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Liquid Rocket Propellant

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Overview

Large stockpiles of liquid rocket propellants remain in the stockpiles of many countries, with many concentrated in Asia, Eastern Europe, and the Commonwealth of Independent States. These liquid rocket propellants were used as the primary propulsion mechanism for a number of weapons systems (see Table 11.1), although how many of each are still in storage is unknown.

Stockpiles of liquid rocket propellants have necessitated a number of technical operations to alleviate the risks they pose, including their safe disposal. This chapter does not aim to provide a detailed technical study of liquid rocket propellants, but rather an overview to illustrate the basic theory of minimizing the risks they pose.

There are numerous reasons why the clearance or disposal of liquid-propellant-fuelled systems hazards may be desirable in a post-conflict or developing country, including: 1) to reduce the risk to human health; 2) to allow the destruction of unserviceable or unstable ammunition; 3) to safeguard the environment; or 4) to permit clearance of the area.

Many of these liquid fuels are stored in the open, or in unventilated buildings that have no drainage channels. Due to the lack of appropriate storage conditions and the effects of climate (humidity and high temperatures), containers have been discovered that are corroded and are not hermetically sealed. The result is a very strong probability of uncontrolled evaporation of the chemicals into the atmosphere and the possibility of wider leakage, leading to significant environmental pollution.

Table 11.1

Summary of weapons systems using liquid propellants

Weapon system		Use	Remarks
Type	NATO* designation		
Volga-2 S-75	SA-2 'Guideline'	Surface to air	China: HQ-2 version Iran: Sayyed-1 version North Korea: own version
Angara/Vega S-200	SA-5 'Gammon'		
R-1	SS-1a 'Scunner'	Surface to surface	Initial design that led to 'Scud' Iraq: Al-Hussein 1 and 2 There was a range of further theatre ballistic missile derivatives, including SS-4 'Scandal' (8K53), etc.
R-11 (8K11), R-17 (8K14), R-300 Elbrus	SS-1b/c 'Scud'		
P-15, P-20, P-21, P-22, P27 Termit	SS-N-2 'Styx' SSC-3 'Styx'	Ship to ship Surface to ship	Also produced in India, North Korea, and possibly Egypt
R-13 (4K50)	SS-N-4 'Sark'	Ship to surface	SS-N-5 also referred to as 'Sark' Submarine-launched ballistic missile
R-21 (4K55)	SS-N-5 'Sark'		
R-27 (4K10)	SS-N-6 'Serb'		
R-29 (4K75)	SS-N-8 'Sawfly'		
R-29K (4K75D)	SS-N-18 'Stingray'		
R-29RM (4K75RM)	SS-N-23 'Skif'		
C-201 SY-1/HY-1	CSS-N-1 'Scrub-brush'	Ship to ship Surface to ship	Also produced in Iran
C-201 HY-2/FL-1/FL-3A	CSS-N-2 'Silkworm' CSS-N-3 'Seersucker'		

* North Atlantic Treaty Organization.

What are liquid propellants?

Liquid propellants are used in some rocket motors, and are divided into monopropellants and bipropellants. Monopropellants consist of a single compound, although some may require the action of a catalyst. They have a low

specific impulse² and tend to be used mainly in small rocket motors, such as thrusters, or in gas generators. They are unsuitable as a main propulsive source in a munition, and therefore they are not discussed further here.

Biropellants use a combination of a liquid fuel and a liquid oxidizer (often called melange). They are stored in separate tanks within the missile and injected into a combustion chamber. They then come into contact and violently react, producing hot gas for the purpose of propulsion. This spontaneous ignition of the fuel and oxidizer is called a hypergolic³ reaction. Highly volatile hypergolic reactions will also occur if leakage or poor storage conditions allow the two components to mix, resulting in a major deflagration event.

Fuels

The most common fuels likely to be encountered in ammunition stockpiles are listed in Table 11.2.

Table 11.2
Common liquid propellant fuels

Compound	Generic name	Chemical formula	Remarks
Unsymmetrical dimethyl hydrazine	UDMH	$(\text{CH}_3)_2\text{N-NH}_2$	Mainly NATO
Monomethyl hydrazine*	MMH	$(\text{CH}_3)\text{NH-NH}_2$	
Triethylamine/xylidene**	Tonka TG-02		Mainly Soviet and Chinese
Kerosene	Kero	C_8H_{18}	The formula varies, as kerosene is a complex mixture of petroleum hydrocarbons and other constituent compounds. The formula given is an 'average'.

* Used with dinitrogen tetroxide.

** Also known as ksilidin, dimethylaminobenzene, dimethylaniline, dimethyl-phenylamine, or aminodimethyl benzene.

The hydrazine fuel family are colourless, oily liquids with ammonia-like or fishy smells. The triethylamine/xylidene mixture is an oily liquid that easily vaporizes under normal climatic conditions. The colour varies from yellow to brown and it has the characteristic scent of oily amines.

Oxidizers

The oxidizer is the most difficult component of the propellant to deal with safely. If oxidizers are stored for lengthy periods, the water composition percentage can significantly increase as a result of shrinkage and corrosion, and the effectiveness of the inhibitor may decrease by 50–60 per cent, thus leading to the destabilization and active decomposition of the oxidizer itself.

The oxidizers most likely to be encountered in ammunition stockpiles are listed in Table 11.3.

Table 11.3
Common liquid propellant oxidizers

Compound	Generic name	Formula	Remarks
Red fuming nitric acid	RFNA	HNO_3	
Inhibited red fuming nitric acid	IRFNA mélange	$\text{HNO}_3 +$	The inhibitor in IRFNA is hydrofluoric acid and is designed to protect the container against corrosion caused by the RFNA.
Dinitrogen tetroxide		N_2O_4	

Technical data for the oxidizers used in missile systems is often difficult to obtain, and will inevitably be inaccurate due to poor storage conditions. The percentage compositions vary, as shown in the examples for IRFNA given in Table 11.4.⁴

Table 11.4
IRFNA chemical composition data⁵

Component	%		Remarks
	Bosnia*	Standard	
Nitric acid (HNO_3)	74.6	82	
Dinitrogen tetroxide (N_2O_4)	22.5	0	
Nitrogen oxide (NO_2)	0	17	
Hydrogen fluoride (HF) Water	4.4	0.7	The Bosnia sample also included H_3PO_4 and water.

* See endnote. 4.

Safe disposal options

Decanting the fuel and oxidizer from storage containers and subsequently disposing of both is a complex process that should only be conducted by an accredited chemical (nitric acid-capable) or waste management company on site, or in its stationary facilities outside the country (if it is an international company). A range of safe and environmentally benign disposal or recycling options is available, but dependent on an economy of scale.

Previous experience of NATO, the Organization for Security and Co-operation in Europe (OSCE), and the UN Development Programme (UNDP) of oxidizer disposal indicates that this 'economy of scale' is an important factor in the selection of disposal options. Small quantities (less than 75 tonnes) are sometimes more cost-effectively disposed of through a competitive commercial contract. For larger quantities (greater than 300 tonnes), it is often more cost-effective to build national capacity 'on site'—through the procurement of specialist equipment, which is used to convert the oxidizer into fertilizer—or to develop the capability for destructive disposal in the host country.

In the case of South-eastern and Eastern Europe, disposal and/or recycling operations must be in accordance with the appropriate international and European Union environmental and safety hazardous goods and waste transport and disposal directives.⁶ Previous safe disposal options within the region have included those given in Table 11.5, although some of these have not complied with environmental safety requirements.

Table 11.5 **Liquid propellant disposal options**

Disposal option	Fuel	Oxidizer	Remarks
Leak sealing and overpacking	Yes	Yes	Prior to removal to commercial waste disposal facility
Acid dilution/neutralization	No	Yes	
Incineration	Yes	Yes	
Fertilizer conversion	No	Yes	
Open burning	Yes	No	Environmental limitations
Decanting and contained burning	Yes	No	Requires integrated pollution control system for environmental compliance
Dilution with low-grade fuel	Yes	No	Recycling option Improves fuel octane rating

Toxic risks

For any given substance, toxic risk depends on: 1) the toxicity of the substance; 2) the duration of exposure; and 3) the intensity of exposure. The main routes by which any toxic substance may enter the body are: 1) ingestion;⁷ 2) percutaneous entry;⁸ 3) ocular entry;⁹ and/or 4) inhalation.

A compound's toxicity alone is an insufficient guide to the level of risk it may pose due to inappropriate storage or during disposal operations. For example, in the case of contaminant vapours, the volatility of the parent compound must be considered in addition to its toxicity. In practice, a compound with a higher volatility may pose a greater hazard than a more toxic compound with lower volatility. This is because, at a given ambient temperature, higher volatility compounds are present in the immediate atmosphere in higher concentrations than less volatile compounds. There is no universally recognized method of quantifying risk on the basis of both volatility and toxicity, but one simple method uses the 'Hazard Index':

$$\text{Hazard Index (HI)} = \text{Volatility} / \text{Toxic dose}$$

To illustrate the relationship among toxicity, volatility, and risk, a comparison has been made between UDMH and MMH in Table 11.6.

Table 11.6

Toxicity/volatility comparison MMH/UDMH

Compound	Vapour pressure @ 25° C (mm Hg)	Toxicity* Index	Hazard Index
Monomethyl hydrazine (MMH)	49.6	74	0.67
Unsymmetrical dimethyl hydrazine (UDMH)	156.8	252	0.62

* The LC₅₀ limit is the concentration of substance, which under defined conditions, is lethal to 50 per cent of those exposed. In this case, the LC₅₀ limit is for a four-hour period.

While UDMH is nearly four times less toxic than MMH, its higher volatility (caused by much higher vapour pressure) means the two compounds are ranked equally in the Hazard Index. It must be emphasized that the Hazard

Index is not a universally agreed concept, but it does present a rough guide that can be used operationally to assess the relative risk posed by different chemical substances.

Hydrazines

The hydrazine derivatives (MMH and UDMH) tend to be local irritants, convulsants, and blood-destroying agents¹⁰ that are absorbed by all routes of administration to the body. They are almost all suspected of causing cancer in humans. Hydrazine itself is a strong skin and mucous membrane irritant and a moderate blood-destroying agent. It can be absorbed through intact (undamaged) skin. Exposure to the vapour results in: 1) eye irritation; 2) lung congestion; and 3) nervous system convulsions.

Similar effects are exhibited by UDMH contamination, but the compound is less irritating to the skin, and has less severe percutaneous toxic effects. It also has a lower oral toxicity than hydrazine, but its acute vapour toxicity is greater. UDMH therefore poses greater risks in cases of localized atmospheric contamination.

The American Conference of Governmental Occupational Hygienists is an advisory body that sets standards for threshold limit values (TLVs).¹¹ These standards are similar to the United Kingdom health and safety executive occupational exposure limits (HSEOEL), which although internationally preferred, do not publish limits for UDMH and MMH. Therefore, TLVs have to be used, as shown in Table 11.7.

Table 11.7

Threshold limit values (TLV) for hydrazine/MMH/UDMH

Compound	TLV		Remarks
	ppm*	mg.m ³	
Hydrazine	0.1	0.10	UK HSEOEL = 0.10 mg.m ³ . Same as TLV
MMH	0.2	0.35	
UDMH	0.5	1.00	

* Parts per million.

Hazard reduction

Reducing hazards when working in liquid-bipropellant-contaminated environments does not consist solely in adopting the appropriate operating procedures and the provision of suitable personal protective equipment. The following measures are also essential: 1) the education of employees; 2) regular monitoring of the working environment; 3) emergency contingency planning; 4) management of work schedules to reduce exposure; and 5) frequent medical monitoring of worker health. Regrettably, in many countries that still have liquid-propellant stockpiles, little of this is implemented at the operational level, and therefore workers and local communities are exposed to the risks.

Table 11.8

Liquid propellant disposal projects (as of September 2007)

Country	International agency	Quantity (tonnes)	Disposal method	Remarks
Armenia	OSCE	862.0	Conversion to mineral dressing	Ongoing (700 tonnes completed)
Azerbaijan	NATO/NAMSA*	1,200.0	Conversion to liquid soil enhancer	Ongoing (1,000 tonnes completed)
Bosnia and Herzegovina	UNDP	45.6	Over-pack and subsequent removal to Western Europe hazardous waste disposal facility	Complete
Georgia	OSCE	400.0	Conversion to fertilizer	Complete
Kazakhstan	OSCE	410.0	<i>Contractual negotiations ongoing</i>	
Moldova	NATO/NAMSA	250.0	Incineration	Complete
Montenegro	UNDP/OSCE	128.8	<i>Competitive tender process ongoing</i>	
Ukraine	OSCE	16,336.0	<i>Competitive tender process ongoing</i>	
Uzbekistan	To be confirmed	1,500.0	<i>Uzbekistan is still to decide on a partner international organization.</i>	
Total		21,132.4		

* NATO Maintenance and Supply Agency.

Progress to date

National governments, with the support of international organizations and donors, have initiated a range of disposal programmes within South-eastern and Eastern Europe (where the majority of the liquid propellants may be found). These have included projects to dispose of both oxidizers and fuels (see Table 11.8).

Conclusion

The safe disposal of liquid rocket propellants, although a potentially hazardous process, is now well understood, and a range of technical solutions are possible. There is now little doubt as to the potential environmental hazards that the majority of current storage systems present should leakage occur, but the exact scale of the problem has yet to be defined.

The issue of liquid rocket propellant disposal is also beginning to be understood by a range of donors, and disposal projects have, or are being, initiated by NATO, the OSCE, and UNDP. The success of these projects will depend on a sustainable level of donor funding. ■

Notes

- 1 This chapter is based on Wilkinson (2002). It has been condensed for this volume and updated where appropriate.
- 2 This can be defined as the thrust per unit mass rate of burning of the propellant. Ideally, it should be a constant for a given propellant. It is an important performance parameter.
- 3 The spontaneous ignition of two components.
- 4 The following information is based on a technical report and chemical analysis for the disposal of a similar substance by UNDP Bosnia and Herzegovina in 2005. It was AK-20 oxidizer.
- 5 AK-20 oxidizer.
- 6 These directives include: Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000 on the Incineration of Waste; Directive 2003/105/EC of the European Parliament and of the Council of 16 December 2003 on the Control of Major-Accident Hazards Involving Dangerous Substances; Directive 2006/12/EC of the European Parliament and of the Council of 5 April 2006 on Waste; and the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal.
- 7 Entry into the body by eating or swallowing.

- 8 The penetration of substances through the skin.
- 9 Entry into the body via the eyes.
- 10 Agents that can attack and contribute to the destruction of the red blood cells.
- 11 TLV is the maximum concentration levels of a toxic substance in air, which, under certain conditions, is considered acceptable for the exposure of industrial workers.

Further reading

OSCE (Organization for Security and Co-operation in Europe). 2007. *Best Practice Guide: Liquid Rocket Fuel Components Elimination (DRAFT)*. Vienna: OSCE.

Wilkinson, Adrian. 2002. *Technical Note for Mine Action (TNMA) 09.30*. Geneva: Geneva International Centre for Humanitarian Demining.

Bibliography

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