for bigger explosives, despite having slightly lower detonation parameters and a higher melting point than TNT. By directly implementing amino groups into nitroaromatics such as TNT, amino-2,4,6-trinitrotoluenes were obtained, for which the stroke sensitivity is reduced. In 1964, a patent for the preparation of hexanitrobenzophenone by reaction of hexanitrodiphenylmethane (HNDM) with active oxidants was published. It has a higher melting point, but a much better oxygen balance. There are no reports in the literature about the calculated detonation parameters. A very important material that is obtained directly from TNT is E-2,2',4,4',6,6'-hexanitrostilbene (HNS), which melts upon decomposition and shows lower sensitivity to mechanical stimuli with detonation parameters similar to TNT. Due to its high melting point, HNS can also be used as a heat-resistant explosive and as an additive (0.5-1%) to reduce contraction and the risk of cavities in TNT castings. Other compounds in this category are nitro-methyl-diphenylamines obtained from the reduction of TNT. However, due to the presence of mobile hydrogen on the nitrogen bridge, these compounds are characterized by relatively high reactivity in terms of salt formation and corrosion catalysis of metals, so they have been eliminated from common military and civilian applications.

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