

Edyta JANEBA-BARTOSZEWICZ^{*}Marcin KICIŃSKI^{**}Adam ROJEWSKI^{***}

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RISK OF HYDRAZINE USAGE AT CIVIL AIRPORTS

The article presents the safety issue bonded to the Polish Air Force aircrafts, which uses for emergency supply special fuel called hydrazine, which is 70% aqueous solution of toxic hydrazine with designation H-70. For this reason, the rescue services of Polish Air Force bases where this types of aircraft 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 can 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 Aircraft rescue and firefighting.

Keywords: hydrazine, safety, health threat

1. INTRODUCTION

Due to changing requirements in construction of technical objects and aircraft, there is bigger pressure on aspects connected with the safety issue. This is a key element in civil and military aviation. Generally, safety in air transport can be defined as kind of state, in which risk bonded to many kinds of aviation operations related or posting directly support of aircraft is below an acceptable level and it is controlled [Satkowski, Bartoszewicz and Kiciński 2016].

The most important factors which has influence on air traffic safety are as follow: level of aircraft maintenance personnel training, level of aircraft pilots training, level of navigation personnel training, quality of communication/navigation/

^{*} Wielkopolskie Samorządowe Centrum Kształcenia Zawodowego i Ustawicznego nr 1 w Poznaniu, Poznan University of Technology.

^{**} Institute of Machines and Motor Vehicles, Poznan University of Technology.

^{***} Chair of Thermal Engineering, Poznan University of Technology.

supervision systems, organization of airspace, rules and procedures of air space exploitation, organization and functioning of air traffic management systems.

In view of the wide range of factors in the activities of the aviation safety problems should be considered system-wide, because the probability of occurrence injury of persons and property (e.g. aircraft, ground control and navigation resources, air traffic control) should be minimized and maintained at an acceptable level or below.

Considering the above, in the opinion of the authors, the process of identifying potential threats and risk safety management should be continuous. Hence, after implementation into service in the Polish Air Force new aircraft (in this case multi-role F-16 aircraft), it becomes necessary to analyze the safety of their use in the context of potential runaways on which F-16 can land. This is due, among others, with the safety management of liquid fuels. In the case of F-16 aircraft except to F-34 fuel also hydrazine (H-70). It should be noted that in the literature bounded with Polish F-16s the most frequently raised issues are covering storage and maintenance related to the fuel supply of Emergency Power System (EPS) of mentioned aircraft in the air force bases [Ciołek and Demel 2008, Zboina 2014]. In the event of emergency situations, in this area, researchers devote much less attention.

2. EMERGENCY POWER UNIT OF F-16 AIRCRAFT

Multirole F-16 is jet-powered aircraft, and it is used in air forces of nearly 30 countries around the world. Total number of F-16s is currently near to 4,500 aircrafts, and 48 of them are in the Polish Air Force [Satkowski 2016]:

- 31st Tactical Air Base in Krzesiny: 23 aircraft types F-16 C BLOCK 52+ (single-seat model) and 9 aircraft types F-16 D BLOCK 52+ (two-seat model),
- 32nd Tactical Air Base in Łask: 13 aircraft type F-16 C BLOCK 52+ (single-seat model) and 3 aircraft types F-16 D BLOCK 52+ (two-seat model).

This aircraft is equipped with a fly-by-wire control system [Christensen 1979]. This solution is distinguished by the absence of a mechanical connection between the control yoke and the control surfaces. This means the need of providing continuous (uninterrupted) electrical and hydraulic power supply system. In order to ensure the uninterrupted supply-seen situations used emergency power systems – EPS. Behind the dish is restored in a very short time the basic functions of the aircraft to enable it to continue the flight and safe landing. In order to ensure the power supply in unexpected situations, there is emergency power system (EPS) mounted in aircraft. Its task is to restore in a very short time the basic functions of the aircraft to enable further flight and safe landing.

In the F-16 it is possible to distinguish the following main elements of the emergency power system [Christensen 1979, T.O.GR1F-16CJ-12003, Zboina 2014]: nitrogen tank, a portable container with hydrazine, Emergency Power Unit,

the electronic control system. In addition, there are various types of sensors and valves, which supervise and control the different elements of the aircraft.

In the case of normal operation, EPU is in standby mode. In an emergency manifested: pressure drop in the hydraulic system (below 68 [kG/cm²] or approx. 6.67 [MPa] or approx. 1000 [psi] or loss of power supply) or switch off the engine during flight. Any of this situations provides a flow of compressed to 3000 [psi] nitrogen, which causes the ejection of hydrazine from the tank to the EPU decomposition chamber. Hydrazine by proceeding reaction with iron oxides coated on the inner chamber wall decomposes and turns from a liquid to a gas. This reaction is giving off a very large amount of heat. Gasses produced in the reaction are lead to a gas turbine, which speed can reach 75000 rpm in just 2 seconds. During the rapid decomposition temperature of the exhaust gasses can reach 870 °C [Suggs et al. 1979].

Emergency Power Unit gas turbine transmits power to the hydraulic pump and generator, which restores the power of the electrical and hydraulic system and as a result maintain the maneuverability of the aircraft by the pilot to the landing time. It should be emphasized that the Emergency Power Unit simulation system, which uses as a power source of the aqueous hydrazine solution is mainly characterized by [Ciolek and Demel 2008]: a relatively low weight which is important from the point of view of aircraft performance; simplicity of construction; efficiency in the whole range of aircraft flight (this is especially important in the case of low-speed flight, for example during take-off or landing); high reliability of the system.

3. HYDRAZINE CHARACTERISTIC

Hydrazine (diamine) is a compound nitrogen group, in another word it is a compound made of nitrogen and hydrogen. As shown in Fig. 1 is a chemical compound composed of two interconnected N-N amino groups (chemical formula: N₂H₄) [O'Neil, Smith and Heckelman 2013].

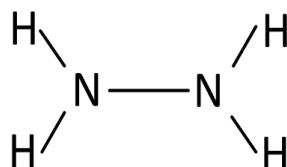


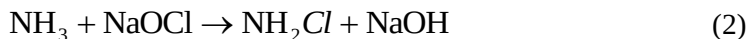
Fig. 1. Molecular formula of hydrazine

Hydrazine can be obtained by:

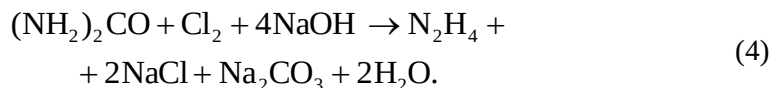
- the reaction of ammonia with chlorine, as in the equation below (1):



– or the reaction of synthesis Raschig i.e. The oxidation of ammonia with sodium hypochlorite (fusion) as in the equations below (2) and (3):

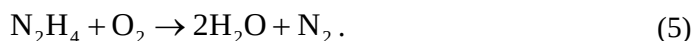


– or by the addition of chlorine to a 20% urea solution and 20% sodium hydroxide. It was written by formula (4), the reaction efficiency is estimated at approx. 50% [<http://dictionnaire.sensagent.laparisien.fr> 2017]:



Hydrazine is a colorless and oily liquid, with a smell similar to ammonia - NH_3 (characteristic for alkyl derivatives of hydrazine). Which in pure form burns with blue or violet flame. It is miscible with water (creates hydrate $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) and alcohols (eg. ethyl or methyl). In the reaction with acids forms salts, which means that it behaves like a weak base ($K_1 = 3 \times 10^{-6}$) [Ciołek and Demel 2008]. In the presence of metals and oxidants, hydrazine can react rapidly. Hydrazine and its derivatives are very strong reducers. This means that the course of the possible reaction is difficult to control. Gniewek and Trzeciak [Gniewek and Trzeciak 2009] emphasize important advantage that the product of the oxidation is nitrogen. Selected physical and chemical quantities of hydrazine are summarized in Table 1.

Hydrazine and its aqueous solution widely applied in industry. For example, in heat power engineering its compound is used for the treatment of process water, ie. adjustment of the water composition [Ignatowicz 2004, Nawrocki and Biłozor 2000]. It is used in diesel powered boilers to reduce the corrosion. The addition of hydrazine to water can be write down in the form of a chemical equation (5):



If there is too much water mixed with hydrazine, its proceed decomposition with the formation of ammonia at the same time. This compound in water binding carbon dioxide, as its present in chemical equation (6):



In addition, the hydrazine is used as an intermediate for the production of various kinds of drugs, e.g. the group of cytostatic anticancer drugs [Pośniak and Bartoszek 2009]. In the chemical industry, hydrazine (or aqueous solution) is used for generating pesticides [Pohanish 2015], insecticides or textile pigments [Jakubowski and Kubczewska-Dobacka 2015]. Hydrazine is also used in the production of various plastics, for example in galvanizing plastics and glass.

The wide range of applications includes explosives for civil use (e.g. pyrotechnic materials of passive safety systems in vehicles) and military [Szala, Szymańczyk and Dziura 2009], the power source of aircraft [Bartoszewicz et al. 2016, Satkowski et al. 2016, Satkowski 2016], rocket, [Aggarwal, Patel and Sharma 2015] or ship engines.

In the case of aviation, fuel hydrazine is used as an aqueous solution (70% N_2H_4 + 30% H_2O). The use of this chemical compound in aircraft was recorded at World War II in a German fighter plane Messerschmitt Me-163B. However, in this case, it was a compound made of methyl alcohol.

Table 1. Selected quantities of hydrazine [Ciołek and Demel 2008, Hydrazine 2017, Hydrazyna 2017, Jakubowski and Kupczewska-Dobacka 2015, National Oceanic... 2017, O'Neil et al. 2013]

Quantity	Unit	Value
Heating value (oxygen in the air)	[J/kg]	$1,941 \cdot 10^7$
Heat of vaporization	[kJ/mol]	45,27
Specific density in temperature: - 5 °C + 15 °C + 20 °C + 25 °C + 35 °C	[g/ml]	1,146 1,011 1,0083 1,0036 0,9955
Explosive limits	[% obj.]	4,7-100
Molecular weight	[g/mol]	32,05
Surface tension	[Nm/m]	66,7
Vapour pressure in temperature + 20 °C + 25 °C	[hPa]	13,3 19,2
Ionization energy	[eV]	8,93
Odor detection threshold	[mg/m ³]	3-5,3 (3-4*)
Solubility in water	[g/l]	1000
Temperature of ignition - in the present of a glass - in the present of stainless steel - in the present of steel sheet - in the present of ferric oxides	[°C]	270 156 132 23
Melting point	[°C]	1,4 (1,4/2*)
Ignition temperature	[°C]	37,88 (38/40*)
Boiling point	[°C]	113,5
Symbols: (*) depending on data source		

4. DANGERS OF HYDRAZINE USE

According to harmonized classification and labeling approved by the European Union, hydrazine (number CAS 302-01-2) is classified as dangerous substance [Centralny Instytut... 2017, European Chemicals... 2017]: Flam. Liq. 3, H226; Carc. 1B, H350; Acute Tox. 3(*), inhale., 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 for living organisms authors noted as follow [Ciolek and Demel 2008, Jakubowski and Kupczewska-Dobacka 2015, Suggs et al. 1979, Toth 2005]: burns and allergic reactions of the skin, eye damage (e.g. conjunctivitis), toxicity if swallowed or inhaled (hyperaemia and degenerative changes in the liver, kidneys, lungs, spleen, heart muscle or bones, a high probability of pulmonary edema), aquatic toxicity, central nervous system stimulation, irritation of nose and throat when exposed to fumes.

In addition, hydrazine is probably carcinogenic. Thus, among the categories of substances Carc. 1B, which are known or presumed to be carcinogenic. The basis for this classification (B1) are the results of tests carried out on animals (mainly in rats, mice, rabbits or dogs). Few accidents with people involved and clinical observation of the effects of acute and chronic toxicity are presented [Jakubowski and Kupczewska-Dobacka 2015]. Confirms the previous studies in this area. Due to the above IMP classified hydrazine as the substance of carcinogenic or mutagenic effect [Instytut Medycyny... 2017].

As stated in the Table 1 hydrazine has a wide range of explosive limit. For this reason, it also creates the risk of fire (cat. Flam. Liq. 3). As pointed out Ciolek and Demel [4], the ignition temperature of hydrazine is reduced to room temperature by the action of metals (copper, platinum, nickel, iron), which increases the potential risk. In addition, this compound and their concentrated aqueous solutions (e.g. H-70) are capable of chemical spontaneous ignition in contact with oxides of certain metals and substances with high surface area (e.g. asbestos, wood, textiles, dry land, slag) [Ciolek and Demel 2008, Federal Emergency... 2017].

Specific hazards of aqueous solutions of hydrazine ($N_2H_4 \cdot H_2O$) and requirements for transportation and storage, with the procedures, are included in the safety data sheets of products, e.g.:

- hydrazine monohydrate 60% produced by Ciech Trading SA [Ciech Trading S.A. 2013],
- hydrazine monohydrate 80% produced by POCH SA [POCH S.A. 2010].

In the event of danger, the magnitude of dangerous concentrations of hydrazine is various depending on the time of its influence and the level of concentration, as shown in the Table 2.

Table 2. Dangerous fumes concentration of hydrazine according to time of influence
[F-16 technical... 2006]

Dangerous level of hydrazine fumes concentration [ppm]	Time of influence [min]
10	60
20	30
30	10

In view of the existing regulations in Poland for hydrazine:

- the highest allowable concentration (TLV-TWA) is 0,05 [mg/m³],
- the highest allowable temporary concentration (TLV-STEL) is 0,1 [mg/m³].

It should be emphasized that the present world tends to limit the impact of the hydrazine and therefore reducing the TLV-TWA and TLV-STEL. In 2015 77 Meeting of the Interdepartmental Committee of Maximum Admissible Concentrations and Intensities of Harmful Factors for Health in the Working Environment has adopted the following values of hydrazine concentration in the work environment: 0,013 [mg/m³] for TLV-TWA and 0.039 [mg/m³] for TLV-STEL [Ciech Trading S.A 2013].

In case of presence of hydrazine in the air [Ciołek and Demel 2008]:

- lethal concentration is 2,60 [g/m³],
- dangerous concentration: 104 [mg/m³],
- deadly dose: 0,06 [g/kg].

5. DANGERS IDENTIFICATION AND CLASSIFICATION OF HYDRAZINE USE AT CIVIL AIRPORT

As indicated earlier hydrazine and its aqueous solution states a serious threat to people and the surrounding environment. Bearing in mind the safety aspects of risk management, places of the risks arise associated with hydrazine can be identified at different angles. Given the basic logistics chain of hydrazine, which is presented in detail in Stokowski's Ph.D. thesis [Satkowski 2016], in a time of peace hazard can occur in storage facilities for hydrazine, in transport between objects and plane (Fig. 2), and when hydrazine is assembled on the airframe. Under the current rules, hydrazine transportation requires on the packaging appropriate pictograms (Fig. 3). Carriage in containers from the warehouse to the F-16 is fulfilled with special HRT trailer (Hydrazine Response Team which is part of the Aircraft Rescue and Fire-fighting). Another potential hazard occurs during the work on the ground with the aircraft, e.g. during the operation of installation or replacement after an emergency landing of filled with hydrazine cylinder. These works are carried out on a single plane by two persons.



Fig. 2. Transport container for hydrazine gas cylinder



Fig. 3 Pictograms used in the European Union (GHS) on the packaging which contains hydrazine [European Chemicals... 2017]

At this point, the authors point out that the greatest risk occurs in the case of emergency situations, e.g.:

1. After starting the emergency power supply system during the flight.
2. During the uncontrolled release of hydrazine from aircraft.

This concerns in particular events where the landing of for example F-16 takes place at the civil airport, where there is no HRT. Taking into account the location of the Polish Air Force bases, the possible HRT transport by road within an acceptable time is impossible because of the distance. A similar situation occurs in situations where the F-16 aircraft is forced to land at the civil airport. In such events are run local emergency services, which should initiate specific safety procedures.

6. CONCLUSION

The issue of security operations in the Air Force of each country is bounded with the certain aircraft exploitation. Their design solutions, the technologies used to create safety procedures determine the occurrence of unexpected events featuring this airplane. These actions in the case of aircraft in which the emergency power supply system fuel is H-70, procedures should be implemented in two ways, and additionally include emergencies at airports which does not have HRT, i.e.:

- in military bases which do not have aircraft using H-70,
- at a civil airport.

First, to restrain the potential consequences for man and the surrounding environment, emergency services should evacuate all people to safety, windy area. Secondly, only personnel equipped with PPE (personal protection equipment, e.g. gas mask, oxygen tank, sealed suit) can approach to the aircraft. If there is no fire

and pilot live is not in danger, emergency services from the civil airport should wait for HRT from military base to come with HRT trailer (supplied with PPE, allows to transport hydrazine tanks safely) and wait for disassemble hydrazine tank from aircraft. It is necessary to train firefighting teams from civil airports in the case of the emergency landing of a military plane with H-70 onboard.

REFERENCES

- Aggarwal R., Patel I., Sharma P.B., 2015, Green Propellant: A Study, *International Journal of Latest Trends in Engineering and Technology*, Vol. 6, Iss. 1 (September), p. 83–87.
- Bartoszewicz J., Kiciński M., Nygard A., 2016, Specyfika gospodarki paliwami w bazach lotnictwa wojskowego (BLW), in: Sulima Z., Szramowiat K., Sornek K., Rzepoka K. (red.), *Energia i paliwa*, WSTN, Kraków, p. 7–14.
- Centralny Instytut Ochrony Pracy – Państwowy Instytut Badawczy, 2017, Hydrazyna: klasyfikacja i oznakowanie, <https://www.ciop.pl> (access on 23.02.2017).
- Christensen W.D., 1979, Hydrazine as a Monopropellant for the F-16 Emergency Power Unit, *The Second Conference on the Environmental Chemistry of Hydrazine Fuels*, 15 February.
- Ciołek Z.J., Demel S., 2008, Hydrazyna – procedury jej przechowywania, wykonywania obsługi na samolotach F-16 oraz zasady postępowania w sytuacjach awaryjnych, *Przegląd Sił Powietrznych*, listopad, p. 42–71.
- F-16 Technical Order 00-105 E-9, 2006.
- Flight Manual F-16C/D Blocks 50 and 52+. T.O.GR1F-16CJ-1, 15 June 2003.
- Gniewek A., Trzeciak A.M., 2009, Nanocząsteczki metali przejściowych – synteza i aktywność katalityczna, *Wiadomości chemiczne*, nr 11–12, p. 953–984.
- Emergency Management Agency United States Fire Administration, *Hazardous Materials Guide to Fire Protection*, <http://www.d.umn.edu/ehso/hazguide.pdf> (access on 22.02.2017).
- Hydrazine, <https://pubchem.ncbi.nlm.nih.gov> (access on 22.02.2017).
- International Civil Aviation Organization (ICAO), 2013, *Safety Management System*, Anex 19.
- Ignatowicz K., 2004, Uzdatnianie wody kotłowej z zastosowaniem Kotaminy C, *Ochrona Środowiska*, 26, nr 3, s. 25–27.
- Jakubowski M., Kupczewska-Dobacka M., 2015, Hydrazyna. Dokumentacja proponowanych dopuszczalnych wielkości narażenia zawodowego, *Podstawy i Metody Ochrony Środowiska Pracy*, nr 3(85), p. 35–65.
- POCH S.A., 05.01.2010, Karta charakterystyki substancji/preparatu: hydrazyny wodzian r-r 80% nr cz-476023429.
- Ciech Trading, 13.03.2013, Karta charakterystyki: wodzian hydrazyny 60% nr 048400, wydanie 8.
- National Oceanic and Atmospheric Administration U.S. Department of Commerce, Karta: Hydrazine, <https://cameochemicals.noaa.gov/chris/HDZ.pdf> (access on 22.02.2017).
- Nawrocki J., Biłozor S. (red.), 2000, *Uzdatnianie wody. Procesy chemiczne i biologiczne*, Wydawnictwo Naukowe PWN, Warszawa–Poznań.
- O’Neil N.J., Smith A., Heckelman P.E. (eds.), 2013, *The Merck Index: An Encyclopedia of Chemicals, Drugs, and Biologicals*, Royal Society of Chemistry, Cambridge.

- Pohanish R.P., 2015, *Sittig's Handbook of Pesticides and Agricultural Chemicals* (Second Edition), Elsevier.
- Pośniak M., Bartoszek D.D., 2009, *Analiza i ocena zagrożeń chemicznych w procesie produkcji leków*, CIOP-PIB, Warszawa.
- Satkowski W., Bartoszewicz J., Kiciński M., 2016, Hydrazyna jako paliwo systemu awaryjnego zasilania wielozadaniowych samolotów F-16, in: *materiały konferencyjne Poznań – Lotnictwo dla obronności*, Politechnika Poznańska, Poznań, 26.08.
- Satkowski W., 2016, *Gospodarka materiałami niebezpiecznymi w bazach lotnictwa wojskowego w zmiennych warunkach działania*, rozprawa doktorska, Politechnika Poznańska, Poznań.
- Sensagent – dictionnaire, <http://dictionnaire.sensagent.leparisien.fr> (access on 22.02.2017).
- European Chemicals Agency, Substance information: Hydrazine, <https://echa.europa.eu/substance-information/-/substanceinfo/100.005.560> (access on 23.02.2017).
- Suggs H.J., Luskus L.J., Kilian H.J., Mokry J.W., 1979, *Exhaust Gas Composition of the F-16 Emergency Power Unit*, Report SAM-TR-79-2, USAF School of Aerospace Medicine Texas.
- Szala M., Szymańczyk L., Dziura R., 2009, Wysokoazotowe materiały wybuchowe do zadań specjalnych, „Biuletyn WAT”, Vol. 58, nr 3, p. 37–55.
- Toth B., 2005 *Hydrazines and Cancer: A Guidebook on the Carcinogenic Activities of Hydrazines, Related Chemicals, and Hydrazine Containing Natural Products*, Harwood Academic Publishers.
- Instytut Medycyny Pracy im. Prof. J. Nofera w Łodzi, Wykaz substancji zaklasyfikowanych jako substancje o działaniu rakotwórczym lub mutagennym w środowisku pracy na podstawie klasyfikacji zharmonizowanej, <http://www.imp.lodz.pl/upload/centra/wykaz%20substancji%202015.pdf> (access on 23.02.2017).
- Zboina J. (red.), 2014, *Bezpieczeństwo na lądzie, morzu i w powietrzu w XXI wieku*, Wydawnictwo CNBOP-PIB, Józefów.
- Grzesik N., 2010, *Uzbrojenie samolotu F-16*, Wydawnictwo Wyższej Szkoły Oficerskiej Sił Powietrznych, Dęblin.

ZAGROŻENIA STOSOWANIA HYDRAZyny W PORTACH LOTNICZYCH

Streszczenie

W artykule przedstawiono zagadnienie bezpieczeństwa związanego z eksploataowaniem w Siłach Powietrznych RP samolotów wykorzystujących jako paliwo do systemu awaryjnego wodnego roztworu hydrazyny o oznaczeniu H-70. Z tego też względu służby ratownicze polskich baz lotnictwa wojskowego, w których stacjonują samoloty korzystające z hydrazyny, musiały zostać odpowiednio dostosowane. Zwrócono uwagę, że w przypadku wystąpienia konieczności awaryjnego lądowania takiego statku powietrznego na innych lotniskach mogą pojawić się trudności związane z ewentualnym wyciekiem hydrazyny czy jej neutralizacji z uwagi na brak wyspecjalizowanych zespołów HRT, będących częścią Grupy Ratownictwa Lotniskowego.

Słowa kluczowe: hydrazyna, bezpieczeństwo, zagrożenie zdrowia