Formation of explosive compounds in acid-contaminated leaded rubber gloves Part I: theoretical analysis

B. Mishra *, A.G. Raraz, D.L. Olson, W.A. Averill

Kroll Institute for Extractive Metallurgy, Colorado School of Mines, Golden, CO 80401, USA

Abstract

The formation of explosive compounds has been reported in the chemical reaction system where leaded rubber gloves have been in contact with nitric acid. It is speculated that this explosive compound is lead fulminate. An extensive literature review does not show a clear picture regarding the formation of lead fulminate. On the other hand, a complex scenario in the reaction system can be justified which might lead to the formation of several organo-lead compounds that are explosive materials but do not have fulminate ions in their structure. The production of 'lead fulminate' by the reaction of leaded Neoprene rubber with nitric acid and its identification are technically difficult. Part I of this paper presents the theoretical anaylsis and suggests possible reaction products, and Part II of the work describes the experimental verification of the reaction system. © 1997 Elsevier Science B.V.

Keywords: Lead fulminate; Leaded rubber gloves; Nitric acid contamination; Explosive compounds; Organo-metallic compounds; Nitration

1. Introduction

During the evaluation of the hazardous characteristics of a variety of residues at the USDOE's Rocky Flats Environmental Technology Site (RFETS), there were conflicting reports on the evidence for the formation of unstable compounds which exhibit flammability or explosivity when Neoprene and/or Hypalon lined gloves are exposed to nitric acid. These leaded rubber gloves have three layers—a red lead oxide (Pb_3O_4)–

---

* Corresponding author. Tel.: + 1 303 273-3893; fax: + 1 303 384-2189; email: bmishra@mines.edu

Neoprene layer sandwiched between two layers of Hypalon. Lead oxide is incorporated for radiation shielding and these gloves were used in gloveboxes that had a radioactive environment.

A potential safety concern has been indentified with those waste drums that contain leaded rubber gloves contaminated with nitric acid. Two incidents occurred 26 years ago involving drums of leaded rubber gloves. The first incident was an explosion at the Mound facility that occurred when flammable vapors ignited while the gloves were being heated in a muffle furnace [1]. The second incident was a minor fire that occurred in a drum of leaded gloves at the RFETS. The specific cause of these fires was never determined. Subsequent studies identified nitrated lead-organic compounds as the shock-sensitive material [2,3].

In the technical literature, it is suggested that an unstable nitrated lead-organic compound could form that might be explosive. The explosive reaction could be spontaneous or initiated by light, heat, friction, impact, or a catalyst [4]. Davies also has reported that explosions can be initiated by introducing stimuli or by amplifying normally passive environments. It has been indicated also that static electricity and vibration are other stimuli for accidental explosion [5,6]. In this case, it was concluded that the most likely sources were heat and impact [5].

On the basis of the two referred incidents at RFETS and reported examples of explosive reactions [4], it was suspected at RFETS that the unstable compound formed by reaction of nitric acid with leaded rubber gloves is lead fulminate. Therefore, the objective of this research was to identify and characterize the products formed when leaded rubber glove samples are exposed to nitric acid at different concentrations, temperatures and times. To accomplish this objective, it was necessary to consider two aspects: (1) theoretical analysis of lead fulminate formation, and understanding its relevance to the reactants in the system in order to design the experimental matrix, and (2) experimental study of the reacting system of leaded rubber gloves and nitric acid to produce and identify the products. This present study deals with the theory of lead fulminate formation and the relevant reacting systems. Experimental work will be described in the following paper.

2. Synthesis of lead fulminate

In 1882, Wislicenus [7] mentioned the formation of mercury and silver fulminates in the presence of mercury or silver salts, alcohol, nitric acid, and sometimes in nitrous acid. Wöhler and Weber [8] in 1929 studied the formation of several fulminate compounds including the 2-pyridine lead fulminate. The starting materials were lead amalgam, mercury fulminate and pyridine. Grignard et al. [9] published in 1949 that, among several fulminates, lead fulminate can be obtained from its amalgam. None of these early publications addresses the lead fulminate production and recovery process or the method of proper identification.

Singh [10] reported in 1959 on the recovery of lead fulminate and included the IR spectroscopy data for this product. However, there are no details on the recovery method, composition, color, or appearance. It is possible that the author followed the method reported by Taylor and Rinkenbach [11] for silver fulminate, which consists of

Table 1
Organolead compounds reported as lead fulminates [12]

No.	Compound	Properties
1	Ph_3PbCNO	colorless crystal, m.p. 174–175°C
2	Ph_3PbNCO	thermal arrangement of (1) at 155–165°C
3	Pr_3PbCNO	yellow crystal, explosive
4	Me_3PbNCO	decomposes at 220°C

treating a silver compound with nitric acid and alcohol. It could also have been an application of Wöhler's method [8].

In 1964, Beck and Schurierer [12] obtained and analyzed by IR spectroscopy several organometallic fulminates including triphenyllead fulminate, tripropyllead fulminate and trimethyllead fulminate. Beck and Schurierer's IR values are different from the values reported by Singh [10], perhaps because of the difference in absorption of the triphenyl and tripropyl moieties. However, the tripropyllead fulminate has closer spectroscopic values than the triphenyllead fulminate. Triphenyllead fulminate, a colorless crystal, is made from triphenyllead hydroxide in chloroform with a dilute solution of sodium fulminate and shows a thermal rearrangement. Tripropyllead fulminate, a yellow crystal, is the result of a neutralization reaction of organolead oxide (Pr_2PbO) and hydroxide (Pr_3PbOH) with sodium fulminate and dilute sulphuric acid. This tripropyllead fulminate is explosive (see Table 1 [12]).

The lead fulminates reported in the organic chemistry literature thus correspond to organo-lead fulminates. These compounds are not a typical lead fulminate having the chemical representation of $Pb(CNO)_2$, as is seen from the reported fulminates of other metals such as mercury, silver, cadmium etc.

## 3. Possible chemical reactions in the system

To predict some possible reactions in the leaded glove–nitric acid system, and to learn about the possible source of some precursor compounds already present in the glove material, some properties and characteristics of the three layers of the gloves have to be understood. The outer and inner layers are Hypalon and the center layer is a mixture of red lead oxide (Pb_3O_4) and Neoprene. The following is a review of the pertinent chemistry of these inorganic and organic compounds.

Red lead oxide (Pb_3O_4) can react with nitric acid in the following way [13]:

$$Pb_3O_{4(s)} + 4HNO_{3(aq)} \rightarrow 2Pb(NO_3)_{2(aq)} + PbO_{2(s)} \downarrow + 2H_2O \tag{1}$$
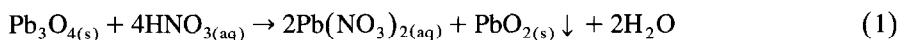
Lead dioxide, PbO_2, can be prepared by reaction (1) and is dark brown or black and slightly soluble in concentrated nitric acid. This oxide is a strong oxidizing agent in the presence of nitric acid and reacts with sulphur dioxide to yield lead sulphate. If rubbed with sulphur it ignites and forms lead sulphide, PbS [14]. It is known that lead dioxide tends to give salts of Pb^{2+} with liberation of O_2 when treated with nitric acid. Due to its oxidizing property, PbO_2 is used in matches and pyrotechnics [15]. Crystalline lead nitrate is also used in matches and pyrotechnics as a source of oxygen [16].

Neoprene® (trade mark of chloroprene rubber with a chemical name of polychloro-prene [mainly *trans*]) has the following unit structure [17]:

-(-CH₂-C=CH-CH₂-)-
|
Cl
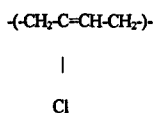
Neoprene often contains ZnO and MgO, which are used as vulcanizing agents, and sometimes has additions of organic accelerators [18,19]. There are several types of Neoprene [19–21]. According to Noller [21], N-phenyl-b-naphthylamine can be used as a stabilizer in the production of Neoprene. Sulphur and organic rubber accelerators can be used for vulcanization. Bever [22] indicates that Neoprene is decomposed by nitric acid.

Hypalon® (trade mark of chlorosulphonated polyethylene) is the other organic compound in the leaded rubber glove. There are several types of Hypalon. The processing of these organic compounds involves mixing with various fillers, plasticizer, processing aids, etc.; the product is then shaped and crosslinked in its final form. It has been mentioned that one of the methods for crosslinking includes hydrolysis of the sulphonyl chloride group with a carboxylic acid, i.e. stearic acid, which produces water at curing temperatures [17]. It is reported that Hypalon coatings have excellent resistance to nitric acid [22].

It has been reported [23] that compounds such as trimethyllead cyanamide, triethyl-lead cyanamide, tripropyllead cyanamide and triphenyllead cyanamide can be used as stabilizers for PVC. There is a report on modification of elastomer properties with nitro-compounds [24]. C-nitration products (see Section 4.2) are effective modifiers of elastomers. On the basis of the addition of these nitrogen–carbon compounds in the production of elastomers and rubbers, it can be concluded that these materials may also be present in the reacting system under study. In a study on electrochemical oxidation of rubbers [25], it has been reported that diene rubbers (=C=C=) react with inorganic acids (in particular HNO_3, H_2SO_4 and HCl) and form C=O groups without an electrochemical action.

The compounds that result from the reaction between leaded rubber gloves and nitric acid, as reported in literature, have been analyzed by X-ray diffraction, IR spectroscopy and mass spectrometry. A colorless lead nitrate with trace amounts of PbO or ZnO has been identified. The explosive yellow material was identified as a mixture of unsaturated organic compounds (=C=C=), methyl pyridine, dimethyl imidazole, nitro-carboxylic compound, which corresponds to some nitro group (–NO_2 and –COOH), and some organic acids [2,3,26]. The previous report on the explosive yellow material established that the gases evolved from the explosion do not include any lead [2,3]. The detonation products of fulminates usually contain the metallic element; e.g., the explosion products of mercury fulminate include CO, CO_2, N_2, C and Hg [27].

Twelve organic lead compounds have been reported as having a common characteris-tic: they are considered explosive materials and their chemical composition is not related

Table 2
Organolead compounds with explosive characteristics [28]

No.	Compound	Main properties
1	tetramethyllead: Me_4Pb	shock sensitive and explosive
2	tetraethyllead: Et_4Pb	explosion hazard comparative to (1)
3	—$^a(CH_2-CH_2-CH)_4Pb$	explodes on heating in air
4	$Et_3PbC\equiv C-CH_2=CH$	explodes on heating
5	$Et_3PbC\equiv CH_2=CMe$	explodes on heating
6	$PhPb(N_3)_2$	explodes at 190–200°C
7	$Et_3PbO(C_6H_2(NO_2)_3)$	mildly explosive
8	$Me_3PbOSiMe_3$	detonates in air at 140°C
9	$Et_2Pb(OBz)_2$	explosive
10	$[m-O_2NC_6H_4C(NO_2)_2]_2Pb$	orange, explosive solid
11	$Et_2Pb(O_2CCF_3)_2$	detonates during combustion, m.p.185°C [23].
12	lead picrate, $Pb(C_6H_2N_3O_7)_2 \cdot H_2O$	yellow, needles, explosive [28]

^{a}Cyclic.

to fulminates. Table 2 includes all of these compounds [28]. If the explosive compound does not include lead, the reaction is conceivably more complicated than has been understood in the past.

4. Explosives, nitration and nitrogen compounds

4.1. Explosives and propellants

Explosives and propellants have relatively large amounts of available energy stored compactly but readily deliverable. Explosives and propellants are chemical compounds or mixtures that rapidly produce large volumes of hot gases when properly initiated. Explosives detonate at rates of kilometers per second and propellants burn at relatively lower rates measured in centimeters per second. On the other hand, pyrotechnic materials evolve large amounts of heat but much less gas than propellants and explosives [27].

Urbanski [29] indicated that explosives can be classified both from the chemical standpoint and according to their uses. From the chemical point of view the following classification may be used: (a) nitro compounds; (b) nitric esters; (c) nitramines; (d) derivatives of chloric and perchloric acids; (e) azides; and (f) different compounds, such as fulminates, acetylides, nitrogen-rich compounds such as tetrazene, peroxides, ozonides, etc.

In general, there are eight definite structural groupings existing in explosive materials, as given below [29]:

(1) $-NO_2$ and $-ONO_2$ in both organic and inorganic materials;

(2) $-N=N-$ and $-N=N=N-$ in organic and inorganic azides;

(3) $-NX_2$, where X is a halogen, as in NCl_3;

(4) $-O-N=C$ in fulminates;

(5) $-OClO_2$ and $-OClO_3$ in organic and inorganic chlorates and perchlorates;

(6) –O–O– and –O–O–O– in organic and inorganic peroxides and ozonides, respectively;

(7) –C≡C– in acetylene and metal acetylides;

(8) M–C, metal bonded with carbon in some organometallic compounds.

Therefore, for the present system of leaded rubber gloves and nitric acid, the possibility of several structural groups may be considered. Perhaps groups 2, 6 and 7 in the list shown above are the likely exceptions for this reacting system under study.

4.2. Nitration and nitration agents

According to Urbanski [29], nitration can be defined as the introduction of the nitro group (NO_2) in place of a hydrogen atom or by adding it to a double bond; alternatively, it may be added indirectly by introducing into a compound a group which can readily be substituted by the nitro group.

For direct introduction of the nitro group, the following are nitrating agents [29]:

1. concentrated nitric acid;
2. mixtures of concentrated nitric and sulphuric acids (or oleum) in different proportions which are known as nitrating mixtures;
3. alkali nitrates in the presence of sulphuric acid;
4. dilute nitric acid;
5. nitrogen dioxide;
6. a solution of nitrogen dioxide in sulphuric acid;
7. nitrogen dioxide in the presence of catalysts.

It has been reported that more expensive nitrating agents may be used, such as solutions of nitric acid in inert organic solvents (chloroform, carbon tetrachloride, ether, nitromethane etc.), or a solution of nitric acid in phosphoric or acetic acid or in acetic anhydride [29].

Indirect methods of nitrating consist of the presence of a group which can readily be substituted by a nitro group. One common method is the reaction of a sulphonated compound with nitric acid, where the sulpho group is replaced by the nitro group. This method is used in the nitration of phenols [29]. The chemical structure of compounds resulting from nitration processes is related to the three nitration reactions [29]:

(1) C-nitration: resulting in the formation of 'true' nitro compounds having the nitro group attached to a carbon atom

$$\equiv C - NO_2$$
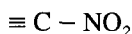
(2) O-nitration: leading to the formation of nitric acid esters, where the nitro group is attached to an oxygen atom

$$\equiv C - ONO_2$$
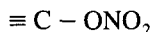
(3) N-nitration: resulting in the formation of nitramines with the nitro group attached to a nitrogen atom of an amine or amide group
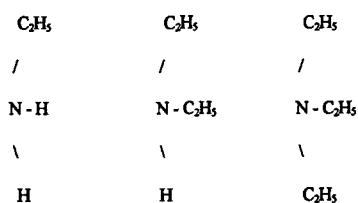
$$= N - NO_2$$

There is no information available on the nitration of elastomers or synthetic rubbers. However, a model was developed by Michael and Carlson to understand the mechanism

of the nitration process for organic materials [30]. It is considered that nitric acid, as $H + ONO_2$, reacts with the ethenic carbon:

```
\/                    \/
C       H            C - H
||  +   |    ⇒        |
C      ONO₂          C - ONO₂
/\                    /\
```
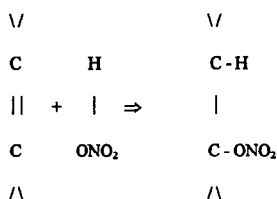
$$(2)$$

This kind of reaction yields the nitric ester of the corresponding alcohol, and most of these materials are explosives [29]. Nitration cannot be related to direct products, but can be the causative reaction of derivatives of the organic materials with nitrous gases which are formed in the deoxidation of the nitric acid. This type of reaction is known as indirect nitration [29]. On the basis of the definitions of several compounds, it is possible to set up another possible mechanism to obtain the fulminate nitro group [31]. The replacement of the hydrogen atoms in ammonia by alkyl groups forms amines:

```
C₂H₅           C₂H₅           C₂H₅
/              /              /
N - H          N - C₂H₅       N - C₂H₅
\              \              \
H              H              C₂H₅
```

The reaction of a salt of these amines with Na or K cyanates results in cyanic acid. Cyanic acid can also be obtained by decomposition of nitrourea. After polymerization, cyanic acid can result in fulminic acid, cyamelide and cyanuric acid. Fulminic acid is the nitro group that could form a fulminate by replacing the hydrogen with an atom of the base metal. Cyanuric acid forms fulminuric acid by thermal rearrangement, and fulminurates can then be obtained. Fulminurates and cyamelides are not considered explosive materials. Fig. 1 shows these relationships.

4.3. Nitrogen oxides and nitric acid

Nitrogen forms a series of oxides in which the oxidation state of nitrogen can vary from $+1$ (N_2O) to $+5$ (N_2O_5). The most common oxides are N_2O (colorless gas, anesthetic, $+1$), NO (usually colorless, $+2$) and NO_2 (brown gas, $+4$). N_2O gas is found in the reduction of reactive metals (Zn) with dilute nitric acid. The reduction of less reactive metal (Cu) with dilute nitric acid produces NO gas; however, with concentrated nitric acid the reduction by-product is NO_2 gas. In addition, NO can react with NO_2 to generate N_2O_3 [13].
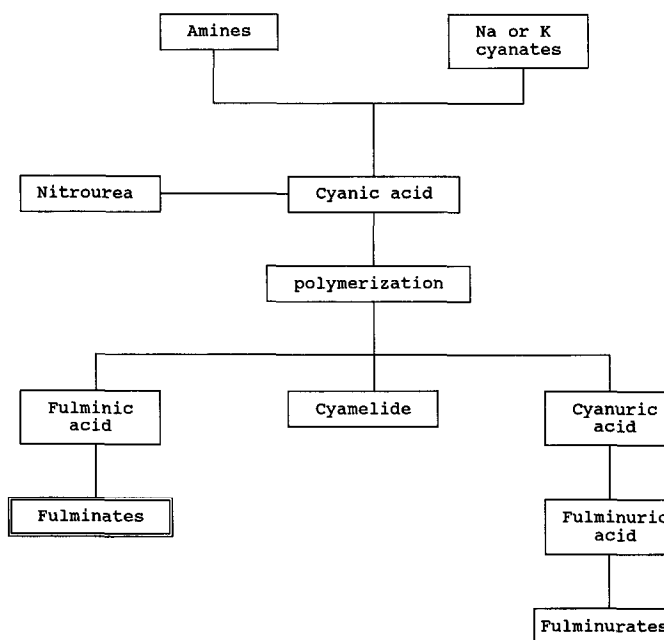
Fig. 1. Possible mechanism to obtain fulminates in a reacting system [31].

Nitric acid reacts with nonmetallic elements, generally with the formation of an oxyacid and NO gas [13]. Concentrated nitric acid has a specific gravity of 1.51 and melting and boiling points of $-41.6°C$ and $86°C$, respectively. The concentration of 69% HNO_3 is 15.4 M [22]. Slightly above its melting point, nitric acid undergoes partial decomposition according to the reaction [13]:

$$2HNO_3 \rightarrow 2NO_{2(g)} + H_2O + \tfrac{1}{2}O_{2(g)} \tag{3}$$

For organic compounds nitric acid can be both a nitrating and an oxidizing agent. The reaction depends on the organic compound and on the concentration of the nitric acid. It is expected that concentrated nitric acid acts as a nitrating agent and, for dilute nitric acid, its nitrating action diminishes and eventually starts on an oxidizing action. The more dilute the nitric acid, the more oxidizing nature it possesses. The limiting concentration of nitric acid varies according to the organic compounds involved [29,32].

5. Conclusions

1. The formation of lead fulminate, $Pb(CNO)_2$, has not been reported in the technical literature. However, organo-lead compounds, which imply the formation of organic lead fulminates, have been studied.

2. The absence of alcohol in the reacting system of leaded rubber gloves with nitric acid may help in avoiding the formation of fulminic acid or fulminates, as reported for mercury and silver fulminates.

3. The reaction of the Neoprene layer with nitric acid is theoretically possible, considering the feasibility of the formation of nitrated organic compounds. These compounds may have explosive characteristics.

4. The lead compound (lead nitrate or lead dioxide) formed by reaction of red lead oxide with nitric acid may be part of the explosive compound as a source of oxygen. It may also be a precursor for any organic lead compound.

Acknowledgements

References

[1] Johnson, T.C. and Lindsay, J.W., Flammability of leaded dry-box gloves, Rocky Flats Report RFP-1354, Dow Chemical Co., Golden, CO, 1969, pp. 13–23.

[2] Long, J.L., Identification and thermal studies of the residue from nitric acid reaction with leaded Neoprene glove, Report MSL 2507, Dow Chemical Co., Rocky Flats Division, Golden, CO, 1973, pp. 24–34.

[3] Long, J.L. and Smith, C.J., Unstable material formed by reacting leaded rubber gloves with nitric acid, Rocky Flats Report RFP-2648, Rockwell International, Golden, CO, 1977, pp. 1–12.

[4] Patnaik, P., A Comprehensive Guide to the Hazardous Properties of Chemical Substances, Van Nostrand Reinhold, New York, 1992, pp. 22–23.

[5] P.A. Davies, Accidental initiation of condensed phase explosives during road and rail transport, J. Hazard. Mater. 38 (1994) 75–88.

[6] K. Raha, J.S. Chhabra, Static charge development and impact sensitivity of high explosives, J. Hazard. Mater. 34 (1993) 385–391.

[7] Wislicenus, J., Organic Chemistry, translated and edited by W.H. Hodgkinson and A.J. Greenaway, D. Appleton & Co., New York, 1882.

[8] Wöhler, L. and Weber, A., 1929. Neue Salze der Knallsäure (New salts of fulminic acid), Berichte der Deutschen C Chemischen Gesellschaft, 62 (1929) 2742–2758.

[9] Grignard, V. et al., Traité de Chimie Organique, Masson, Paris, 1949.

[10] Singh, K., Structure of fulminate ion, J. Chem. Soc. Lond. (1959) 459–461.

[11] Taylor, C.A. and Rinkenbach, Wm.H., A sensitive form of silver fulminate, Army Ordnance, VI(36) (1926) 448.

[12] Beck, W. and Schurierer, E., Übertriorganometallfulminate von Silicium, Germanium, Zinn und Blei, Chem. Berichte, 97 (1964) 3517–3523.

[13] Petrucci, R.H., General Chemistry, Principles and Modern Applications, 4th edn, Macmillan, New York, 1985.

[14] Durrant, P.J. and Durrant, B., Introduction to Advanced Inorganic Chemistry, 2nd edn, John Wiley and Sons, New York, 1970.

[15] Greenwood, N.N. and Earnshaw, A., Chemistry of the Elements, Pergamon Press, Oxford, 1984.

[16] van Thoor, T.J.W. (Ed.), Chemical Technology: an Encyclopedic Treatment, Vol. I, Barnes and Noble, New York, 1968.

[17] Kirk-Othmer (Ed.), Encyclopedia of Chemical Technology, 4th edn, Vol. 8, John Wiley and Sons, New York, 1993.

[18] Codd, L.W. et al. (Eds.), Chemical Techonology: an Encyclopedic Treatment, Vol. V, Barnes and Noble, New York, 1972.

[19] Saunders, K.J., Organic Polymer Chemistry, Chapman and Hall, London, 1973.

[20] Kauffman, G. and Seymour, R.B., Elastomers II. Synthetic rubbers, J. Chem. Educ., 68(3) (1991) 217–220.

[21] Noller, C.R., Chemistry of Organic Compounds, W.B. Saunders, Philadelphia, 1965.

[22] Bever, M.B. (Ed.), Encyclopedia of Materials Science and Engineering, Vol. 2, Pergamon Press, Oxford, 1986.

[23] Weiss, R.W., Organometallic Compounds, Vol. II: Compounds of germanium, tin and lead, including biological activity and commercial applications, First Supplement, Springer-Verlag, New York, 1973.

[24] Ososhnik, I.A., Modification of elastomers with nitroso compounds, Polym. Int. Sci. Technol., 13(8) (1986) T/10–T/17.

[25] Neklyudov, Yu.G. et al., Electrochemical oxidation of rubbers, Int. Polym. Sci. Technol., 18(12) (1991) T/19–T/22.

[26] Thiel, R.D. and Santiago, W.F., Identification of flammable compound formed from the contact of nitric acid with leaded gloves, Interim Report, RDT 255-94, EG and G Rocky Flats, Golden, CO, 1994, pp. 35–37.

[27] Kirk-Othmer (Ed.), Encyclopedia of Chemical Technology, 4th edn, Vol. 10, John Wiley and Sons, New York, 1993.

[28] Dub, M. (Ed.), Organometallic Compounds, Vol. II: Compounds of germanium, tin and lead, including biological activity and commercial applications, Springer-Verlag, New York, 1967.

[29] Urbanski, T., Chemistry and Technology of Explosives, Vol. I, PWN–Polish Scientific Publishers, Warsaw, 1964.

[30] Michael, A. and Carlson, G.H., On the mechanism of the nitration process, J. Am. Chem. Soc., 57 (1935) 1268–1276.

[31] Parker, S.P., Dictionary of Scientific and Technical Terms, 5th edn, McGraw-Hill, New York, 1994.

[32] Jolly, W.L., The Inorganic Chemistry of Nitrogen, W.A. Benjamin, New York, 1964.