

ANALYSIS OF HAZARDS OCCURRING DURING THE USE OF HYDRAZINE

Edyta Janeba-Bartoszewicz

*Poznan University of Technology
Institute of Machines and Motor Vehicles
Piotrowo Street 30, 61-138 Poznan, Poland
e-mail: edyta.janeba-bartoszewicz@put.poznan.pl*

Adam Rojewski

*Poznan University of Technology
Chair of Thermal Engineering
Piotrowo Street 30, 61-138 Poznan, Poland
tel.: +48 791450322
e-mail: adam.m.rojewski@doctorate.put.poznan.pl*

Abstract

The article presents the safety issue bonded to the Polish Air Force F-16 multirole aircraft. The authors pointed out the issue of fuel used for emergency supply system of these aircrafts. The article emphasized the fact that these aircrafts require special fuel with designation H-70, which is 70% aqueous solution of toxic hydrazine. For this reason, the rescue services of Polish Air Force bases where Polish F-16 are stationed had to be adjusted accordingly. Just as importantly, authors noticed that in the event of an emergency landing of this aircraft at different airports could receive difficulties associated with the possible leakage of hydrazine, or its neutralization in the absence of specialized Hydrazine Response Team, which are part of the Airport Rescue Group. After the introduction of new aircraft for use in the Polish Air Force (in this case F-16 multirole aircraft), it is necessary to analyse the safety of their use in the context of potential places on which they can land. This is related, among others, to the safety of managing liquid fuels. In the case of F-16 aircraft, one must bear in mind besides the F-34 fuel, also hydrazine (H-70). The article presents a functional diagram of EPU system of emergency power supply EPS of F-16 multirole aircraft.

Keywords: aviation fuel, hydrazine, airport rescue group

1. Introduction

Due to the changing requirements in the area of construction of technical facilities, including aircraft, more and more attention is paid to aspects related to broadly understood security. This element plays a key role in both civilian and military transport. As emphasized by Satkowski et al. [24], this term has many meanings, depending on the areas of science considered. In general, safety in air transport can be defined as a certain state in which risks associated with various types of aviation activities related to or constituting direct support of aircraft operations are reduced to an acceptable level and are controlled [23].

According to the authors, the process of identifying potential threats and managing the security risk should be continuous. Therefore, after the introduction of new aircraft for use in the Polish Air Force (in this case F-16 multirole aircraft), it is necessary to analyse the safety of their use in the context of potential places on which they can land. This is related, among others, to the safety of managing liquid fuels. In the case of F-16 aircraft, one must bear in mind besides the F-34 fuel, also hydrazine (H-70). At this point, it should be noted that the issues related to the storage, provision of fuel-related services for emergency power systems (EPS) of these aircraft in bases are

most often addressed in the letter concerning the Polish F-16 aircraft, military aviation [5, 31]. When it comes to emergency situations, researchers devote much less attention to the area.

2. The emergency power unit in jet aircraft

Multi-purpose F-16s are aircraft with a jet engine, used in the armed forces of nearly 30 countries around the world. The total number of them currently amounts to approximately 4500 items, including 48 items in the Polish Air Force [25]:

- 31 Tactical Air Base in Krzesiny: 23 items of type F-16 C BLOCK 52+ (single-seater) and 9 pieces of type F-16 D BLOCK 52+ (two-seater),
- 32 Tactical Aviation Base in Łask: 13 pieces of type F-16 C BLOCK 52+ (single-seater) and 3 pieces of type F-16 D BLOCK 52+ (two-seater).

This aircraft is equipped with a fly-by-wire control system [4]. Such a solution is distinguished by the lack of a mechanical connection between the control bodies and the control surfaces. The following main elements of the EPS system can be distinguished in the F-16 [4, 7, 31]: nitrogen tank, portable hydrazine container, turbine drive unit, electronic control system. In addition, various types of sensors and valves supervise and control individual elements of the aircraft system. A simplified diagram of the principle of operation of the EPU system is shown in Fig. 1. Hydrazine undergoes decomposition due to the reaction with iron oxides sputtered on the inner walls of the chamber and passes from liquid to gaseous form. This reaction is accompanied by the release of a very large amount of thermal energy. Separated gases are directed to a gas turbine whose rotational speed in just 1-2 seconds can reach 75 thousand rpm. At the time of rapid decomposition, the temperature of exhaust gases can reach 870°C [27].

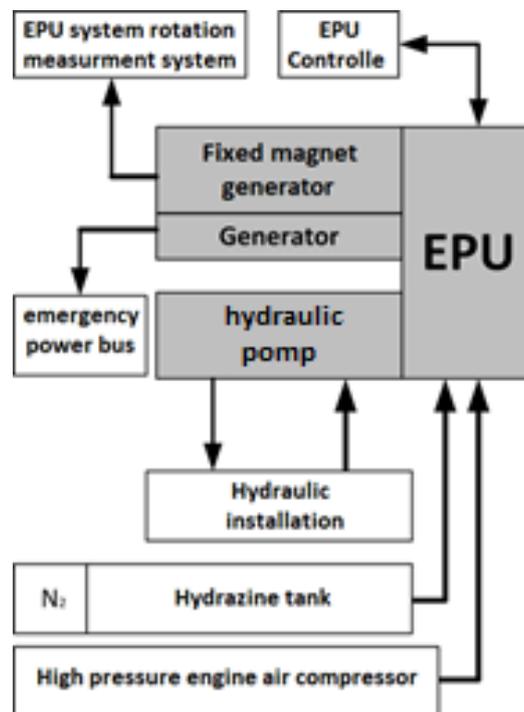


Fig. 1. A functional diagram of EPU system of emergency power supply EPS of F-16 multirole aircraft

3. Hydrazine

Hydrazine (Fig. 2) (diamine, diamine, with the name hydrazine) belongs to nitrates that are compounds of elements with hydrogen. Is a chemical compound composed of two amino groups connected with each other by the N-N bond (chemical formula: N_2H_4) [20].

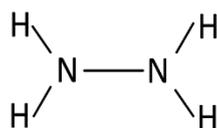


Fig. 2. The molecular formula of hydrazine

Hydrazine can be obtained as a result of:

- the reaction of ammonia with chlorine, as recorded in formula (1):



- or the Rasching synthesis reaction, i.e. the ammonia oxidation of sodium hypochlorite (synthesis), which is recorded by the following formulas (2) and (3):



- or by adding chlorine to 20% urea solution and 20% sodium base, as recorded in formula (4):



In the latter case, the response efficiency is estimated at approx. 50% [10]. Hydrazine is a colourless and oily liquid, with an ammonia-like odour – NH_3 (characteristic of alkyl hydrazine derivatives). Being in its pure form, it burns with a violet or blue flame. Mix well with water (to form $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ hydrate) and with alcohols (e.g. ethyl or methyl). In acidic reactions, it forms salts, which means that it behaves like a weak base ($K_1 = 3 \cdot 10^{-6}$) [5]. In the presence of metals and oxidants, it can react violently. Hydrazine and its derivatives are extremely powerful reducers. This means that the course of a possible reaction is more difficult to control. Nevertheless, as emphasized by Gniewek and Trzeciak [8], an important advantage is the fact that the product of its oxidation is nitrogen.

Hydrazine and its aqueous solution are widely used in the industry. For example, in thermal energy, this compound is used for the treatment of process water, i.e. the adjustment of its composition [14, 19]. It is used in the case of the firing of high-pressure boilers in order to reduce the adverse phenomenon of corrosion. The addition of hydrazine to water can be saved in the form of a chemical equation (5):



If too much hydrazine is added to the water, it is simultaneously disintegrated to form ammonia. This compound in water binds carbon dioxide according to the chemical equation shown (6):



In addition, hydrazine is used as an intermediate for the production of various medicines, e.g. those belonging to the group of cytostatic anticancer drugs [22]. In turn, in the chemical industry, this compound (or its aqueous solution) is used to produce: pesticides [21], insecticides or textile dyes [15]. Hydrazine is also used in the production of various plastics, e.g. in the galvanic treatment of plastics and glass. A wide range of applications also includes explosives for civilian applications (e.g. pyrotechnic materials of passive safety devices of cars) and military [28], sources of propulsion for aircraft engines [2, 24, 25], carriages [1] or ships. In the case of aviation fuel, its aqueous solution (70% $\text{N}_2\text{H}_4 + 30\% \text{H}_2\text{O}$) is used. The use of this chemical compound for aircraft propulsion was recorded during the Second World War in the German fighter aircraft Messerschmitt Me-163B. However, in this case, it was a flat containing additionally methyl alcohol.

Hazards associated with hydrazine according to the CLP (Harmonized Classification and Labelling) labelling approved by the European Union, hydrazine (CAS No. 302-01-2) is a dangerous substance [13, 26]: Flam. Liq. 3, H226; Carc. 1B, H350; Acute Tox. 3 (*) inhalation, H331; Acute Tox. 3 (*) dermal, H311; Acute Tox. 3 (*) oral, H301; Skin Corr. 1B, H314; Skin Sens. 1, H317; Aquatic Acute 1, H400; Aquatic Chronic 1, H410. Among the most frequently mentioned threats to living organisms can be included [5, 15, 26, 29]: burns and allergic reactions of the skin, eye damage (e.g. conjunctiva or cornea), toxicity after ingestion or in the sequence of inhalation (congestion and changes degenerative in the liver, kidneys, lungs, spleen, myocardium or bone marrow, high likelihood of pulmonary edema) toxicity to the aquatic environment, stimulation of the central nervous system, eyes, nose and throat in case of contact with vapours. In addition, it is probably carcinogenic. Hence, it belongs to the category of Carc. 1B, which is known or alleged that are cancerous. Few human accidents and clinical observations of the effects of acute and chronic toxicity are presented in paper [15]. They confirm the previous research in this area. Due to the above, the IMP classified hydrazine as carcinogenic or mutagenic substances [30].

As emphasized by Ciołek and Demel [5], that the temperature of hydrazine self-ignition is reduced to room temperature due to the action of metals (copper, platinum, nickel, iron), which increases the potential hazard. In addition, this compound and its concentrated aqueous solutions (e.g. H-70) are capable of chemical spontaneous combustion in contact with oxides of certain metals and surface-expanded substances (e.g. asbestos, wood, fabrics, dry earth, slag) [5, 9]. Detailed hazards of the produced hydrazine water solutions ($N_2H_4 \cdot H_2$) and requirements for transport and storage as well as the rules of conduct are included in the product safety data sheets, e.g.: hydrazine hydrate 60% produced by Ciech Trading SA [17], hydrazine hydrate 80% produced by POCH SA [16]. Taking into account, the applicable regulations, in Poland for hydrazine: the highest admissible concentration (NDS) is 0.05 mg/m^3 , the highest permissible temporary concentration (NDSch) 0.1 mg/m^3 . It should be emphasized that the current in the world is aimed at limiting the impact on hydrazine and, therefore, lowering the values of NDS and NDSch. In 2015, the 77th meeting of the Inter Ministerial Commission for Maximum Permissible Concentrations and Strengths of Factors Detrimental to Health in the Work Environment adopted the following values of hydrazine concentrations in the work environment: 0.013 mg/m^3 for NDS and 0.039 mg/m^3 for NDSch [15]. In the case of hydrazine in the air, [5]: lethal concentration is 2.60 g/m^3 , dangerous concentration: 104 mg/m^3 , lethal dose: 0.06 g/kg .

4. Conclusions

The issue of the safety of operations in the air forces of each country is associated with the operation of certain aircraft. Their structural solutions and applied technologies determine the creation of safety procedures during the occurrence of unforeseen events involving aircraft. According to the authors of this article, these actions in the case of F-16 Polish Armed Forces, where H-70 fuel is used for emergency power systems, should be implemented in two ways and also include emergency situations at airports where there are no specialized teams. HRT, i.e.: in military bases where F-16s are not stationed, on civilian airplanes. Few, but emerging, dangerous events indicate that the problem occurs and requires more precise identification in terms of limiting the potential effects on people and the surrounding environment.

References

- [1] Aggarwal, R., Patel, I., Sharma, P. B, *Green propellant: A study*, International Journal of Latest Trends in Engineering and Technology, Vol. 6, pp. 83-87, 2015.
- [2] Bartoszewicz, J., Kiciński, M., Nygard, A., *Specyfika gospodarki paliwami w bazach lotnictwa wojskowego (BLW)*, w: Sulima, Z., Szramowiat, K., Sornek, K., Rzepoka, K., (red.), *Energia i paliwa*, pp. 7-14, WSTN, Krakow 2016.

- [3] Christensen, W. D., Martone, J. A., *The F-16 aircraft and hydrazine – An industrial hygiene perspective*, SAE Technical Paper Series 851971, California (USA) 1985.
- [4] Christensen, W. D., *Hydrazine as a monopropellant for the F-16 emergency power unit*, The Second Conference of the Environmental Chemistry of Hydrazine Fuels, 15 February 1979.
- [5] Ciołek, Z. J., Demel, S., *Hydrazyna – procedury jej przechowywania, wykonywania obsługi na samolotach F-16 oraz zasady postępowania w sytuacjach awaryjnych*, Przegląd Sił Powietrznych, pp. 42-71, 2008.
- [6] F-16 Technical Order 00-105 E-9, 2006.
- [7] Flight Manual F-16C/D Blocks 50 and 52+. T.O.GR1F-16CJ-1, 15 June 2003.
- [8] Gniewek, A., Trzeciak, A. M., *Nanocząsteczki metali przejściowych – synteza i aktywność katalityczna*, Wiadomości chemiczne, 63, Nr 11-12, pp. 953-984, 2009.
- [9] *Hazardous materials guide to fire protection*, Federal Emergency Management Agency United States Fire Administration, <http://www.d.umn.edu/ehso/hazguide.pdf>, access 22.02.2017.
- [10] <http://dictionnaire.sensagent.leparisien.fr>, access 22.01.2018.
- [11] *Hydrazine MSDS*. ScienceLab.com, 11.06.2008, access 22.01.2018.
- [12] *Hydrazine*, <https://pubchem.ncbi.nlm.nih.gov>, access 22.01.2018.
- [13] *Hydrazyna: klasyfikacja i oznakowanie*, Centralny Instytut Ochrony Pracy – Państwowy Instytut Badawczy, <https://www.ciop.pl>, access 22.01.2018.
- [14] Ignatowicz, K., *Uzdatnianie wody kotłowej z zastosowaniem Kotaminy C*, Ochrona Środowiska, 26, Nr 3, pp. 25-27, 2004.
- [15] Jakubowski, M., Kupczewska-Dobecka, M., *Hydrazyna. Dokumentacja proponowanych dopuszczalnych wielkości narażenia zawodowego*, Podstawy i Metody Ochrony Środowiska Pracy, Nr 3 (85), pp. 35-65, 2015.
- [16] *Karta charakterystyki substancji/preparatu: hydrazyny wodzian r-r 80% nr cz-476023429*, POCH S.A., 05.01.2010.
- [17] *Karta charakterystyki: wodzian hydrazyny 60% nr 048400*, Ciech Trading SA, wydanie 8, 13.03.2013.
- [18] *Karta: Hydrazine*, National Oceanic and Atmospheric Administration U.S. Department of Commerce, <https://cameochemicals.noaa.gov/chris/HDZ.pdf>, access 22.01.2018.
- [19] Nawrocki, J., Biłozor, S. (red.), *Uzdatnianie wody. Procesy chemiczne i biologiczne*, Wydawnictwo Naukowe PWN, Warszawa-Poznan 2000.
- [20] O’Neil, N. J., Smith, A., Heckelman, P. E., (eds.), *The Merck Index: An encyclopedia of chemicals, drugs, and biologicals*, Royal Society of Chemistry, Cambridge 2013.
- [21] Pohanish, R. P., *Sittig’s handbook of pesticides and agricultural chemicals* (2nd edition), Elsevier Inc 2015.
- [22] Pośniak, M., Bartoszek, D. D., *Analiza I ocean zagrożeń chemicznych w procesie produkcji leków*, CIOP-PIB, Warszawa 2009.
- [23] *Safety Management System*, Anex 19 International Civil Aviation Organization – ICAO 2013.
- [24] Satkowski, W., Bartoszewicz, J., Kiciński, M., *Hydrazyna jako paliwo systemu awaryjnego zasilania wielozadaniowych samolotów F-16*, Materiały konferencyjne, Poznan – Lotnictwo dla obronności, Politechnika Poznańska, Poznan 2016.
- [25] Satkowski W., *Gospodarka materiałami niebezpiecznymi w bazach lotnictwa wojskowego w zmiennych warunkach działania*, rozprawa doktorska, Politechnika Poznańska, Poznan 2016.
- [26] *Substance information: Hydrazine*, European Chemicals Agency, <https://echa.europa.eu/substance-information/-/substanceinfo/100.005.560>, access 23.02.2017.
- [27] Suggs, H. J., Luskus, L. J., Kilian, H. J., Mokry, J. W., *Exhaust gas composition of the F-16 emergency power unit*, Report SAM-TR-79-2, USAF School of Aerospace Medicine, Texas 1979.

- [28] Szala, M., Szymańczyk, L., Dziura, R., *Wysokoazotowe materiały wybuchowe do zadań specjalnych*, Biuletyn WAT, Vol. LVIII, Nr 3, pp. 37-55, 2009.
- [29] Toth, B., *Hydrazines and cancer: A guidebook on the carcinogenic activities of hydrazines, related chemicals, and hydrazine containing natural products*, Harwood Academic Publishers, 2005.
- [30] Wykaz substancji zaklasyfikowanych jako substancje o działaniu rakotwórczym lub mutagennym w środowisku pracy na podstawie klasyfikacji zharmonizowanej, Instytut Medycyny Pracy im. Prof. J. Nofera w Łodzi, <http://www.imp.lodz.pl/upload/centra/wykaz%20substancji%202015.pdf>, access 23.02.2017.
- [31] Zboina, J., (red.), *Bezpieczeństwo na lądzie, morzu i w powietrzu w XXI wieku*, Wydawnictwo CNBOP-PIB, Józefów 2014.

Manuscript received 06 July 2018; approved for printing 10 September 2018