

This article is available in PDF-format, in colour, at:

http://www.wydawnictwa.ipo.waw.pl/materialy-wysokoenergetyczne/materialy-wysokoenergetyczne12/2/HEM_0202.pdf

Materiały Wysokoenergetyczne / High Energy Materials, 2020, 12 (2), 139 – 145; DOI 10.22211/matwys/0202
ISSN 2083-0165

Copyright © 2020 Lukaszewicz Research Network - Institute of Industrial Organic Chemistry, Poland



Article is available under the Creative Commons Attribution-Noncommercial-NoDerivs 3.0 license CC BY-NC-ND 3.0.

Research paper / Praca doświadczalna

The illegal synthesis of picric acid in the context of applicable legal regulations *Nieuprawniona synteza kwasu pikrynowego w kontekście obowiązujących regulacji prawnych*

Mateusz Polis*, Zenon Wilk, Karolina Nikolczuk

Lukasiewicz Research Network – Institute of Industrial Organic Chemistry, Branch in Krupski Młyn, 1 Zawadzkiego Street, 42-693 Krupski Młyn, Poland

*E-mail: mateusz.polis@ipo.lukasiewicz.gov.pl

Abstract: *Homemade explosives (HME) are increasingly used in terrorist attacks. These materials can be defined as physical mixtures of commonly available raw materials or those obtained by synthesis e.g. picric acid. For most compounds there are at least several synthesis routes which allow a suitable route to be matched for the available materials. The aim of the task was to investigate the possibility of producing picric acid using raw materials and equipment available to the average user. The obtained product was tested for safety, i.e. sensitivity to friction and impact was determined.*

Streszczenie: *Samodziałowe materiały wybuchowe (HME – z ang. homemade explosive) są coraz częściej stosowane w zamachach terrorystycznych. Materiały te możemy zdefiniować jako uzyskane poprzez fizyczne mieszanie powszechnie dostępnych surowców lub syntezę. W przypadku materiałów wybuchowych, otrzymany w wyniku syntez, można wymienić m.in. kwas pikrynowy. Dla większości związków chemicznych istnieje co najmniej kilka ścieżek syntezy, co umożliwia jej dopasowanie do dostępnych materiałów. Celem pracy było zbadanie możliwości uzyskania kwasu pikrynowego, korzystając z dostępnych dla przeciętnego użytkownika surowców i aparatury. Otrzymany produkt poddano badaniom bezpieczeństwa, tj. określono wrażliwość na tarcie oraz uderzenie.*

Słowa kluczowe: *kwas pikrynowy, materiał wybuchowy, prekursorzy materiałów wybuchowych*

Keywords: *picric acid, explosive material, explosive material precursors*

1. Introduction

1.1. General

Homemade explosives (HMEs) are being more and more frequently used in terrorist attacks [1]. In 2011, ANFO (ammonium nitrate-fuel oil) type charges were used in an attack in Oslo. The charges were initiated with detonators utilising picric acid (2,4,6-trinitrophenol) [2]. An analysis of the explosives used in these attacks showed that most of them were homemade explosives (HMEs). Attention should be drawn to the hazards associated with explosives being made by a person without either expert knowledge or specific raw materials. Many instructions on how to make various explosives are available on the internet. Despite legal restrictions,

many explosive precursors are available commercially without any or insufficient limitations regarding sales. Picric acid was first synthesized in 1742 [3]. Initially used as a dye, antiseptic and intermediate product for other syntheses in the pharmaceutical and dye industries, since 1830 it has also been used as an explosive [4]. The solubility of picric acid in water is relatively low; at 20°C it is 1.11 g per 100 g of solvent. The solubility in sulfuric acid decreases up to 20 wt.% sulfuric acid concentration, and increases with further increases in sulfuric acid concentration; an inverse relationship can be observed in nitric acid solutions [5]. Its solubility in organic solvents is higher than in water, and its distribution coefficient is better in organic liquids [5]. According to [4] the detonation velocity is 7350 m/s at 1.70 g/cm³, and according to [6] it is 7260 m/s at 1.70 g/cm³. The heat of explosion is given as 3800-3970 kJ/kg [5, 7].

Due to the strong resonance effect (as a result of overlapping π orbitals in the aromatic ring and nitro groups stabilizing the phenolate anion), it exhibits high acidity ($pK_a = 0.38$) [3, 7]. It crystallizes to form colourless or yellow crystals with a melting point of 122-123 °C and decomposes explosively if heated to over 300 °C. Due to its strong corrosive properties, toxicity, sublimation and the formation of unstable salts, *i.e.* picrates, it was replaced in explosive applications by the much more stable, less sensitive and safer 2,4,6-trinitrotoluene (TNT) [5, 8]. Direct nitration of phenol yields macromolecular products due to an increase in reactivity of the aromatic ring caused by the hydroxyl group. Synthesis is usually conducted by an initial sulfonation of phenol (forming mainly *p*-phenylsulfonic acid and *o*-phenylsulfonic acid, the presence of the disulfonic derivative requiring higher reaction temperatures, however, it is beneficial due to an increased nitration yield) [5, 7]. The next stage involves nitration of the product obtained in the previous stage. Direct nitration is also possible, provided that the concentrations and temperatures are maintained at sufficiently low levels [9]. Another method involves nitration of 2,4-dinitrophenol with concentrated nitric acid or base hydrolysis of picryl chloride (2,4,6-trinitrochlorobenzene) [5, 7, 9].

1.2. Legal regulations in Poland

Methods of obtaining and legally using explosives in Poland are limited by law. A licence to manufacture and market explosives, weapons, ammunition, products and technologies for military and police applications, is required. The licence is issued to a manufacturer by the Ministry of the Interior and Administration, following approval by the Military Institute of Armament Technology of the manufacturer's technical and organisational compliance. The purchasing, storage and use of explosives for civil applications requires a licence issued by the provincial government following approval by the regional Chief of Police. In both cases, employees permitted to work with explosives, must undergo training and meet the requirements laid down in the regulations.

In Europe, Regulation (EU) No. 98/2013 of the European Parliament and of the Council of 15 January 2013 on the marketing and use of explosive precursors, is in effect. A corresponding act is the Polish Regulation of 13 April 2016 on the safety of marketing of explosive precursors. This lists substances which are liable to being used in the manufacture of explosives and thus require registration, purchase and sales restrictions. Explosive precursors are substances which can be used as substrates in the production of explosives or as components of explosive compositions. According to the regulations [10], the concentration of a restricted precursor must be higher than a specified concentration limit value; this also applies to mixtures containing this precursor. The regulations control the issue of customer access to the restricted substances. A total and complete ban on using explosives precursors would be irrational, and the restrictions only apply to users not holding relevant licences. The system is based on two categories of explosive precursors. The first group includes substances which shall not be individually made available to members of the general public, or in mixtures or substances including them, except if the concentration is equal to or lower than the limit values set out below. One of the provisions allows for an appropriate licence to be obtained to purchase those substances for relevant economic activities, in concentrations higher than those specified in the regulations. Apart from that, the registration system allows users access to the substances provided that the transaction is registered for those substances listed in the regulations. The second group includes substances for which suspicious transactions

shall be reported. The regulation requires that suspicious transactions and thefts must be reported to the national contact centres by establishing a registration system. The competent authorities should take the necessary measures to investigate the hard evidence, including the authenticity of the relevant economic undertaking, exercised by a professional user involved in a suspicious transaction. The register shall comprise at least the following information:

- personal data of the client,
- quantity of the substance, including its concentration,
- its intended use,
- the date and place of the transaction.

The problem is that the seller or intermediary decides which transaction is suspicious. A more lenient treatment of this group of substances results from their relatively low potential for use as explosives precursors.

Additional regulations concerning ammonium nitrate need to be discussed. Regulation (EU) No. 1907/2006 of the European Parliament and of the Council of 18 December 2006 [11] restricts the supply of ammonium nitrate direct to users if it can be used directly in the production of explosives. It can be supplied to some groups of users including farmers, however, the implication is that any suspicious transactions should be reported. The regulation [10] also assumes the possibility of including additional substances in the system, also by use of urgency procedures, if justified by circumstances.

Regulation (EU) No 273/2004 of the European Parliament and of the Council of 11 February 2004 on drug precursors [12], should also be mentioned. This classifies and distinguishes substances which can be used as drug precursors. It includes the following compounds: potassium permanganate, toluene and acetic anhydride. Customer declaration and documentation may not be required if the annual turnover of a specific substance is lower than the limits laid down in the regulation. For example, the limit for acetic anhydride is 100 dm³, and for potassium permanganate it is 100 kg [12].

On 30 November 2018, a draft replacement for Regulation (EU) No 98/2013 of the European Parliament and of the Council of 15 January 2013 was published [13]. The aim was to toughen the requirements. The list of substances subject to suspicious transaction reporting would include magnesium nitrate hexahydrate, magnesium powder and aluminium powder, provided that the particle size was lower than 200 µm and that the content of one of the metals was higher than 70 wt.%. The draft also included tightened regulations on substances which are not to be made available to the general public. The draft has been approved as Regulation (EU) 2019/1148 of the European Parliament and the Council of 20 June 2019, on the marketing and use of explosives precursors, amending Regulation (EC) No 1907/2006 and repealing Regulation (EU) No 98/2013. The Regulation comes into effect on 21 February 2021. Until then, the previous Regulations apply.

2. Experimental section

2.1. Raw materials

The following substances were used in the synthesis of picric acid :

- Commercially available product containing 500 mg of acetylsalicylic acid,
- Sulfuric acid, concentrated (manufacturer: Chempur),
- Potassium nitrate, pure (manufacturer: *Zakłady Azotowe* in Chorzów),
- Ethanol solution (manufacturer: Chempur).

2.2. Synthesis method

A portion of acetylsalicylic acid was ground in a porcelain mortar. The ground material was transferred to a round-bottomed flask and ethanol was added. A reflux condenser was connected to the flask and the mixture was heated until boiling and kept at the boiling point for 30 min. After cooling, the suspension was filtered, and the filtrate was added to an open beaker and heated until all the solvent had evaporated. The separated acetylsalicylic acid was re-crystallized from ethanol and dried to a constant mass. A portion of sulfuric acid was added to

a round-bottomed flask with a stirrer and a thermometer and placed in a cooling bath. The mixture temperature was maintained at low values, and portion of potassium nitrate was added in batches over approximately 60 min. After all the potassium nitrate was added, the mixture was stirred. Portion of crystallised acetylsalicylic acid was weighed and added in batches to the mixture over 60 min. The temperature of the reaction was maintained at constant value. Once the crystallised acetylsalicylic acid had been added, a reflux condenser was connected to the flask, and the mixture was heated with constant stirring. The system was then left to cool down. The mixture was transferred to a vessel containing demineralised water. The precipitate was filtered and rinsed several times with cold water until a characterising test failed to detect sulphate ions. The filtered and rinsed picric acid was transferred to a porcelain tray and dried.

2.3. Test methods

2.3.1. Determining the melting point of the product

Melting point is one of the characteristic physical properties of organic compounds and a good criterion of their purity. Pure crystalline organic compounds will melt within a narrow range of 1 °C. A 10 mm glass capillary was filled to half of its volume with the test material and compacted by gently tapping on a ceramic plate. The capillary was inserted into a Tottoli apparatus (Fig. 1) filled with a heating medium, *i.e.* oil. The apparatus stirrer was started and the temperature measured until it had stabilized. The system was heated at a rate of 1 °C/min and was continued until a phase change was observed in the sample. The melting point was taken as being in the range between the point at which the melted sample starts to flow down the capillary walls and the point at which the capillary is completely filled with liquid. The test was repeated 5 times.



Figure 1. Tottoli apparatus

According to [8], the melting point of picric acid is between 122-123 °C. In [9] it is given as 122.5 °C. In the above experiments, the results indicated that the melting point lies between 119 °C and 123 °C.

2.3.2. Sensitivity to friction and impact

Sensitivity to friction and impact was evaluated in accordance with [14] and [15], using a Peters friction apparatus and a Kast drop hammer. Table 1 shows the test results and literature data.

Table 1. Sensitivity test results

Sensitivity to friction [N]		Sensitivity to impact [J]	
Test result	Literature data	Test result	Literature data
> 360	> 353 [7]	25	15.8 [3] 7.4 [7]

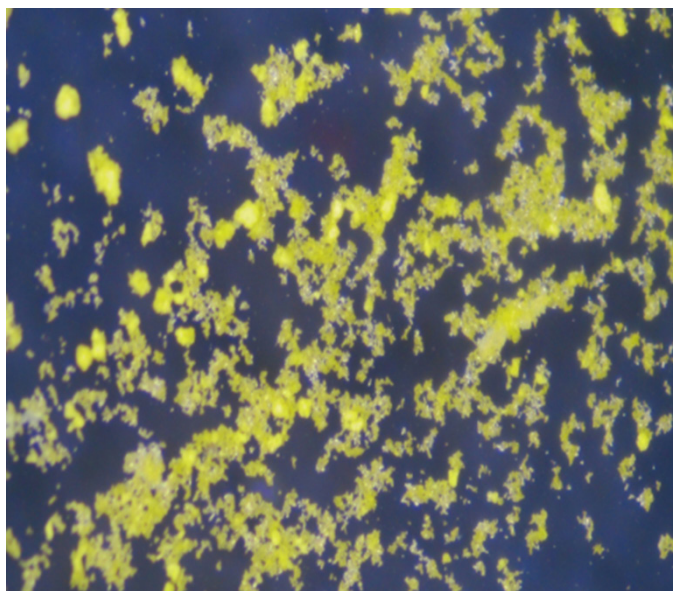
The synthesised product was not additionally refined (the microscope image shows remnants of potassium nitrate) and was not recrystallized. This may imply desensitisation of the explosive. The significant difference in sensitivity to impact may result from the crystalline structure and a size reduction of the tested crystals.

2.3.3 Microscopic image

An image of picric acid, synthesized without refining and recrystallization, was taken using an optical microscope (Fig. 2).



(a)



(b)

Figure 2. Optical microscope image – optical magnification: (a) $\times 4.5$, (b) $\times 0.7$

3. Test results and discussion

Current legal regulations are totally inadequate, which was demonstrated by the synthesis of picric acid despite limited access to explosive precursors. Regulations restricting the concentration of a compound available without a licence, can be circumvented by its sale in mixtures with inert additives which can be easily separated (e.g. water soluble chlorate salts mixed with sand). The regulations cover a small number of substances which can be used in the synthesis of explosives. With many different synthesis paths available, it is very likely that some precursors not covered by the regulations (e.g. acetylsalicylic acid), can be used. The draft Regulation of November 2018, approved on 20 June 2019 extends the current scope, however, it might still be insufficient. Details of synthesis parameters presented in experimental part (par.2.2. Synthesis method) were intentionally avoided.

4. Summary

The main conclusion from the study is the empirical validation of insufficient legislation restricting access to explosive precursors. It has been shown that it is possible to develop and synthesize explosives using information available on the internet.

References

- [1] Saska P., Klimentowski F., Kowalczyk P. Characteristics of Improvised Explosive Devices Used in the Iraqi Conflict. (in Polish) *Zeszyty Naukowe WSOWL* **2008**, *1*: 41-57.
- [2] *Reducing the Threat of Improvised Explosive Device Attacks by Restricting Access to Explosive Precursor Chemicals*. Washington (D.C.): National Academies Press, **2018**.
- [3] Şen N., Nazir H., Atçeken N., Hope K.S., Acar N., Atakol O. Synthesis, Characterisation and Energetic Performance of Insensitive Energetic Salts Formed Between Picric Acid and 2,3-Diaminotoluene,

- 2,4-Diaminotoluene. *J. Mol. Struct.* **2020**, *1205*, 127580: 1-13.
- [4] Cooper P.W. *Explosives Engineering*. New York: Wiley-VCH, **1997**.
- [5] Urbański T. *Chemistry and Technology of Explosives*. Oxford: Pergamon Press, **1985**; ISBN 0-08-010401-0.
- [6] Cybulski W. *Investigation of Detonation of Explosives Using Rotating Mirror Camera Method*. (in Polish) Katowice: Biuro Wydawnictw Technicznych INBPW, **1948**.
- [7] Srivastava K.K., Srivastava S., Alam M.T. An Overview on Picric Acid. *Der Pharma Chem.* **2017**, *9*(9): 64-75.
- [8] Korzun M. *A 1000 Words about Explosives and Explosion*. (in Polish) Warsaw: Wyd. Ministerstwa Obrony Narodowej, **1986**; ISBN 83-11-07044-X.
- [9] Ledgard J.B. *The Preparatory Manual of Explosives*. 3rd ed. Independently Published, **2014**.
- [10] Regulation (EU) No. 98/2013 of the European Parliament and of the Council of 15 January 2013 on the Marketing and Use of Explosives Precursors, **2013**.
- [11] Regulation (EU) No. 1907/2006 of the European Parliament and of the Council of 18 December **2006**.
- [12] Regulation (EU) No 273/2004 of the European Parliament and of the Council of 11 February 2004 on Drug Precursors, **2004**.
- [13] Regulation (EU) 2019/1148 of the European Parliament and of the Council of 20 June 2019 on the Marketing and Use of Explosives Precursors, Amending Regulation (EC) No 1907/2006 and Repealing Regulation (EU) No 98/2013, **2019**.
- [14] PN-EN 13631-3:2005. *Explosives for Civil Uses – High Explosives – Part 3: Determination of Sensitiveness to Friction of Explosives*. (in Polish) **2005**.
- [15] PN-EN 13631-4:2005. *Explosives for Civil Uses – High Explosives – Part 4: Determination of Sensitiveness to Impact of Explosives*. (in Polish) **2005**.

Received: August 31, 2020

Revised: November 18, 2020

Published first time online: November 25, 2020