DoD EXPLOSIVES SAFETY STANDARDS FOR ENERGETIC LIQUIDS PROGRAM

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ABSTRACT

The Department of Defense Explosives Safety Board (DDESB) is sponsoring the DoD Explosives Safety Standards for Energetic Liquids Program to study issues and develop revised safety standards concerning explosives equivalence, compatibility mixing, and quantity-distance (Q-D) criteria for liquid propellants and related energetic liquids. Energetic Liquid has been defined as - a liquid, slurry, or gel, consisting of or containing an explosive, oxidizer, fuel, or combination of the above, that may undergo, contribute to, or cause rapid exothermic decomposition (thermal explosion), deflagration, or detonation. Fundamental to the program are tasks to 1) review energetic liquid accident and realistic large-scale test data, and 2) to review other guidelines used in the commercial sector for application to energetic liquids. Data generated in these activities is forming the basis for proposed revisions to current standards. In addition, an interagency advisory board, the Liquid Propellants Working Group (LPWG), has been established to provide oversight in the assessment of available information with respect to historical and operational requirements, and ultimately to deliberate on the formulation of recommendations. This paper summarizes the rationale for the program and discusses technical information developed from the accident and test review with respect to hazards controlling quantity-distance criteria for energetic liquids. Furthermore, preliminary proposals on the hazard classification of energetic liquids and associated Q-D criteria are developed and presented.

INTRODUCTION

Explosives safety standards for liquid propellants such as liquid oxygen (LO2), liquid hydrogen (LH2), hydrazines, nitrogen tetroxide and other materials used in launch vehicles and some weapons systems are based on information and data comprising the state of knowledge from over thirty years ago. Regulations promulgated by the Department of Defense Explosives Safety Board (DDESB) for these materials are covered in DoD 6055.9-STD *DoD Ammunition and Explosives Safety Standards* Chapter 9 Paragraph F.

Much additional data have been developed from research efforts and analyses conducted since the original criteria were established. Studies by Napadensky (1993) and Tomei (1989) have questioned the validity of current requirements in general, and also as applied to liquid rocket static testing and launch facility siting, respectively. A number of inconsistencies and

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irregularities in the current standards have been identified. Among these are the inappropriate generalization of hydrogen vapor cloud fireball effects data in the implementation of quantity-distance (Q-D) criteria, and inconsistencies in the hazard classification and storage compatibility group mixing requirements for energetic liquids. Another problem area is the inaccurate characterization of blast overpressure hazards of liquid bipropellant explosions (TNT equivalence values). In addition, current standards do not specifically address materials such as gelled propellants and concepts such as hybrid rocket systems. Finally, inconsistencies exist between guidelines promulgated by DoD and a variety of other government agencies and commercial organizations such as Department of Transportation (DOT), Occupational Safety and Health Administration (OSHA), National Aeronautics and Space Administration (NASA), and the National Fire Protection Association (NFPA). The Explosives Safety Standards for Energetic Liquids Program has been established to address all of these concerns.

The program is divided into two separate task areas. The first part is addressing hazard classification and Q-D guidelines for fuels, oxidizers, and monopropellants when isolated from other incompatible energetic liquids. The second part of the study is addressing TNT equivalence and associated explosives safety siting guidance for liquid bipropellant combinations held in close proximity such as in fueled launch vehicles and static test stands. This paper focuses on the issue of fuels, oxidizers, and monopropellants. A discussion of the bipropellant issue can be found in a recent paper by Tomei (1998) of The Aerospace Corporation.

CURRENT DoD STANDARDS

As specified in DoD 6055.9-STD, liquid propellants are classified into Hazard Groups I through IV, as well as Compatibility Groups (A through F) that are uniquely defined. Group I identifies the least hazardous materials, that are considered to have a fire hazard potential only. Group II comprises strong oxidizers that may yield a more serious fire hazard when combined with combustible materials. Group III comprises materials that may give rise to fragment hazards from pressure rupture of a container resulting from fire, deflagration, or vapor phase explosion. Group IV materials present blast overpressure and fragment hazards indicative of Hazard Division 1.1 mass detonating explosives.

Compatibility Groups for liquid propellants are specified in DoD 6055.9-STD without subsequent definition; however, working definitions are identified in CPIA Publication 394 *Hazards of Chemical Rockets and Propellants* (Hannum, 1984b). These definitions should not be confused with standard hazard classification Compatibility Groups defined for Class 1 materials in other sections of DoD 6055.9-STD. Group A comprises strong oxidizers mainly of acidic character. Group B was formerly used for concentrated hydrogen peroxide. Group C consists of fuels such as hydrocarbons and hydrazines. Group D materials act mainly as fuels, but individual chemicals may react as oxidizers in some combinations. Group E consists of pressurizing gases. Group F materials are characterized by a significant sensitivity to detonation by shock or impact. Group G comprises monopropellants that may have an adverse chemical reaction with either fuels or oxidizers. Table 1 compiles Hazard Group/Compatibility Group information for some representative materials.

Table 1. Hazard Group/Compatibility Group Designations for Selected Liquid Propellants

PROPELLANT	HAZARD GROUP	STORAGE GROUP
Hydrocarbon Fuels (RP-1)	I	C
Hydrazines	III	C
Nitrogen Tetroxide	I	A
Otto Fuel II	I	G
Nitromethane	IV	F
Hydrogen Peroxide(> 52%)	II	A
Liquid Oxygen	II	A
Ethylene Oxide	III	D
Liquid Hydrogen	III	C

Quantity-distance criteria are mainly determined for Hazard Groups (I - III) based on liquid hydrogen/air flame data (Napadensky, 1993; Zabetakis and Burgess, 1961). Quantity-distance criteria for Hazard Group IV materials are determined from Hazard Division 1.1 Q-D tables using specifically assigned TNT equivalence values. Likewise, when incompatible Hazard Group (I - III) propellants are contained in the same vicinity at less than specified distances and without implementation of adequate provisions to prevent mixing, Hazard Division 1.1 Q-D tables are used in conjunction with specified TNT equivalence values to determine separation distances. Current TNT equivalence criteria for some energetic liquids are shown in Table 2.

Table 2. Selected Liquid Propellant Explosive Equivalents

PROPELLANT COMBINATIONS	TNT EQUIVALENCE	
	STATIC TEST STANDS	RANGE LAUNCH
LO2/LH2	60%*	60%*
LO2/LH2 + LO2/RP-1	Sum of (60% for LO2/LH2)* + (10% for LO2/RP-1)	Sum of (60% for LO2/LH2)* + (20% for LO2/RP-1)
Nitromethane	100%	100%

*Change 1 to DoD 6055.9-STD (Aug 97) will include a revision for LO2/LH2 as a result of work conducted under the auspices of the bipropellant task of the Explosives Safety Standards for Energetic Liquids Program as follows: "For siting launch vehicles and static test stands, the explosive equivalent weight is the larger of: (1) The weight equal to $8W^{2/3}$ where W is the weight of LO2/LH2, or (2) 14 percent of the LO2/LH2 weight."

FUELS, OXIDIZERS, AND MONOPROPELLANTS

A thorough review of fire and explosion hazards associated with fuels, oxidizers, and monopropellants when isolated from other incompatible energetic liquids has been performed, based on actual incidents and full scale tests that simulate realistic accident scenarios. Tables 3a and 3b compile information on incidents and notable tests identified with various materials of interest, including brief descriptions of event failure scenarios involved and hazard characteristics observed. Details can be found in previous reports (Cocchiaro, 1998; Cocchiaro, 1997).

Table 3a. Incidents and Tests with Fuels and Monopropellants

Material	# Events	Failure Scenario	Hazard Characteristics
Hydrazine	3	explosion of storage drums and propellant tanks in fires	violent explosion with pressure vessels (near field blast); no mass sympathetic reaction; far field fragment hazards
Otto Fuel II	3	fuel tank explosion during static testing; explosion in transfer pipeline in fire; explosion of propellant tank in fire	finite propagation of low velocity detonation with heavy confinement or ullage (blast and fragment hazards similar to Class 1.1); minor explosion with lower confinement (near field fragment hazards)
Ethylene Oxide	5	major chemical plant explosion; major explosion from storage tank rupture; minor sterilization facility explosion; fires from ruptured tank car and pipeline	major vapor explosions (far field blast and fragment hazards); possible near field fragment effects from minor explosions
Liquid Hydrogen	7	fires from ruptured pipelines and processing equipment; 2 vapor explosions from tank failures	major vapor explosion potential (intermediate blast and fragment hazards); normal fire hazards otherwise
Hydroxyl-ammonium Nitrate	4	spontaneous explosion of storage tanks, processing vessels, and pipeline	violent explosion with pressure vessels (near field blast); no mass sympathetic reaction; near field fragment hazards
Monomethyl-amine Nitrate	1	major explosion of rail tank car	mass detonation similar to Class 1.1
Nitromethane	1	major explosion of rail tank car	mass detonation similar to Class 1.1

SUMMARY OF ENERGETIC LIQUID HAZARD BEHAVIOR

These materials demonstrated a wide variance in degree of hazard in accidents and realistic field test scenarios. Although blast effects were observed at relatively close range in incidents involving liquids such as hydrazine and hydroxylammonium nitrate (HAN) based materials (depending on confinement), the primary hazard (without consideration of toxic hazards) governing quantity-distance requirements for these materials appears to be fragment throw for static situations such as liquid storage. The analogous behavior between hydrazine and HAN based liquids is due to a propensity towards self sustained exothermic decomposition (as a negative characteristic) but shock insensitivity and resistance to mass detonation (as positive characteristics) - relative to typical high explosives. It is further assumed that fragment distance and dispersion would likely be independent of the number of containers involved since these materials do not undergo mass detonation, although the number of containers that end up reacting is important in determining how many fragments are eventually produced and dispersed. It should be noted that specific packaging configuration does appear to have a significant influence on hazard response. While quantitative information on blast and fragment effects from analogous incidents with hydrogen peroxide, ethylene oxide, and Otto Fuel II was not obtained in all cases, these materials exhibit a similar characteristic of self sustainable exothermic decomposition and thus may be considered to produce similar hazard effects (at a minimum) in a storage environment. Liquids such as Otto Fuel II may also exhibit more predominant blast hazards in situations involving pumping or propulsion system testing due to vapor phase explosion or effects of confinement. Nitromethane and monomethylamine nitrate may also exhibit significant blast hazards in circumstances involving bulk quantities of the materials. Finally, energetic liquids such as hydrogen and ethylene oxide may exhibit more pronounced hazards due to vapor explosions. On the other hand, the primary hazard with materials such as nitrogen tetroxide, nitric acid, halogen fluorides (chlorine trifluoride/pentafluoride), and in many cases liquid hydrogen appears to be either dispersion of toxic vapors from the unreacted materials or normal fire. These materials did not exhibit a susceptibility to violent self sustained exothermic decomposition in the bulk liquid similar to many other energetic liquids.

Table 3b. Incidents and Tests with Oxidizers

Material	# Events	Failure Scenario	Hazard Characteristics
Hydrogen Peroxide	7	fires/explosions with storage drums, processing vessels, and during aerospace system testing	minor explosions causing localized damage; no mass reaction; potential near field fragment hazards
N2O4/IRFNA	5	tank ruptures	toxic cloud release hazards only
Chlorine Trifluoride	1	minor explosion and toxic cloud release from run tank failure	Primarily toxic cloud hazards; minor explosion potential

The National Fire Protection Association (NFPA) Instability Hazard Rating system defined in NFPA 704 *Standard System for the Identification of the Hazards of Materials for Emergency Response, 1996*, and utilized in hazard descriptions provided in NFPA 49 *Hazardous Chemicals Data, 1994*, provides one method for categorizing the majority of these energetic liquids with respect to observed hazards. The Instability Hazard Rating Index of NFPA 704 provides a ranking methodology addressing the degree of susceptibility of materials to release energy (explosive potential). The degrees of hazard are ranked according to ease, rate, and quantity of energy that may be released. Table 4 summarizes the instability hazard criteria. Besides using a qualitative determination of several important properties, the ranking system also employs a quantitative measure of instantaneous power density (IPD) from the decomposition of a material (product of the Heat of Reaction and initial reaction rate at 250 °C).

Table 4. NFPA 704 Instability Hazard Rating Criteria

HAZARD RATING	Instant. Power Density (W/ml)	OTHER PROPERTIES
NFPA = 0	< 0.01	Normally stable, even under fire conditions; no reaction with water; no exotherm at T < 500 °C
NFPA = 1	0.01 < IPD < 10	Normally stable, but can become unstable at elevated temperatures and pressures; react vigorously with water; change or decompose upon exposure to air, light, or moisture
NFPA = 2	10 < IPD < 100	Undergo violent chemical change at elevated temperatures and pressures; may react violently or form explosive mixtures with water
NFPA = 3	100 < IPD < 1000	Capable of detonation or explosive decomposition from a strong initiating source or heating under confinement; react violently with water without heat or confinement; sensitive to thermal or mechanical shock at elevated temperatures and pressures
NFPA = 4	> 1000	Capable of detonation or explosive decomposition at normal temperatures and pressures; sensitive to thermal or mechanical shock

Tables 5 and 6 compile NFPA classification data for energetic liquids determined to be of direct relevance to this program. Materials such as hydrazine, methylhydrazine, nitromethane, ethylene and propylene oxide, and hydrogen peroxide have Instability Hazard Rating assignments of 2 or greater. Examining hazard descriptions of NFPA 49, these materials are all characterized as giving rise to potential hazards associated with violent rupture of closed containers upon heating. Otto Fuel II is also characterized in a Navy manual (NAVSEA, 1993) as exhibiting container rupture due to rapid decomposition upon heating. Otto Fuel II may also be subject to explosion when explosively-boosted sufficiently or when heated under heavy confinement (NAVSEA, 1993). This behavior is consistent with an Instability Hazard Rating of 3, and thus, an unofficial designation (not submitted to NFPA for approval) for Otto Fuel II has been assigned. Likewise, technical data for HAN based energetic liquids is consistent with the definition of an Instability Hazard Rating of 2/3 (Cocchiaro, 1998). Again, unofficial designations for HAN based materials have been assigned in the tables. Chlorine trifluoride and liquid fluorine have assigned Instability Hazard Ratings of 3 and 4; however, this is probably due to special fire fighting considerations associated with violent reaction with water as opposed to an indication of instability of the neat materials. Nitromethane can be considered analogous to detonable high explosives (Instability Hazard Rating of 4) under some conditions. On the other hand, energetic liquids such as hydrocarbon, liquid hydrogen, and UDMH fuels and liquid oxygen, nitric acid, and nitrogen oxides (N2O4 and mixed oxides of nitrogen [MON]) oxidizers have Instability Hazard Ratings of less than 2. With the exception of hydrogen, these materials do not appear to be subject to violent hazard behavior (as characterized in NFPA 49). Unfortunately, NFPA 704 does not have provisions covering vapor phase explosion hazards important with materials such as ethylene oxide and hydrogen that may exhibit different types of hazard behavior.

The NFPA Instability Hazard Rating concept, with consideration for possible confinement effects of the energetic liquid packaging configuration, appears to provide a methodology for categorizing energetic liquids for Q-D purposes. In most cases, fuels, oxidizers, and monopropellants of concern can be segregated into a few distinct categories: 1) energetic liquids having an Instability Hazard Rating of 4, which might be treated similarly to conventional high explosives using Hazard Division 1.1 criteria for Q-D purposes; 2) energetic liquids having an Instability Hazard Rating of 2 or 3, where Q-D requirements may vary from specific minimum fragment distances assigned for packaging in either a pressure vessel or a commercial storage/transport configuration, to less restrictive criteria depending on confinement effects; 3) energetic liquids having an Instability Hazard Rating of less than 2, with minimal Q-D requirements based on fire hazard considerations only; and 4) energetic liquids that are subject to vapor phase explosion, where special provisions may need to be developed. A special exception to these requirements should be made for halogen fluorides and fluorine, which aside from water reactivity, exhibit behavior more consistent with normal oxidizers with an Instability Hazard Rating less than 2.

ENERGETIC LIQUID HAZARD CLASSIFICATION

In general, replacement of the current Hazard Group (I - IV)/Compatibility Group (A - F) classification scheme for liquid propellants with United Nations (UN) hazard classification nomenclature as defined in *Recommendations on the Transport of Dangerous Goods* has been justified. Thus, the main hazard classification designator for energetic liquids would become either Class 1 (explosives), Class 2 (compressed or liquefied gases), Class 3 (flammable liquids), Class 4 (flammable solids, self-reactive materials), Class 5 (oxidizers), Class 6 (toxic/infectious substances), Class 8 (corrosive), or Class 9 (miscellaneous). UN transportation hazard classifications for energetic liquids are also compiled in Tables 5 and 6.

The design and logistics of modern weapons sometimes require that consideration be given to permitting storage or operations involving energetic liquids in a storage structure containing solid explosives. For example, it may be necessary to store hydrocarbon-fueled cruise missiles having high explosive warheads with fueled configurations not containing explosive warheads. Another example is the storage of liquid gun propellant with explosive ammunition components. Since two energetic liquids might each be compatible with certain explosive ammunition stores, but incompatible with each other, a two-part compatibility group designation may be assigned to an energetic liquid.

The first element is the storage and transportation Compatibility Group (CG) designation. The alpha designations are the same as the Compatibility Group designations for UN hazard Class 1, with the same definitions. However, a CG may also be assigned to an energetic liquid in a hazard class other than Class 1 for storage and handling purposes. [The absence of a CG

Table 5. HAZARD CLASSIFICATION MATRIX – Fuels and Monopropellants

NAME	UN Hazard Class	OSHA/NFPA Flammable Liquid Class[1,4]	NFPA Instability Hazard Rating[2]	NFPA Health Hazard Rating[2]	NFPA Flammability Hazard Rating[2]	Current DoD Storage Class	Proposed DoD Storage Hazard Class[3]
Flammable liquids, N.O.S. (JP-10)	3	II (CL)	0		2	I C	3 (LB)
kerosene (RP-1)	3	II (CL)	0	0	2	I C	3 (LB)
Hydrogen, Refrig Liq	2.1	N/A	0	3	4	III C	2.1 (LB)
Hydrazine, Anhydrous or > 64% aq	8	II (CL)	3	3	2	III C	8 (LC)
Aerozine 50	6.1					III C	6.1 (LC)
Methylhydrazine	6.1	IB (FL)	2	4	3	III C	6.1 (LC)
Dimethylhydrazine, unsym	6.1	IB(FL)	1	4	3	III C	6.1 (LC)
Nitromethane	3	IC (FL)	4	1	3	IV F	3 (LE)
Ethylene oxide	2.3	IA (FL)	3	3	4	III D	2.3 (LD)
Propylene Oxide	3	IA (FL)	2	3	4	N/A	3 (LD)
HAN Monopropellants	1.3 C	N/A	3		N/A	N/A	1.3 C (LE)
Otto Fuel II	9	IIIB (CL)	3		1	I G	9 (LE)

NOTES:

1. Calculated from Flash Point/Boiling Point data (from CPIA and NFPA) versus NFPA 30 criteria: CL = Combustible Liquid FL = Flammable Liquid
2. As specified in NFPA 49 (and/or calculated from NFPA 704).
3. New DoD Energetic Liquid Compatibility Group identified in parentheses.
4. Calculated from reported Flash Point/Boiling Point data (from CPIA and NFPA) versus 29 CFR 1910.106 (OSHA) criteria.

Table 6. HAZARD CLASSIFICATION MATRIX - Oxidizers

NAME	UN Hazard Class	NFPA Oxidizer Classification[1]	NFPA Instability Hazard Rating[2]	NFPA Health Hazard Rating[2]	NFPA Flammability Hazard Rating	Current DoD Storage Class	Proposed DoD Storage Hazard Class[3]
Hydrogen Peroxide, aq (>60%)	5.1	3	3	2	N/A	II A	5.1 (LA)
Nitric acid, red fuming	8	3	1	4	N/A	I A	8 (LA)
Nitrogen Tetroxide/MON	2.3	2	0	3	N/A	I A	2.3 (LA)
Liquid Oxygen	2.2	N/A	0	3	N/A	II A	2.2 (LA)
Hydroxylammonium Nitrate	4.1		2		N/A	N/A	4.1 (LE)
Halogen Fluoride (ClF3/ClF5)	2.3		3 *	4	N/A	II A	2.3 (LE)
Liquid Fluorine	2.3		4	4	N/A	II A	2.3 (LE)
Nitrogen Trifluoride	2.2				N/A	N/A	2.2 (LE)

NOTES:
1. Specified in NFPA 430.

2. As specified in NFPA 49 and/or calculated from NFPA 704.

3. New Energetic Liquid Compatibility Group identified in parentheses.

* Due to violent reaction with water.

indicates incompatibility with solid explosives.] The second element is a new Energetic Liquid Compatibility Group (ELCG) designation. The ELCG applies to mixed storage of energetic liquids or ammunition components containing energetic liquids. The ELCG is specified in parentheses as the last element of the hazard classification. The ELCG designations and definitions are:

LA - Energetic liquids that are strong oxidizers, mainly of acidic character. These materials may cause or contribute to the combustion of other material, possibly resulting in serious flare fires or explosions. Includes, but is not limited to, nitrogen tetroxide and mixed oxides of nitrogen, inhibited red fuming nitric acid, liquid oxygen, hydrogen peroxide (52 % or greater), and gels, slurries, or emulsions of the above.

LB - Energetic liquids that are readily combustible when exposed to, or ignited in the presence of an oxidizing agent, but that are not strong reducing agents. Some may be hypergolic with group LA materials. Includes, but is not limited to, hydrocarbons such as kerosenes and strained ring ramjet fuels; liquid hydrogen; and gels, slurries, or emulsions of the above.

LC - Energetic liquids that are readily combustible when exposed to, or ignited in the presence of an oxidizing agent, and are also strong reducing agents. These will likely be hypergolic with group LA substances. Includes, but is not limited to, hydrazines and other amines, including slurries or gels of these.

LD - Energetic liquids that act mainly as combustible fuels, similar to groups LB and LC, when exposed to, or ignited in the presence of oxidizing agents but that may act as oxidizers in some combinations. They may be a monopropellant with the right catalyst, or may be pyrophoric and ignite upon release to the atmosphere. Examples are ethylene and propylene oxides, and boranes.

LE - Energetic liquids having characteristics that do not permit storage with any other energetic liquid. They may react adversely with either fuels (reducing agents) or oxidizers. Examples are nitromethane, nitrate ester based formulations such as Otto Fuel II, liquid monopropellants containing hydroxyl ammonium nitrate (HAN), halogen fluorides and fluorine, and gels, slurries, or emulsions of the above.

Different energetic liquids in the same ELCG may be stored together with the exception of dissimilar liquids of Group LE. Mixed storage is prohibited between energetic liquids of different ELCG designations, with one exception: liquids of groups LB and LC should not be stored together if possible, especially for storage areas containing primarily materials of group LB; however, mixed storage is permitted if circumstances require. Hydrazines (Group LC) may ignite if leaked onto a rusted surface and in turn cause a hydrocarbon (Group LB) fire in a mixed storage environment. Absence of hydrazine in a hydrocarbon storage area would reduce the probability and/or consequences of an accident.

This compatibility scheme is reflected in the hazard classification for the HAN based liquid gun propellant XM-46:

1.3C(LE)

This hazard classification reflects the conventional storage and transportation CG “C” - which means the propellant can be stored in the same magazine with CG “C” solid propellants. Since CG “C” can be mixed in storage with CG “D” (reference Table 3-1, DoD 6055.9-STD), CG “D” high explosive projectiles could also be present. On the other hand, hydrocarbon fuel such as JP-10 would not be permitted in this storage scenario, because its ELCG (LB) indicates incompatibility with the liquid gun propellant (LE).

Some miscellaneous observations that assisted in the determination of compatibility group designations for a few materials, where mixed storage could yield increased accident probability and/or consequences, are described below:

Nitromethane (LE) - sensitized to detonation by amines (LC) and strong acids (LA); contact with strong oxidizers(LA) may cause fire or explosion; mixtures with hydrocarbons (LB) are highly flammable; also may react violently with amines (LC) and hydrocarbons (LB).

HAN (LE) - decomposition is catalyzed by nitric acid (Group LA). Also, the commonality of the spontaneous ignition scenario identified in several accidents with HAN based liquids indicates that these materials should probably be segregated from unlike energetic liquids in storage unless other provisions are enforced with respect to facility design or configuration.

Halogen fluorides and Fluorine (LE) - hypergolic with water; violent reaction between 90% hydrogen peroxide (LA) and chlorine pentafluoride (LE) at -78 C.

Hydrogen peroxide (LA) - Segregated storage or facility/operational contamination control measures may be advisable for hydrogen peroxide given the common root cause of contamination observed in several incidents. Without these controls, assignment to ELCG (LE) may be warranted

Each new energetic liquid, or new non-bulk packaging configuration of an energetic liquid, developed by a DoD Component or adopted for DoD use, will be examined and assigned a hazard classification in accordance with the process described in TB 700-2/NAVSEAINST 8020.8B/TO11A-1-47/DLAR 8220.1 *Department of Defense Ammunition and Explosives Hazard Classification Procedures*.

Quantity-distance criteria associated with this hazard classification protocol (described below in Table 7) include separation requirements for bulk quantities, and in some cases, minimum distances for pressure vessels and other commercial packagings. If the hazards of a particular new packaging configuration are not adequately addressed by the separations prescribed in the following tables, a different minimum distance may be assigned during the hazard classification process, and indicated parenthetically, in hundreds of feet, as the first element of the hazard classification. For example, if a new liquid oxygen pressure vessel configuration is hazard classified: "(10)2.2(LA)", a minimum distance of 1000 feet would apply, rather than the criteria of Table 13 (as specified in Table 7). Again, the absence of a conventional storage and transportation CG indicates incompatibility with solid explosives.

ENERGETIC LIQUID QUANTITY-DISTANCE CRITERIA

Since many energetic liquids are not classified as UN Class 1 explosives, conventional Q-D storage criteria do not generally apply to these materials. At the same time, the (non-Class 1) UN transportation hazard classifications for many energetic liquids appear to be inappropriate and/or inadequate for application to storage safety (based on available accident and test data). For example, hydrazine has a UN hazard classification of 8 (corrosive), while it also is subject to dangerous fire and explosive behavior. Thus, the implementation of Q-D criteria for energetic liquids should be based on an independent determination of the predominant hazard presented by the material in the storage environment.

Examining the NFPA Instability Hazard Rating methodology along with available accident and test data discussed previously, it appears that several materials require minimum blast or fragment distance criteria. Rational for the minimum distance requirements is discussed below.

The most appropriate option for assigning Q-D requirements for items containing hydrazine and methylhydrazine could be to use specific fragment distances assigned for packaging in either a pressure vessel or a commercial storage/transport configuration. Based on maximum debris ranges observed in accident and test events, appropriate fragment distances appear to be 300 feet for hydrazine drums and 800 feet for hydrazine pressure vessels (Cocchiaro, 1998). This is reasonably consistent with current Q-D criteria for hydrazines, which designates a 600 foot Inhabited Building Distance (IBD) for quantities up to 10,000 pounds based on vessel fragment hazards. In the absence of adequate test and/or accident data, Aerozine 50 (50/50 mixture of hydrazine and unsymmetrical dimethylhydrazine) will be considered equivalent to hydrazine.

Several levels of hazardous behavior may be indicated for Otto Fuel II. Where the material is maintained under heavy confinement such as during underwater static testing, significant blast hazards may be present thus requiring Otto Fuel II to be treated for Q-D purposes as equivalent to conventional Hazard Division 1.1 explosives. For these circumstances, the standard Hazard Division 1.1 Q-D tables can be used in conjunction with a specific TNT equivalency value assigned for the energetic liquid. Based on accident and test data discussed previously (Cocchiaro, 1998), a proposed TNT equivalence value for Otto Fuel II is 100% (for underwater static test stands only). On the other hand, potential fragment hazards may govern Q-D requirements for storage of Otto Fuel II pressure vessels. Based on the maximum debris range observed in a cookoff test of an Otto Fuel II propellant tank (Cocchiaro, 1998), a benchmark fragment distance for Otto Fuel II pressure vessels would be about 200 feet (150 feet plus a 33% safety factor). In other packaging conditions, the hazards associated with Otto Fuel II appear to be minimal, analogous to other (low vapor pressure) stable combustible liquids.

Two distinct hazard levels are apparent with hydrogen. In many cases, hydrogen may present normal fire hazards, and thus, might be treated as non-explosive for Q-D purposes. However, due to a potential for vapor explosion, blast and fragment hazard effects may need to be considered. This will be examined in more detail later.

For Q-D purposes, two levels of hazard appear to be involved with ethylene oxide. When fuel-air vapor explosion of large quantities of the liquid is possible, ethylene oxide might be treated analogous to conventional Hazard Division 1.1 explosives using a TNT equivalence of 100% conservatively indicated in one accident (Cocchiaro, 1998). Otherwise, ethylene oxide might be appropriately considered for fragment hazards. Although a recommended minimum fragment distance cannot be inferred from the accident data, ethylene oxide could be treated as equivalent to hydrazine, unless proven otherwise from approved test data, based on equivalent NFPA Instability Hazard Rating assignments. In the absence of adequate test and/or accident data, propylene oxide will be considered equivalent to ethylene oxide.

Several levels of hazardous behavior may be indicated for HAN based energetic liquids. One option for assigning Q-D requirements for pressure vessels containing HAN based materials could be to use specific fragment distances assigned for either monopropellant mixtures or neat HAN solutions. [In the absence of sufficient data, however, neat HAN solutions and HAN monopropellants will be considered equivalent.] Based on possible blast effects observed in one incident (Cocchiaro, 1998), a minimum distance could be set at approximately 150 feet (110 feet plus a 33% safety factor). On the other hand, fragment debris hazards could increase the minimum Q-D to levels consistent with hydrazine and other similar liquids. For packaging in lower confinement such as commercial shipping/storage containers, HAN monopropellants may be treated according to Hazard Division 1.3 requirements while neat HAN solution might be considered for fire hazards representative of an oxidizer. This is consistent with recommendations provided by Cruice (1981). Based on small scale test results discussed previously (Cocchiaro, 1998), Cruice recommended a hazard classification of Hazard Division 1.3 (old military Class 2) for HAN based monopropellants when packaged in the lowest possible confinement such that gaseous decomposition products can be vented quickly and easily under fire exposure. On the other hand, Cruice suggested that the neat HAN solution may be categorized as an oxidizer for transportation classification purposes. The US Army has obtained an approved UN hazard classification for the HAN monopropellant XM-46 as Hazard Division 1.3C. However, this classification does not take localized blast and potential fragment hazards into consideration that have been observed in incidents with the propellant packaged in a pressure vessel configuration.

Again, different levels of hazard appear to be involved with hydrogen peroxide. Appropriate Q-D guidelines for hydrogen peroxide when packaged in a pressure vessel configuration might be based on the potential for fragment throw. Although a recommended minimum fragment distance cannot be inferred from the accident data, hydrogen peroxide could be treated as equivalent to hydrazine, unless proven otherwise from approved test data, based on equivalent NFPA Instability Hazard Rating assignments. However, it is unclear if similar hazards apply for hydrogen peroxide packaged in a less confining configuration. Thus, more appropriate

Q-D criteria for storage in commercial shipping containers might be based on oxidizer fire hazard considerations only.

Hazards presented by energetic liquids such as normal hydrocarbon and unsymmetrical dimethylhydrazine (UDMH) fuels as well as nitric acid, nitrogen tetroxide, halogen fluoride, and fluorine oxidizers appear to be limited to normal fire. Consistent with a demonstrated less reactive behavior, more appropriate Q-D requirements for these energetic liquids might be limited to fire hazard considerations only.

For the more conventional fuels and oxidizers, and also where minimum blast and/or fragment hazards are not required due to low confinement packaging, Q-D standards can be adopted from OSHA (as specified in 29 CFR 1910) and/or NFPA guidelines. [In many cases it appears that OSHA and NFPA guidelines are equivalent.] This could be beneficial for some facilities through the elimination of multiple (and perhaps conflicting) regulatory requirements. In general, the categorization of energetic liquids according to the ELCG assignment provides a reasonable filter relating the respective materials to appropriate NFPA and OSHA guidance for flammable liquids, oxidizers, and flammable and oxidizing compressed gases.

Table 7 provides a master matrix, which cross-references each particular energetic liquid with a particular set of Q-D requirements. Derivation of criteria for conventional fuels and oxidizers, where no specific minimum guidance is provided, is described below.

Flammable Liquids – excluding Liquid Hydrogen

29 CFR 1910.106 (paragraph d.5.vi.a) requires a separation distance of 50 feet between storage buildings containing flammable and combustible liquids in containers (less than 60 gallon) or portable tanks (less than 660 gallon) and “a building or line of adjoining property that may be built upon” without restrictions on the construction of the storage building. Subparagraph d.5.vi.b further indicates that the total quantity for storage is unlimited; however, additional restrictions on the interior storage configuration are imposed. NFPA 30 *Flammable and Combustible Liquids Code, 1996* provides further commercial guidance on storage separation and other fire protection aspects for normal, less reactive fuels. NFPA guidelines are directed at confining a fire to its storage array and/or preventing propagation of a fire through thermal radiation (DDESB, 1997). NFPA 30 (paragraph 4-4.2.1) also recommends a 50 foot separation distance between storage sites and “an important building or line of adjoining property that can be built upon” with no restrictions on facility construction. Important building is defined in NFPA 30 as “a building that is considered not expendable in an exposure fire” to include “occupied buildings, control buildings, or buildings that contain high value contents or critical equipment or supplies.”

Table 7. Minimum Distances for Selected Energetic Liquids

Energetic Liquid	NFPA Instability Hazard Rating	DoD Storage Hazard Class	Minimum Q-D
RP-1; JP-10	0	3 (LB)	Table 11
Liquid Hydrogen	0	2.1 (LB)	Table 17 or risk assessment
Hydrazine, > 64%	3	8 (LC)	800[1] or 300[2] ft
Aerozine 50		6.1 (LC)	800[1] or 300[2] ft
Methylhydrazine	2	6.1 (LC)	800[1] or 300[2] ft
UDMH	1	6.1 (LC)	Table 11
Nitromethane	4	3 (LE)	Use H/D 1.1 Q-D with TNT Equiv = 100%
Ethylene Oxide	3	2.3 (LD)	H/D 1.1 Q-D[3] with TNT Equiv = 100%, or 800[1] or 300[2] ft
Propylene Oxide	2	3 (LE)	H/D 1.1 Q-D[3] with TNT Equiv = 100%, or 800[1] or 300[2] ft
HAN Monopropellants	3	1.3C (LE)	150[1] ft or use H/D 1.3 Q-D
Otto Fuel II	3	9 (LE)	Use H/D 1.1 Q-D[4] with TNT Equiv = 100%, or 200[1] ft, or Table 11
Hydrogen Peroxide, > 60%	3	5.1 (LA)	800[1] ft or Table 12
IRFNA	1	8 (LA)	Table 12
Nitrogen Tetroxide/MONs	0	2.3 (LA)	Table 12
Hydroxylammonium Nitrate	2	4.1 (LE)	150[1] ft or Table 12
Liquid Oxygen	0	2.2 (LA)	Table 13
Halogen Fluorides (ClF3/ClF5)	3*	2.3 (LE)	Table 12
Liquid Fluorine	4	2.3 (LE)	Table 12
Nitrogen Trifluoride		2.2 (LE)	

1. Packaged in pressure vessel configuration
2. Packaged in commercial shipping/storage container.
3. When vapor cloud explosion of large quantities is likely.
4. For underwater static test stands only.

* Due to violent reaction with water.

Based on the NFPA definition of "important building," it seems reasonable that the 50 foot distance would apply to Inhabited Building Distance (IBD), Intraline Distance (ILD), and Above Ground Magazine distance. With respect to ILD and magazine distances, this requirement implies a very low probability of fire propagation from one energetic liquid site to another. Thus, the proposed IBD for flammable energetic liquid container storage is 50 feet. Although neither 29 CFR 1910.106 nor NFPA 30 provide specific guidance for separation of flammable/combustible liquid container storage buildings from public transportation routes, it would seem that a Public Traffic Route (PTR) distance of 50 feet or perhaps less would be reasonable also. In the case of ILD and Above Ground Magazine distance, a separation distance of 50 feet provides a starting point, at least for container storage inside buildings (this will be expanded on in subsequent paragraphs). In general, Class IA, IB, IC, II, and IIIA liquids (OSHA/NFPA designations) are treated equivalently with regard to safe separation requirements in both 29 CFR 1910.106 and NFPA 30 requirements. Neither 29 CFR 1910.106 nor NFPA 30 provide specific guidance for storage separation between different classes of flammable and/or combustible liquids (analogous to Intragroup ILD as defined in DoD 6055.9-STD). In fact, NFPA 30 allows mixed storage of different classes of flammable/combustible liquids in the same building, subject to some minor restrictions. NFPA 30 also includes additional guidelines on interior storage configuration, diking/grading, and other facility requirements important to fire protection concerns.

NFPA 30 (paragraph 2-3.2.3) provides additional separation distance guidelines for flammable/combustible liquid storage in fixed tanks and large portable tanks (greater than 660 gallons). Table 8 summarizes NFPA 30 guidance in this area. Again, the "nearest important building" distance can be viewed as representing IBD and possibly ILD/Above Ground Magazine distance (if adjacent storage is in containers inside of a building). In this case, the "nearest side of any public way" distance can be viewed as representing PTR distance. Distances shown were derived for tanks with operating pressure of 2.5 psig or for tanks equipped with emergency vents that permit pressures exceeding 2.5 psig. NFPA 30 provides less stringent requirements for lower pressure tanks; however, the 2.5 psig case is selected here as a conservative representation to cover most circumstances. NFPA 30 also provides less stringent criteria for OSHA/NFPA Class IIIB liquids such as Otto Fuel II – again, these have been disregarded here for reasons of simplicity. Other guidelines apply for diking, tank venting, etc.

Table 8. NFPA 30 Separation Distance Criteria for Flammable/Combustible Liquid Storage in Fixed Tanks and Large Portable Tanks (> 660 gallons)

Capacity (gallons)	Distance to Nearest Side of Any Public Way or to Nearest Important Building (ft)
up to 100,000	25
100,001 - 500,000	37.5
500,001 - 1,000,000	52.5
1,000,001 - 2,000,000	67.5
2,000,001 - 3,000,000	82.5
3,000,001 or more	90

The quantities included in Table 8 extend well beyond practical energetic liquids storage requirements. For example, assuming a density for RP-1 rocket fuel of 6.8 pounds/gallon, the first two rows of Table 8 represent 680,000 and 3.4 million pound tank capacities, with corresponding recommended distances of 25 and 37.5 feet, respectively. Thus, for practical purposes, these requirements can be incorporated into the recommended criteria for container storage (50 feet) by allowing provisions for reducing the distance for tank storage.

NFPA 30 (paragraph 2-3.3) also provides guidelines applicable to the separation of any two adjacent flammable/combustible liquid tanks. For tank sizes less than 150 feet in diameter, the recommended distance is one sixth of the sum of the adjacent tank diameters, with a minimum of three feet. As before, OSHA/NFPA Class I through IIIA liquids are treated the same regardless of NFPA classification. This separation requirement can be interpreted as providing an additional variation for ILD and Above Ground Magazine distance for compatible flammable/combustible liquid storage in fixed and large portable tanks.

Other NFPA standards, mainly NFPA 430 *Code for the Storage of Liquid and Solid Oxidizers, 1995* and NFPA 50 *Standard for Bulk Oxygen Systems at Consumer Sites, 1996* provide commercial guidance on the storage separation of flammable/combustible liquids from incompatible oxidizers. NFPA 430 represents guidelines for oxidizers that are either solid or liquid at ambient conditions; therefore oxygen is excluded. NFPA 50 covers guidelines for oxygen stored in either liquid or gaseous form. In addition, 29 CFR 1910.104 also provides OSHA requirements for siting of liquid/gaseous oxygen systems.

Table 9 summarizes oxidizer siting distance guidelines derived from NFPA 430 (paragraphs 4-2.3, 4-5, 5-2.4, 5-5, 6-2.2, and 6-3.3). Actual distances are dependent on the NFPA classification for the oxidizer. [NFPA oxidizer classifications for energetic liquids of interest to this program are indicated in Table 6.] Other requirements for interior storage configuration, building construction, diking, container materials, and facility venting also apply.

Table 9. NFPA 430 Separation Distance Criteria for Oxidizer Storage in Detached Buildings and Tanks[1]

		Distance to Inhabited Building, Public Highway, Other Tank[2], Other Combustible Material, or Flammable/Combustible Liquid/Gas Storage (ft)	
NFPA Oxidizer Class	Quantity (lbs)	Non Sprinklered Building	Sprinklered Building
2	up to 600,000	50	
	up to 4,000,000		35
3	up to 400,000	75	
	up to 3,000,000		50
4	10 - 100	75	75
	101 - 500	100	100
	501 - 1,000	125	125
	1,001 - 3,000[3]	200	200
	3,001 - 5,000		300
	5,001 - 10,000		400

Notes:

1. Quantity and distance requirements do not apply to storage of NFPA Class 2 and 3 oxidizers in approved fixed tanks (NFPA 430 paragraph 1-7.2).

2. Where tanks containing Class 4 oxidizers are not separated from each other by 10 percent of the distance specified in the table for the largest tank, the total contents of all tanks shall be used (NFPA 430 paragraph 6-3.4).

3. Limit of 2,000 pounds of Class 4 oxidizers may be stored inside of a non-sprinklered building.

Fundamental requirements applicable to oxygen Q-D from 29 CFR 1910.104 (paragraph b.3) and NFPA 50 (paragraph 2-2) are summarized in Table 10. In either case, separation distance requirements are independent of oxygen quantity, but for adjacent flammable liquid/gas storage, are dependent on the quantities of these materials. OSHA and NFPA requirements vary somewhat however. NFPA 50 specifically states that compliance with the standard should serve to minimize the risk of the oxygen system becoming involved in an adjacent fire. Additional guidelines and/or requirements relating to equipment assembly and installation, facility design (diking), and other fire protection issues are also provided in both sources.

Table 10. OSHA and NFPA 50 Minimum Distance Requirements (Feet) From Oxygen Storage to Exposures[1]

	Flammable Material Quantity					
Type of Exposure	to 1000 gal Liq	Over 1000 gal Liq	to 25,000 ft^3 Gas	Over 25,000 ft^3 Gas	to 5,000 ft^3 Gas	Over 5,000 ft^3 Gas
Flammable/Combustible Liquid Storage (NFPA)	25	50				
Flammable Liquid Storage (OSHA)	50	90				
Flammable Gas Storage (NFPA)	25	50	25	50		
Flammable Gas Storage (OSHA)					50	90
Liquid Hydrogen Storage (NFPA)	75					
Class IIIB Combustible Liquid Storage (NFPA)	15					
Combustible Liquid Storage (OSHA)	25	50				
Combustible Buildings (NFPA/OSHA)	50					
Exterior Fire Resistive Buildings (OSHA)	25					
Places of Public Assembly (NFPA)	50					
Public Sidewalk or Parked Vehicles (NFPA)	10					

Notes:

1. Distances may be reduced where protective structures having an NFPA fire resistance rating of at least two hours interrupts the line of site between the oxygen system and the exposure.

These guidelines suggest additional restrictions applicable to incompatible ILD and Above Ground Magazine distance criteria for flammable energetic liquids. In fact, using the conservative, non-sprinklered building criteria of NFPA 430 to cover most situations with normal solid and liquid oxidizers, these requirements take precedence over NFPA 30 distances for incompatible ILD/Above Ground Magazine storage with one exception - quantity and distance requirements do not apply to storage of NFPA Class 2 and 3 oxidizers in approved fixed tanks. Since the purpose of NFPA 430 is to prevent the propagation of fire at an oxidizer storage site to another site, the rationale for this is presumably due to a lower risk of oxidizer-initiated fires at tank installations. Similarly, CFR 1910.104 or NFPA 50 requirements take precedence for separation of oxygen storage systems and flammable materials. Choice of the conservative OSHA requirements (as opposed to corresponding NFPA guidelines) for oxygen would maintain consistency with other federal regulations.

Table 11 compiles all of these requirements into proposed Q-D criteria for flammable energetic liquid storage in conventional DoD tabular format, including some possible footnotes covering additional details from NFPA 30 recommendations and also attempting to explain the variations discussed in proceeding paragraphs.

Table 11. Proposed Q-D Criteria for Flammable Energetic Liquid (excluding Liquid Hydrogen) Storage in Detached Buildings or Tanks[1]

Quantity	IBD/PTR (ft)	ILD/Above Ground Magazine (ft)
unlimited[2]	50 or less[3,4]	Note 5

Notes:

1. Other guidelines for diking, tank or container construction, tank venting, and facility construction apply. Refer to 29 CFR 1910.106 and NFPA 30 *Flammable and Combustible Liquids Code, 1996*, for further guidance on liquid storage and fire protection.

2. Guidelines on interior storage configuration (for container storage inside buildings) also apply with the following exceptions: (a) If the storage building is located at least 100 ft from any exposed building (under the direct jurisdiction of a fire protection organization) or property line; or (b) If the storage building is located at least 200 ft from any exposed building (not under the direct jurisdiction of a fire protection organization) or property line. Refer to 29 CFR 1910.106 and NFPA 30 *Flammable and Combustible Liquids Code, 1996* for further guidance on liquid storage and fire protection.

3. For container storage inside of a building, distance may be less than 50 ft if the storage building is constructed of fire resistive exterior walls (NFPA Fire Resistance rating of two hours or more).

4. For large tank storage, Q-D shall be 25 feet for tank capacities up to 100,000 gallons, and 37.5 feet for capacities between 100,001 and 500,000 gallons.

5. For flammable liquid container storage inside of a building, ILD/Above Ground Magazine distance is 50 feet (accept as in Note 3), or for adjacent incompatible oxidizer storage, distances specified for energetic liquid oxidizers. For flammable liquid storage in fixed or large portable tanks, ILD/Magazine distance is either (1) for compatible energetic liquids, equal to one sixth of the sum of the diameters of the two adjacent tanks, or distances specified in Note 4 for adjacent container storage inside of a building; or (2) for adjacent incompatible oxidizer storage, distances specified for energetic liquid oxidizers.

NFPA 30 also has separation distance provisions for unstable liquid storage in fixed and large portable tanks. Unstable liquid is defined in NFPA 30 (paragraph 1-6) as “a liquid that, in the pure state or as commercially produced or transported, will vigorously polymerize, decompose, undergo condensation reaction, or become self reactive under conditions of shock, pressure, or temperature." These requirements were considered for application to other flammable energetic liquids covered by the program such as hydrazine; however, the provisions were determined to be inappropriate for more reactive liquids (DDESB, 1997). According to Benedetti (DDESB, 1997), NFPA guidance is considered to provide minimum acceptable criteria for relatively stable flammable liquids that primarily present normal fire hazards. From a practical standpoint, "unstable liquid" is defined in relatively benign terms with respect to energetic liquids of concern to this program. For example, acrylates that undergo mild exothermic polymerization are considered unstable in NFPA 30.

Liquid Oxidizers – excluding Liquid Oxygen

Table 9 derived from NFPA 430 (discussed in the flammable liquids section) provides the fundamental Q-D criteria for most energetic liquid oxidizers. Table 12 shows proposed liquid oxidizer criteria (excluding liquid oxygen) derived from the non-sprinklered (for conservatism) building requirements in NFPA 430 and converted to a conventional DoD format. Inhabited Building and PTR distances are transcribed directly from NFPA 430 guidelines (as shown in Table 9) with one caveat. As discussed previously, NFPA 430 guidelines indicate that quantity and distance requirements do not apply to storage of NFPA Class 2 and 3 oxidizers in approved fixed tanks, presumably due to a lower risk of fire occurrence at tank installations. This is detailed in a footnote. On the other hand, IBD and PTR distances do apply for NFPA Class 4 oxidizers even for tank storage. In general, ILD and Above Ground Magazine distances apply only for incompatible storage adjacent to flammable/combustible energetic liquids. One could make the argument that the IBD requirement for oxidizer container storage in buildings could also be applied to adjacent oxidizer storage as a precaution to prevent the propagation of a source fire from one oxidizer site to another; however, since oxidizers are not combustible in and of themselves, there is little risk of fire propagation through thermal radiance. Indeed, NFPA 430 does not explicitly state any guidelines for separation of oxidizer storage buildings. Again, quantity and distance requirements also do not apply for ILD and Above Ground Magazine storage of NFPA Class 2 and Class 3 oxidizers in approved fixed tanks. Additional guidelines found in NFPA 430 are included as footnotes. Also note that these requirements apply to both liquid and solid oxidizers.

Liquid Oxygen

Table 10 derived from 29 CFR 1910.104 and NFPA 50 (discussed in the flammable liquids section) provides the fundamental requirements for liquid oxygen Q-D criteria. Table 13 shows proposed Q-D requirements from Table 10, converted to a standard DoD format. Inhabited Building Distance is adapted from OSHA and NFPA guidance for combustible buildings and places of public assembly. The OSHA exception for buildings made of fire resistive exterior construction is included as a footnote. Public Traffic Route distance is taken from the NFPA guidance for public sidewalks/parked cars. The reason for a reduced distance (compared to places of public assembly) is not specified in NFPA 50; however, one might assume that the rationale could be based on the transient nature of fire threat posed by such intermittent sources.

Intraline and Above Ground Magazine distances (for incompatible flammable materials) are derived using the more conservative OSHA requirements for the combination of flammable and combustible liquids and gases, also distinguishing between threshold levels of adjacent flammable material storage. Several footnotes are also provided to capture various other exceptions and also to recommend additional guidelines for facility design with respect to fire protection.

Table 12. Proposed Q-D Criteria for Energetic Liquid Oxidizer (excluding Liquid Oxygen) Storage in Detached Buildings or Tanks[1,2]

NFPA Oxidizer Class	Quantity (lbs)	IBD/PTR/ILD/Above Ground Magazine[3] Distance (ft)
2	up to 600,000	50
3	up to 400,000	75
4[4]	10 - 100	75
	101 - 500	100
	501 - 1,000	125
	1,001 - 3,000[5]	200
	3,001 - 5,000	300
	5,001 - 10,000	400

Notes:

1. Quantity and distance requirements do not apply to storage of NFPA Class 2 and 3 oxidizers in approved fixed tanks.

2. Other requirements for interior storage configuration, building construction, diking, container materials, facility venting, etc. also apply. Refer to NFPA 430 *Code for the Storage of Liquid and Solid Oxidizers, 1995* for further guidance on oxidizer storage and fire protection.

3. ILD and Above Ground Magazine distances apply only for incompatible storage adjacent to flammable/combustible energetic liquids.

4. Where tanks containing NFPA Class 4 oxidizers are not separated from each other by 10 percent of the distance specified in the table for the largest tank, the total contents of all tanks shall be used.

5. Limit of 2,000 pounds of NFPA Class 4 oxidizers may be stored inside of a non-sprinklered building

Table 13. Proposed Q-D Criteria for Liquid Oxygen[1,2]

	IBD (ft)	PTR (ft)	ILD/Above Ground Magazine[3] (ft)	
Quantity			1000 gal liq or 5000 cubic ft gas[6]	Over 1000 gal or 5000 cubic ft gas[6]
Unlimited[4]	50[5]	10	50[7,8]	90[7,8]

Notes:

1. Distances may be reduced where protective structures having an NFPA fire resistance rating of at least two hours interrupts the line of site between the oxygen system and the exposure.

2. Additional guidelines relating to equipment assembly and installation, facility design (diking), and other fire protection issues also apply. Refer to 29 CFR 1910.104 and NFPA 50 *Standard for Bulk Oxygen Systems at Consumer Sites, 1996* for further guidance.

3. ILD and Above Ground Magazine distances apply only to incompatible storage adjacent to flammable/combustible energetic liquids.

4. Q-D is independent of oxygen quantity.

5. Distance may be reduced to 25 feet if the exposed building includes a sprinkler system or if a building is made of exterior walls having an NFPA fire resistance rating of at least two hours.

6. Quantity of adjacent incompatible energetic liquids.

7. The distances shown may be reduced to 25 and 50 feet, respectively, for adjacent combustible (OSHA/NFPA Class II) energetic liquids.

8. Minimum distance for adjacent hydrogen storage is 100 feet (as indicated by liquid hydrogen requirements).

Liquid Hydrogen

29 CFR 1910.103 (paragraph c.2.ii.b) and NFPA 50B *Standard for Liquified Hydrogen Systems at Consumer Sites, 1994* (paragraph 3-2.2) provide OSHA and other commercial guidance, respectively, for the siting of liquid hydrogen storage. Fundamental requirements applicable to Q-D are compiled in Table 14. In this case, OSHA and NFPA requirements differ in some areas. NFPA 50B explicitly states that compliance with the standard will minimize the risk of an adjacent fire affecting a liquid hydrogen storage area, as well as the risk of a hydrogen storage facility fire affecting surrounding premises. Additional guidelines concerning facility design, diking, and operations for fire safety are included in these standards.

Table 14. OSHA and NFPA 50B Minimum Distance Requirements (Feet) From Liquified Hydrogen Systems to Exposures[1]

	Storage Capacity (gallons)		
Type of Exposure	to 3,500	3,501-15,000	15,001-30,000 (OSHA) -75,000 (NFPA)
Fire-resistive building and fire walls (OSHA)	5	5	5
Noncombustible building (NFPA)			
noncombustible contents	5	5	5
combustible contents, unsprinklered, fire resistance > three hours	5	5	5
Noncombustible Building (OSHA)	25	50	75
Noncombustible Building (NFPA) combustible contents, unsprinklered, fire resistance < three hours	25	50	75
Other Buildings (OSHA)	50	75	100
Combustible Building (NFPA)			
sprinklered	50	50	50
unsprinklered	50	75	100
Flammable/Combustible Liquids (OSHA/NFPA)	50	75	100
Stationary Hydrogen Containers (OSHA/NFPA)	5	5	5
Flammable Gas Storage (OSHA)	50	75	100
Flammable Gas Storage (NFPA)	50	75	75
Liquid Oxygen and Other Oxidizers (OSHA)	100	100	100
Liquid Oxygen and Other Oxidizers (NFPA)	75	75	75
Combustible Solids (OSHA/NFPA)	50	75	100
Concentrations of People/Public Assembly (OSHA/NFPA)	75	75	75
Public Ways and Property Lines (NFPA)	25	50	75

Note:

1. Distances for some buildings (rows 3, 4, 5, and 6), flammable/combustible liquid, solid, and gas storage, and public ways may be reduced where protective structures, such as firewalls equal to height of top of the container, to safeguard the liquid hydrogen storage system, are located between the hydrogen storage installation and the exposure.

Selected requirements from Table 14 can be converted to a conventional DoD format to form potential liquid hydrogen criteria. Candidate Q-D requirements based on OSHA/NFPA are shown in Table 15. Inhabited Building Distances were conservatively derived from the requirements specified for buildings that may be constructed of combustible materials and which may not have fire protection (sprinkler) systems. Public Traffic Route Distances were taken directly from NFPA distances for “Public Ways.” Intraline and Above Ground Magazine

Distances were taken directly from the combined requirements for adjacent flammable/combustible liquid, flammable gas, and combustible solid storage. In the case of flammable gas storage where a discrepancy exists between OSHA and NFPA 50B for large quantities, the more conservative OSHA requirement was selected. In addition, special provisions representative of incompatible oxidizer, as well as similar (compatible) liquid hydrogen tank ILD/Above Ground Magazine Distances are proposed through additional footnotes. For oxidizer storage, the more conservative OSHA requirements are proposed. The distances specified in Table 14 for "concentrations of people/public assembly" were determined to apply only to situations where liquid hydrogen systems are installed in a room connected to an occupied building, circumstances that were assumed to be unrealistic for energetic liquids facilities, and thus, these guidelines were ignored. Additional constraints from both OSHA and NFPA are discussed in other footnotes.

Table 15. Possible Q-D Criteria for Liquid Hydrogen[1,2]

Quantity (gal)	IBD (ft)	PTR (ft)	ILD/Above Ground Magazine (ft)[3,4]
3,500	50	25	50
3,501 - 15,000	75	50	75
15,001 - 75,000	100	75	100

Notes:

1. Distances may be reduced (except as in Note 3) where protective structures, such as firewalls equal to height of top of the container, to safeguard the liquid hydrogen storage system, are located between the hydrogen storage installation and the exposure (see Note 2).

2. Other guidelines for facility and tank design, diking, and operations also apply. Refer to 29 CFR 1910.103 and NFPA 50B *Standard for Liquified Hydrogen Systems at Consumer Sites, 1994* for further guidance on hydrogen storage and fire protection.

3. Distances between hydrogen systems and incompatible oxidizer storage shall be 100 feet independent of quantity.

4. Distance between adjacent, stationary liquid hydrogen containers can be reduced to five feet.

A limitation in the OSHA and NFPA 50B requirements is that the separation distance criteria apply to maximum quantities of 30,000 or 75,000 gallons, respectively. Using a density of 0.59 pounds hydrogen/gallon, the maximum tank capacity covered is about 44,000 pounds. NFPA will be consulted in order to determine appropriate separation criteria for greater quantities that may be expected at some launch facilities.

A major problem with these criteria is that they do not provide acceptable safety distances to account for possible blast effects observed in two vapor explosion incidents with hydrogen. In one incident, rapid venting (120 pounds per second average) of pressurized (3400 psi) hydrogen gas resulted in the ignition and explosion of a hydrogen-air vapor cloud containing about 200 pounds of hydrogen (Reider et al., 1965). Although a total of 2000 pounds of hydrogen was released before the explosion, only 200 pounds was estimated to become involved in the fireball based on stoichiometric considerations in conjunction with the observed fireball size. The physical size of the fireball was determined to be approximately 150 feet high with a diameter of about 30 feet. Assuming a cylindrical geometry, the total cloud volume is calculated to be approximately 106,000 cubic feet. It was postulated that a large percentage of the hydrogen became diluted (below the lower flammability limit) due to the high discharge velocity of the hydrogen gas. Based on engineering considerations, the estimated overpressure from the explosion at a distance of approximately 300 feet was about 0.5 psi. In another incident (Davenport, 1977; Kaye, 1983), failure of a storage tank released 665 pounds of hydrogen gas to atmosphere. The release was fairly rapid, simulating explosive dispersal of the stored hydrogen gas into a cloud. The vapor cloud exploded at a height of about 30 feet above ground. The yield of the event was estimated to be approximately 20 to 40 pounds TNT based on equivalent energy release. Unfortunately, fragment debris data was not reported in either of these incidents.

Analog vapor cloud explosion tests provide additional blast overpressure data for consideration. Woolfolk and Ablow (Kaye, 1983) performed deflagration and detonation tests of stoichiometric mixtures of hydrogen and oxygen held in three and five foot diameter spherical balloons corresponding to cloud volumes of 14 and 65 cubic feet, respectively. Cassutt et al. (1963) [see also Tomei, 1989] performed similar tests with hydrogen-air mixtures of varying stoichiometry in five and eight foot diameter balloons corresponding to cloud volumes of 100 and 400 cubic feet, respectively. Cassutt found that no overpressures were generated when the mixtures were ignited through flame, spark, and hot wire sources. Overpressures were generated from initiation with either two gram Pentolite explosive charges or blasting caps, although the overall reactions from blasting cap initiation were determined to be deflagrations (as opposed to detonations) with significantly reduced explosive yields. Figure 1 shows a composite plot of blast overpressure data as a function of stand-off distance (which has been normalized to the hydrogen cloud charge radius) obtained in these tests as well as the incident described by Reider. The Pentolite initiation data of Cassutt can be ignored since it appears to be somewhat conservative from a safety standpoint due to the strength of the initiator. It should be reasonable to assume that idealized high explosive initiation of a hydrogen vapor cloud would not be a credible scenario, particularly in a storage environment. Ignoring this data, the test and accident data can be interpolated to show that a blast overpressure of 1 psi might be observed up to a distance between 10 and 20 times the cloud charge radius.

The blast overpressure data from the hydrogen-air explosion accident and analog tests could be used to formulate Q-D criteria for hydrogen. A risk-based Q-D criterion could be established based on an analysis of the maximum credible vapor cloud size. Alternatively, one could use the accident described by Reider as a maximum credible event using the normalized range of 20 (stand-off distance divided by hydrogen cloud diameter) and also applying a safety factor of 33% for conservatism. This would result in a fixed IBD requirement for hydrogen of about 400 feet.

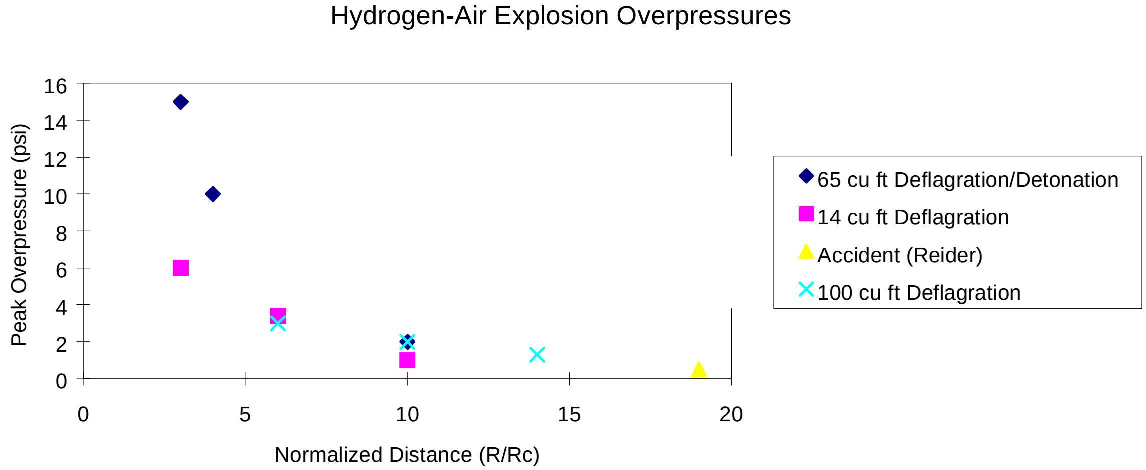

Figure 1. Peak Overpressure versus Distance (Normalized to Cloud Radius) for Hydrogen-Air Explosions

Alternatively, a risk-based explosives safety siting approach could be adopted for hydrogen from fuel-air explosion hazard analysis methods utilized in other (chemical and nuclear) industries. In this method, TNT equivalent yield for a vapor phase explosion is calculated based on the ratio of heats of combustion of the flammable material with respect to TNT (Hudson et al, 1995; Hannum, 1984a). An empirically-derived explosion efficiency factor is also used to account for non ideal mixing, initiation, and other factors. The method also requires an estimate of the amount of spilled material that is above the lower flammability limit for the fuel in air. Equation 1 illustrates the calculational method. ACTA Incorporated (Hudson et al., 1995) has developed a computer model that can be used to perform quantitative risk assessments of vapor cloud explosion scenarios for use by the Air Force. The model employs an explosion efficiency factor of 0.01 (1%) for instantaneous releases and 0.10 (10%) for continuous releases. [Hannum (1984a) recommends a conservative upper limit of 0.20 (20%).]

$$\text{TNT EQ (\%)} = W_{TNT}/W_{material} = \Delta H_{combustion\ (material)} \text{ x (efficiency factor)}/\Delta H_{combustion\ (TNT)} \qquad (1)$$

where (efficiency factor) is found empirically.

On the other hand, it might be feasible to use this method to define a maximum credible event and thus a fixed Q-D criterion for hydrogen. Table 16 shows empirically-determined explosion efficiency factors versus total hydrogen weight for the hydrogen-air accidents and test data discussed previously.

Table 16. Empirical Explosion Efficiency Factors for Hydrogen-Air Explosions

Total Weight Hydrogen (pounds)	Explosion Efficiency Factor (%)
< 0.2 (Cassutt et al., 1963; Kaye, 1983)	7 - 23*
665 (Davenport, 1977; Kaye, 1983)	2** or less
2000 (Reider et al., 1965)	1

* Calculated efficiency factor is dependent on stand-off distance (23% at 14 charge diameters = 35 feet; 7% at six charge diameters = 15 feet)

** Assuming that 10% of total amount spilled was above lower flammability limit analogous to that observed by Reider et al (1965). The calculated value would be 0.2% assuming that all of the 665 pounds of hydrogen was above the flammability limit.

These data show that the explosion efficiency factor decreases significantly as the size of the spill increases. This effect may be manifested in limiting the effective equivalent yield that must be considered for Q-D purposes. Figure 2 shows the relationship between total hydrogen weight spilled and the product of explosion equivalency factor and hydrogen weight involved in the fireball reaction (referred to here as the "Yield Factor," which is proportional to TNT equivalent yield according to equation 1) for the accidents and tests included in Table 16. The effective TNT equivalent yield is then the product of the "Yield Factor" and the ratio of heats of combustion (which for hydrogen and TNT is equal to 28.65). As shown in the figure, the Yield Factor appears to approach a limiting value of between three and four, which would convert to a maximum explosion yield of between 86 and 115 pounds of TNT for most credible hydrogen spills. The upper limit would yield a corresponding blast overpressure of 1 psi at a range of about 220 feet. Applying a safety factor of 33% as before, an appropriate IBD criterion might be about 300 feet.

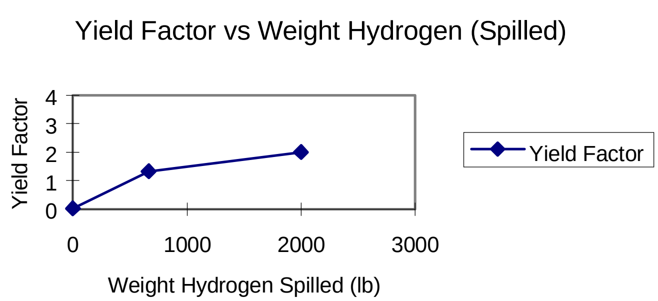

Figure 2. Hydrogen Vapor Explosion Yield Factor Versus Total Hydrogen (Spilled)

Note that, with either approach, a fixed Q-D requirement for vapor phase explosion would only be valid for short duration spill events since it would be extremely difficult to site a facility for all possible scenarios involving the transport and dispersion of an initial vapor cloud with time (prior to vapor explosion).

In addition, consideration for secondary fragment debris hazards may also be warranted. Current DoD regulations establish IBD and PTR distances for hydrogen at 600 feet for quantities up to 10,000 pounds, 1200 feet for quantities between 10,000 and 100,000 pounds, and 1800 feet for larger quantities based on fragment considerations (where protection from fragment debris is not implemented). The fragment distances are greater than potential blast overpressure safety distances for hydrogen-air explosions discussed previously, consistent with observed hazards with other materials such as hydrazine. Thus, the most prudent approach to hydrogen Q-D might be to use the historical fragment distances (as shown in Table 17) as default criteria.

Table 17. Potential Q-D Criteria for Liquid Hydrogen

Quantity (pounds)	IBD/PTR/ILD/Above Ground Magazine Distance (ft)
to 10,000	600
10,001 – 100,000	1200
Over 100,000	1800

SUMMARY

New concepts in explosives safety standards for energetic liquids are being developed based on information gained from accidents, realistic tests, and other (OSHA, NFPA) guidelines used for the commercial sector. The hazard classification and quantity-distance proposals described in this paper represent the authors' interpretation of the results of several iterations through an interagency advisory board (Liquid Propellants Working Group) established to oversee the Explosives Safety Standards for Energetic Liquids Program. [The last meeting of the LPWG was held in April 1998.] Clearly, some details remain to be addressed. The LPWG will meet again in the Fall of 1998 to discuss these proposals and form the basis of draft recommendations applicable to energetic liquid fuels, oxidizers, and monopropellants. Work will also continue on the issue of explosive equivalence and siting criteria for liquid bipropellant combinations at rocket launch and test stands under the auspices of the LPWG.

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