

Explosive Equivalence of Hypergolic Propellants

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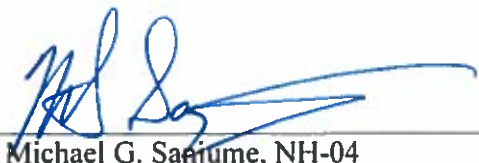
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Michael G. Sanjume, NH-04
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14. ABSTRACT The purpose of this report is to document the explosive equivalence of N ₂ O ₄ /A-50 and other hypergolic energetic liquid bipropellants for inclusion in DESR 6055.09 (Ref. 1). This analysis is similar to the recent report on hydrocarbon propellants that can be found in Aerospace TR-2019-00959 (Ref. 2). The focus of this report will be on revisions to N ₂ O ₄ /A-50 but other combinations [N ₂ O ₄ /N ₂ H ₄ , N ₂ O ₄ /UDMH, IRFNA/UDMH, N ₂ O ₄ /MMH, pentaborane (PB), and chlorine trifluoride/pentafluoride (CTF/CPF) combinations] will be addressed. Based on findings during this latest review additional recommendations for revisions to DESR 6055.09 are included. This revision is intended to apply to DoD facilities siting and construction for operations involving these energetic liquids. It does not govern the storage or handling of energetic liquids for uses other than in launch vehicles, space vehicles, rockets, missiles, and associated static test and processing installations. The yield criteria will envelope test/processing facilities and launch facilities for the pre-launch/pre-ignition state, on-pad engine firing conditions, and post-launch hazards relative to near-pad incidents. Additional assessments are included which apply to other operational facilities and conditions.					
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Abstract

This report documents the explosive equivalence of $\text{N}_2\text{O}_4/\text{A-50}$ and other hypergolic energetic liquid bipropellants for inclusion in Defense Explosives Safety Regulation (DESR) 6055.09 [1]. This analysis is similar to the analysis in the recent report on hydrocarbon propellants (Aerospace Report Number TR-2019-00959 [2]). This report focuses on revisions to $\text{N}_2\text{O}_4/\text{A-50}$, but other combinations ($\text{N}_2\text{O}_4/\text{N}_2\text{H}_4$, $\text{N}_2\text{O}_4/\text{UDMH}$, IRFNA/UDMH, $\text{N}_2\text{O}_4/\text{MMH}$, pentaborane, and chlorine trifluoride/pentafluoride combinations) will be addressed. Based on findings during this latest review, additional recommendations for revisions to DESR 6055.09 are included.

This revision is intended to apply to Department of Defense facilities siting and construction for operations involving these energetic liquids. It does not govern the storage or handling of energetic liquids for uses other than in launch vehicles, space vehicles, rockets, missiles, and associated static test and processing installations. The yield criteria will envelope test/processing facilities and launch facilities for the pre-launch/pre-ignition state, on-pad engine firing conditions, and post-launch hazards relative to near-pad incidents. Additional assessments are included, which apply to other operational facilities and conditions.

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1. Introduction

This report is follow-on to preliminary observations made to the DDESB Liquid Propellant Working Group (LPWG) at the time the LO_2/LH_2 cryogenic analysis was performed, as noted in Reference [3]. This prior effort was reviewed in detail in [2] and will not be repeated here. An additional assessment of hypergolic propellant hazards was conducted in 2008 through 2009 [4]. That assessment was specific to hazardous processing of space vehicles, but additional data were generated during that effort, which expanded the database used in the 1998 timeframe. Appendix A contains backup discussions on the hypergolic bipropellants related to prediction methods, blast asymmetry, impact sensitivity, and past programs.

During the period of LPWG deliberations, the preliminary observations for nitrogen tetroxide (N_2O_4)/Aerzine-50 (A-50) propellants were presented and plans for updating those explosive criteria were put in place. This report presents the follow-on assessments that were deferred at that time. In addition, an addendum is being prepared to update [6] to document the findings from these most recent efforts.

This report details these latest activities and recommends that an adjustment to the explosive siting criteria be made accordingly. In this report, the hypergolic propellants are subcategorized as the hydrazines (typically combined with a nitric acid or nitrogen tetroxide), boranes (B_2H_6 , B_5H_9 , and $\text{B}_{10}\text{H}_{14}$) and halogenated fluorides (ClF_3 and ClF_5). Other hypergolic bipropellant combinations have been proposed, used, and tested in the past (e.g., anilines, amines, furfuryl alcohol, etc.) but are no longer used operationally in the U.S., so they should be addressed separately, as needed.

The data used in the initial release of Department of Defense (DOD) 6055.9-STD [7] accounted for the difference in yield noted during early testing of the N_2O_4 /A-50 propellant combination for missile programs and represented the conclusion as adjusted for propellant mass, i.e., 5% trinitrotoluene (TNT) for test stands and 10% TNT for launch pads. In addition to revising the explosive standard for LO_2/LH_2 , the LPWG entertained a potential change to the N_2O_4 /A-50 standards based on updated test and missile failure data. This test and failure data were reanalyzed and presented to the LPWG, as documented in [5]. For this current report, additional test and failure data were uncovered after the preliminary assessment was prepared and are included herein. In addition to the N_2O_4 /A-50 data, testing with N_2O_4 /hydrazine (N_2H_4), N_2O_4 /monomethylhydrazine (MMH), N_2O_4 /unsymmetrical dimethyl hydrazine (UDMH), $\text{B}_5\text{H}_9/\text{N}_2\text{H}_4$, $\text{N}_2\text{O}_4/\text{B}_5\text{H}_9$, and halogenated fluoride combinations $\text{ClF}_3/\text{B}_5\text{H}_9$ and $\text{ClF}_3/\text{N}_2\text{H}_4$ was uncovered.

The following recommendation options are consistent with the decisions made by the DDESB relative to the current propellant yield curves. Use of a yield curve incorporates the finding that liquid bipropellant explosive yields vary with mass and cannot be accurately approximated with a constant TNT percent equivalent explosive weight (EEW) as currently employed. This report includes recommendations for N_2O_4 /A-50, $\text{N}_2\text{O}_4/\text{N}_2\text{H}_4$, $\text{N}_2\text{O}_4/\text{MMH}$, $\text{N}_2\text{O}_4/\text{UDMH}$, $\text{B}_5\text{H}_9/\text{N}_2\text{H}_4$, $\text{N}_2\text{O}_4/\text{B}_5\text{H}_9$, $\text{ClF}_3/\text{N}_2\text{H}_4$, and $\text{ClF}_5/\text{N}_2\text{H}_4$. It is acknowledged that these hypergolic combinations are no longer used on launch vehicles or missiles. However, the recommendations are made for consistency, to differentiate the various combinations, and for the historical record. In the case of the N_2H_4 , MMH, and UDMH cases, very few tests were conducted to arrive at independent values, but observations can be made for them by comparing similar tests conducted with similar commodities. The pentaborane combinations $\text{B}_5\text{H}_9/\text{N}_2\text{H}_4$ and $\text{B}_5\text{H}_9/\text{N}_2\text{O}_4$ were found to exhibit the greatest yields, while in the case of the chlorine trifluoride/pentafluoride (CTF/CPF) combinations, the explosive yields were extremely small due to their inherent reactivity.

2. Recommendation Summary

2.1 N₂O₄/A-50

The recommended change to the N₂O₄/A-50 liquid propellant explosive equivalence is to replace the current 5% (static test facility) and 10% (launch facility) TNT values in [1], Table V5.E4.T5, with the explosive equivalence from the recommended N₂O₄/A-50 Yield Curves shown in Figure 1. For operations other than static test stands and launch pads (i.e., other potential explosive site (PES)) and quantities less than W_{Pmin} , a separate explosive yield is recommended. The following subsections describe the methods.

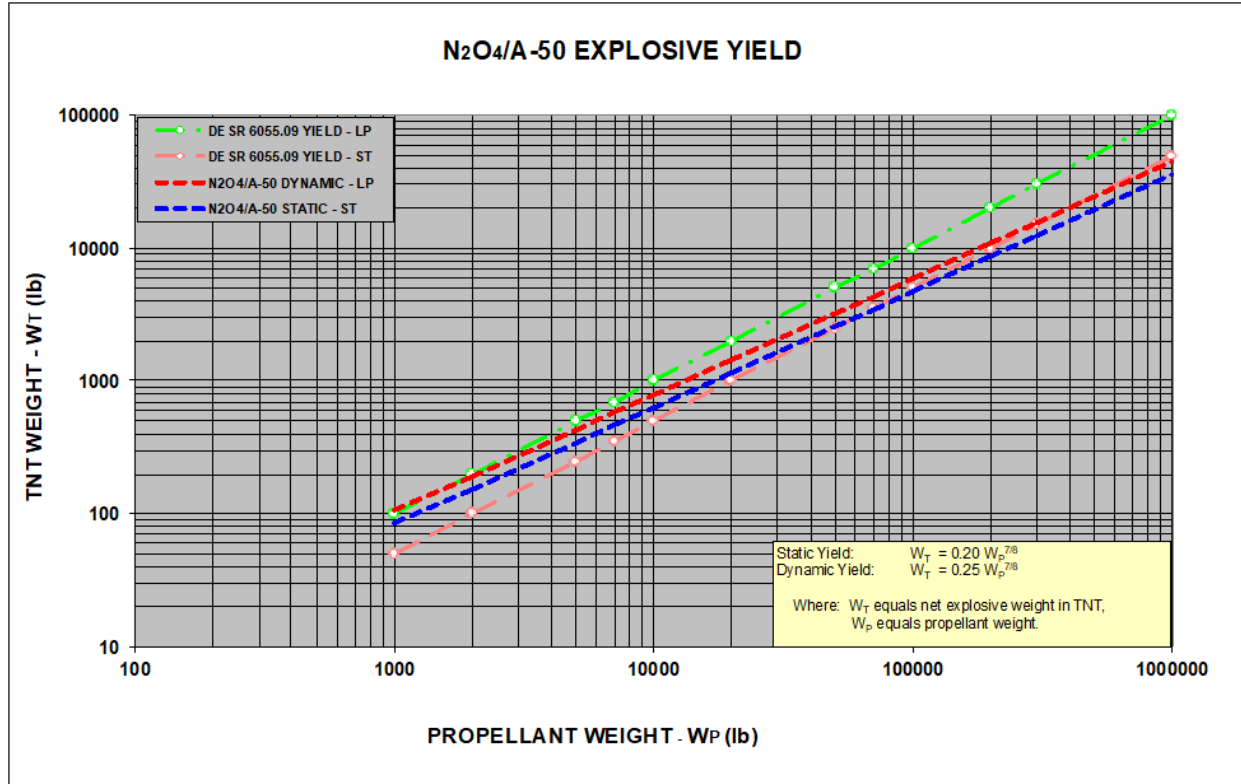


Figure 1. N₂O₄/A-50 proposed explosive Yield Curves.

2.1.1 Static Test or Processing Facilities

For launch vehicles, space vehicles, missiles, stages, engines, or components in static test or processing facilities, the EEW in pounds of TNT is determined by the N₂O₄/A-50 Static Yield Curve shown as ST in Figure 1:

$$W_T = 0.20 W_P^{7/8} \text{ for all } W_P \geq W_{Pmin}$$

2.1.2 Launch Facilities

For launch vehicles, space vehicles, or missiles in the launch configuration, determine the EEW in pounds of TNT is determined by the N₂O₄/A-50 Dynamic Yield Curve shown as LP in Figure 1:

$$W_T = 0.25 W_P^{7/8} \text{ for all } W_P \geq W_{Pmin}$$

2.1.3 Other PESs

For operations other than those for launch vehicles, space vehicles, missiles, stages, engines, or components in static test or processing facilities; launch vehicles or missiles in the launch configuration; or quantities less than W_{Pmin} , the EEW in pounds of TNT is determined by the following:

$$W_T = 14\%W_P$$

where

W_T = net explosive weight (lb) TNT, and

W_P = propellant weight (lb), as defined in [1], V5.E4.5.6.1 and V5.E4.5.6.2, and

$W_{Pmin} = 1,000$ lb, and

mixed oxides of nitrogen (MON) can be substituted for N_2O_4

2.2 N_2O_4/N_2H_4

The recommended change is to include N_2O_4/N_2H_4 as a separate liquid bipropellant combination. Current criteria only call out inhibited red fuming nitric acid (IRFNA)/UDMH explicitly as 10% (static test facility) and 10% (launch facility) TNT explosive equivalence in [1], Table V5.E4.T5, but imply 5% (static test facility) and 10% (launch facility) TNT explosive equivalence values for the N_2O_4/N_2H_4 combination. It is recommended that these values be replaced using the recommended N_2O_4/N_2H_4 Yield Curve shown in Figure 2, using the methods described in the following subsections.

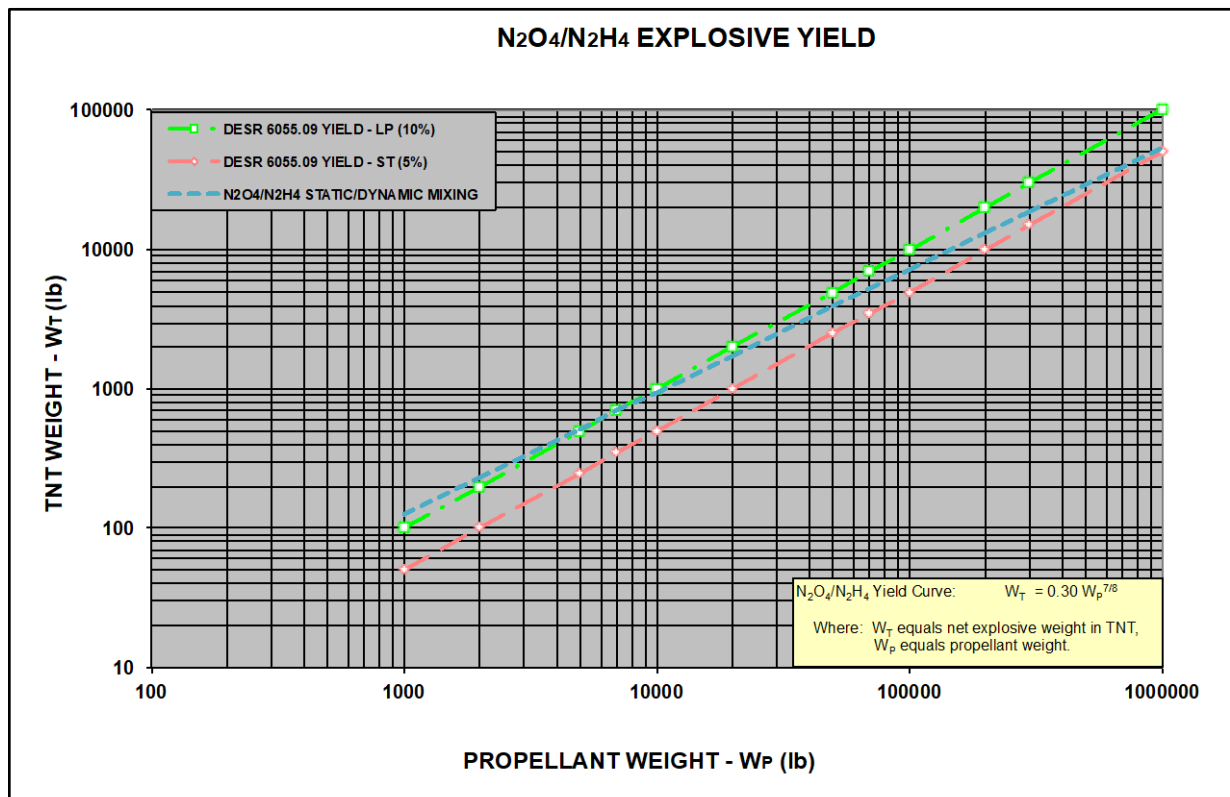


Figure 2. N_2O_4/N_2H_4 proposed explosive Yield Curves.

2.2.1 Static Test or Processing Facilities and Launch Facilities

For launch vehicles, space vehicles, missiles, stages, engines, or components in static test or processing facilities and in the launch configuration, the EEW in pounds of TNT is determined by the N_2O_4/N_2H_4 Yield Curve:

$$N_2O_4/N_2H_4: \quad W_T = 0.30 W_P^{7/8} \text{ for all } W_P \geq W_{Pmin}$$

2.2.2 Other PESs

For operations other than those for launch vehicles, space vehicles, missiles, stages, engines, or components in static test or processing facilities; launch vehicles or missiles in the launch configuration; or quantities less than W_{Pmin} , the EEW in pounds of TNT is determined by the following:

$$N_2O_4/N_2H_4: \quad W_T = 18\% W_P$$

where

W_T = net explosive weight (lb) TNT, and

W_P = propellant weight (lb), as defined in [1], V5.E4.5.6.1 and V5.E4.5.6.2, and

$W_{Pmin} = 1,000$ lb, and

MON can be substituted for N_2O_4

2.3 N_2O_4/MMH

The recommended change is to include N_2O_4/MMH as a separate liquid bipropellant combination. Current criteria only call out IRFNA/UDMH explicitly as 10% (static test facility) and 10% (launch facility) TNT explosive equivalence in [1], Table V5.E4.T5, but imply 5% (static test facility) and 10% (launch facility) TNT explosive equivalence values for the N_2O_4/MMH combination. It is recommended that these values be replaced using the recommended N_2O_4/MMH Yield Curve shown in Figure 3, using the methods described in the following subsections.

2.3.1 Static Test or Processing Facilities and Launch Facilities

For launch vehicles, space vehicles, missiles, stages, engines, or components in static test or processing facilities and in the launch configuration, the EEW in pounds of TNT is determined by the N_2O_4/MMH Yield Curve:

$$N_2O_4/MMH: \quad W_T = 0.28 W_P^{7/8} \text{ for all } W_P \geq W_{Pmin}$$

2.3.2 Other PESs

For operations other than those for launch vehicles, space vehicles, missiles, stages, engines, or components in static test or processing facilities; launch vehicles or missiles in the launch configuration; or quantities less than W_{Pmin} , the EEW in pounds of TNT is determined by the following:

$$N_2O_4/MMH: \quad W_T = 16\% W_P$$

where

W_T = net explosive weight (lb) TNT, and

W_P = propellant weight (lb) as defined in [1], V5.E4.5.6.1 and V5.E4.5.6.2, and

$W_{Pmin} = 1,000$ lb, and

MON can be substituted for N_2O_4

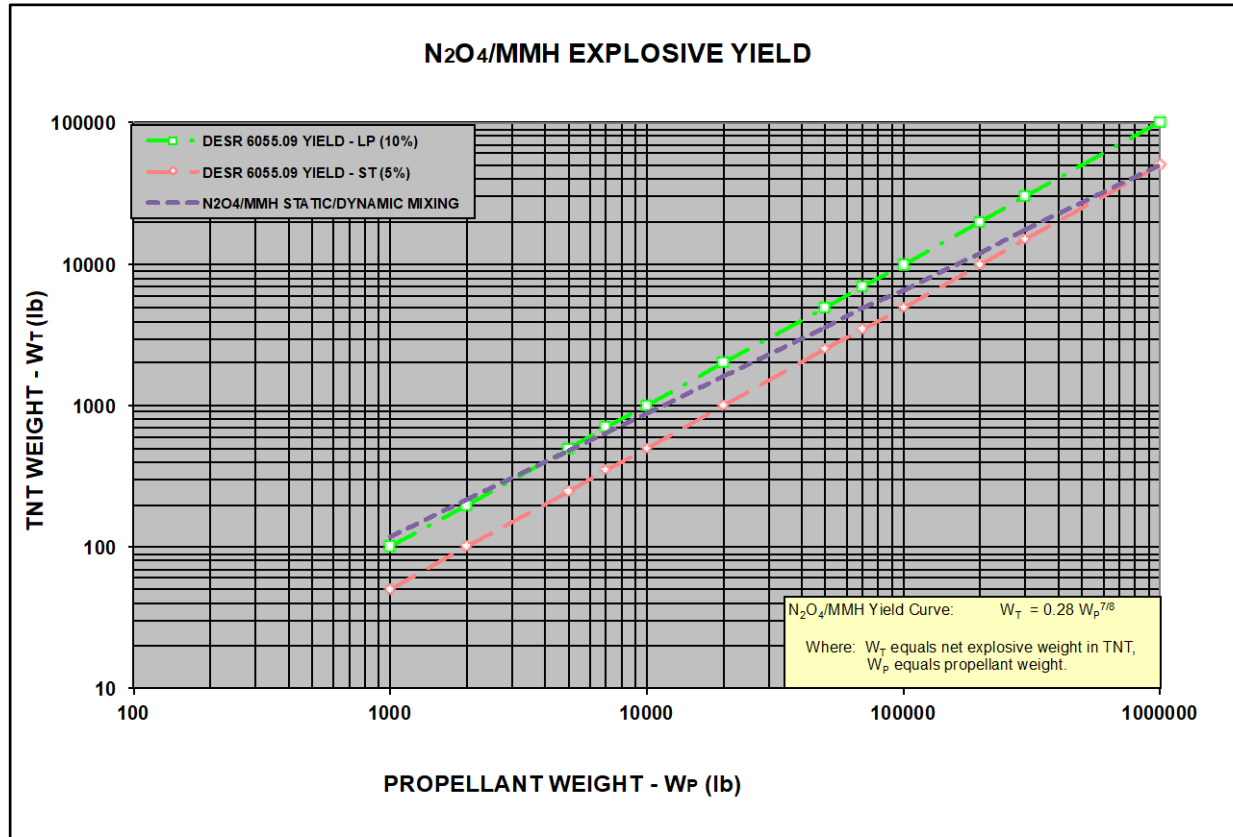


Figure 3. N₂O₄/MMH proposed explosive Yield Curve.

2.4 N₂O₄/UDMH and IRFNA/UDMH

The recommended change is to include N₂O₄/UDMH and IRFNA/UDMH as separate liquid bipropellant combinations. Current criteria only call out IRFNA/UDMH explicitly as 10% (static test facility) and 10% (launch facility) TNT explosive equivalence in [1], Table V5.E4.T5, but imply 5% (static test facility) and 10% (launch facility) TNT explosive equivalence values for the N₂O₄/UDMH combination. It is recommended that these values be replaced using the recommended yield curves shown in Figure 4 using the methods described in the following subsections.

2.4.1 Static Test or Processing Facilities and Launch Facilities

For launch vehicles, space vehicles, missiles, stages, engines, or components in static test or processing facilities and in the launch configuration, the EEW in pounds of TNT is determined by the yield curves:

$$\begin{array}{ll} \text{N}_2\text{O}_4/\text{UDMH:} & W_T = 0.19 W_P^{7/8} \text{ for all } W_P \geq W_{Pmin} \\ \text{IRFNA/UDMH:} & W_T = 0.26 W_P^{7/8} \text{ for all } W_P \geq W_{Pmin} \end{array}$$

2.4.2 Other PESs

For operations other than those for launch vehicles, space vehicles, missiles, stages, engines, or components in static test or processing facilities; launch vehicles or missiles in the launch configuration; or quantities less than W_{Pmin} , the EEW in pounds of TNT is determined by the following:

$$\begin{array}{ll} \text{N}_2\text{O}_4/\text{UDMH}: & W_T = 12\% W_P \\ \text{IRFNA}/\text{UDMH}: & W_T = 15\% W_P \end{array}$$

where

W_T = net explosive weight (lb) TNT, and

W_P = propellant weight (lb) as defined in [1], V5.E4.5.6.1 and V5.E4.5.6.2, and

$W_{Pmin} = 1,000$ lb, and

MON can be substituted for N_2O_4

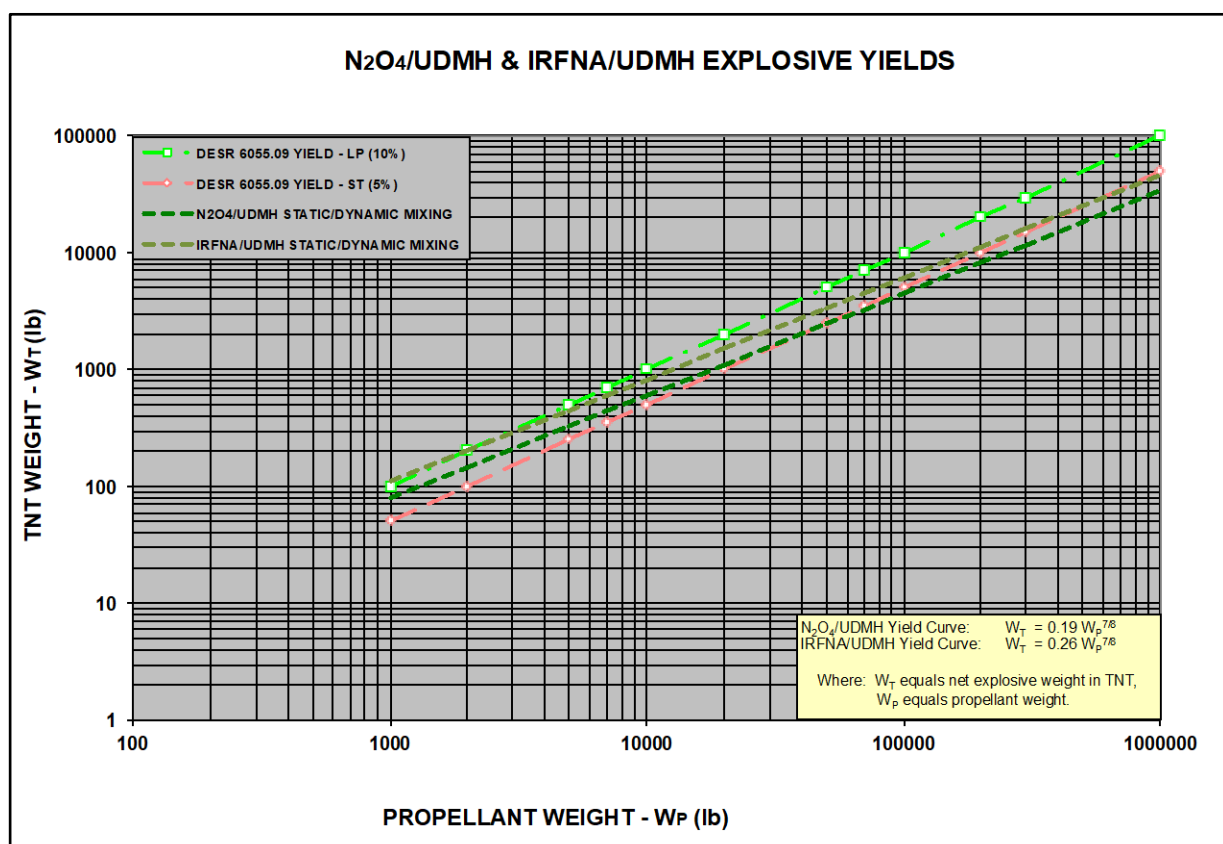


Figure 4. $\text{N}_2\text{O}_4/\text{UDMH}$ and IRFNA/UDMH proposed explosive Yield Curves.

2.5 Pentaborane (PB) Hypergolic Combinations (Tentative Option)

Although no longer available as a rocket propellant, an option to consider is maintaining a database in DESR 6055.09 [1] of alternate propellant combinations including the pentaborane (B_5H_9) hypergolic combinations ($\text{B}_5\text{H}_9/\text{N}_2\text{H}_4$ and $\text{N}_2\text{O}_4/\text{B}_5\text{H}_9$) as separate liquid bipropellant combination entries. Currently these combinations are not included; however, at one time, the tables in [1] included 10% (static test facility) and 20% (launch facility) TNT explosive equivalence values for $\text{B}_5\text{H}_9/\text{N}_2\text{H}_4$ and 60% (static test or launch facility) for $\text{N}_2\text{O}_4/\text{B}_5\text{H}_9$. The explicit values for each combination from this assessment are the PB Yield Curves shown in Figure 5, using the methods described in the following subsections.

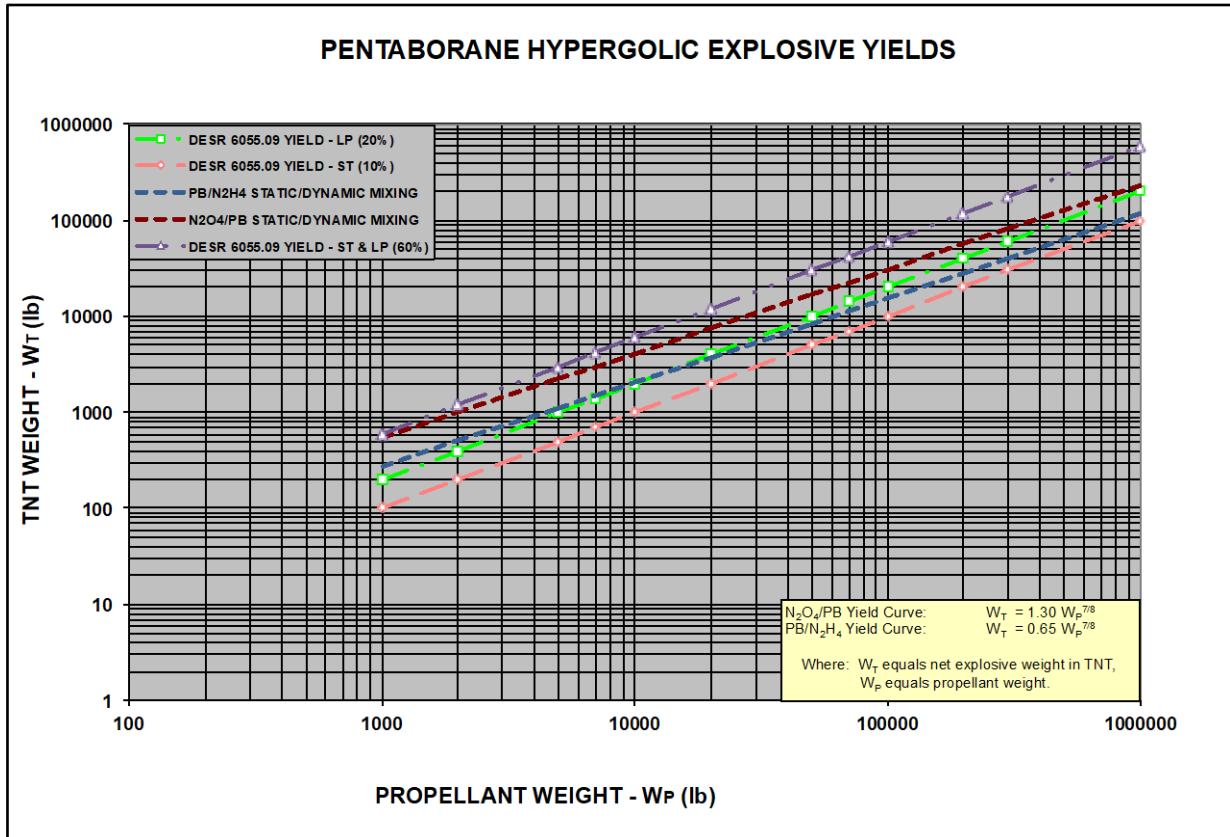


Figure 5. PB/N₂H₄ and N₂O₄/PB proposed explosive Yield Curves.

2.5.1 Static Test or Processing Facilities and Launch Facilities

For launch vehicles, space vehicles, missiles, stages, engines, or components in static test or processing facilities and in the launch configuration, the EEW in pounds of TNT is determined by the PB Yield Curves:

$$\begin{aligned} \text{B}_5\text{H}_9/\text{N}_2\text{H}_4: & \quad W_T = 0.65 W_P^{7/8} \text{ for all } W_P \geq W_{P_{\min}} \\ \text{N}_2\text{O}_4/\text{B}_5\text{H}_9: & \quad W_T = 1.30 W_P^{7/8} \text{ for all } W_P \geq W_{P_{\min}} \end{aligned}$$

2.5.2 Other PESs

For operations other than those for launch vehicles, space vehicles, missiles, stages, engines, or components in static test or processing facilities; launch vehicles or missiles in the launch configuration; or quantities less than $W_{P_{\min}}$, the EEW in pounds of TNT is determined by the following:

$$\begin{aligned} \text{B}_5\text{H}_9/\text{N}_2\text{H}_4: & \quad W_T = 40\% W_P \\ \text{N}_2\text{O}_4/\text{B}_5\text{H}_9: & \quad W_T = 75\% W_P \end{aligned}$$

where

W_T = net explosive weight (lb) TNT, and
 W_P = propellant weight (lb) as defined in [1], V5.E4.5.6.1 and V5.E4.5.6.2, and
 $W_{P_{\min}} = 1,000$ lb, and
 MON can be substituted for N₂O₄

2.6 CTF/CPF Hypergolic Combinations (Tentative Option)

Another option to consider is including CTF/CPF hypergolic combinations (chlorine trifluoride (ClF_3)/ N_2H_4 , ClF_5 / N_2H_4 , and ClF_3 /PB) as separate liquid bipropellant combinations in a DESR 6055.09 [1] database of alternate propellant combinations. Currently these combinations are not included; however, at one time, the tables in [1] included 10% and 20% TNT explosive equivalence values for these combinations. The explicit values for each combination from this assessment are the CTF/ N_2H_4 Yield Curve shown in Figure 6, using the methods described in the following subsections.

2.6.1 Static Test or Processing Facilities and Launch Facilities

For launch vehicles, space vehicles, missiles, stages, engines, or components in static test or processing facilities and in the launch configuration, the EEW in pounds of TNT is determined by the CTF/ N_2H_4 Yield Curve:

$$\begin{array}{ll}\text{ClF}_3/\text{N}_2\text{H}_4: & W_T = 0.003 W_P^{7/8} \text{ for all } W_P \geq W_{P_{\min}} \\ & \text{or use individual commodity siting criteria in [1], Table V5.E4.T3} \\ \text{ClF}_3/\text{B}_5\text{H}_9: & \text{Use individual commodity siting criteria in [1], Table V5.E4.T3}\end{array}$$

2.6.2 Other PESs

For operations other than launch vehicles, space vehicles, missiles, stages, engines, or components in static test or processing facilities; launch vehicles or missiles in the launch configuration; or quantities less than $W_{P_{\min}}$, the EEW in pounds of TNT is determined by the following:

$$\begin{array}{ll}\text{ClF}_3/\text{N}_2\text{H}_4: & W_T = 1\% W_P \\ & \text{or use individual commodity siting criteria in [1], Table V5.E4.T3} \\ \text{ClF}_3/\text{B}_5\text{H}_9: & \text{Use individual commodity siting criteria in [1], Table V5.E4.T3}\end{array}$$

where

W_T = net explosive weight (lb) TNT, and
 W_P = propellant weight (lb) as defined in [1], V5.E4.5.6.1 and V5.E4.5.6.2, and
 $W_{P_{\min}} = 1,000$ lb

Explosive data related to $\text{ClF}_5/\text{N}_2\text{H}_4$ are somewhat obscure due to the classification of this combination during its early testing. Although the performance of CPF is known to be greater than CTF, their hypergolic reactions are similar; therefore, the $\text{ClF}_3/\text{N}_2\text{H}_4$ explosive yields noted above are likely acceptable as interim values for $\text{ClF}_5/\text{N}_2\text{H}_4$. However, a comprehensive test program is needed before an explosive yield can be formally recommended.

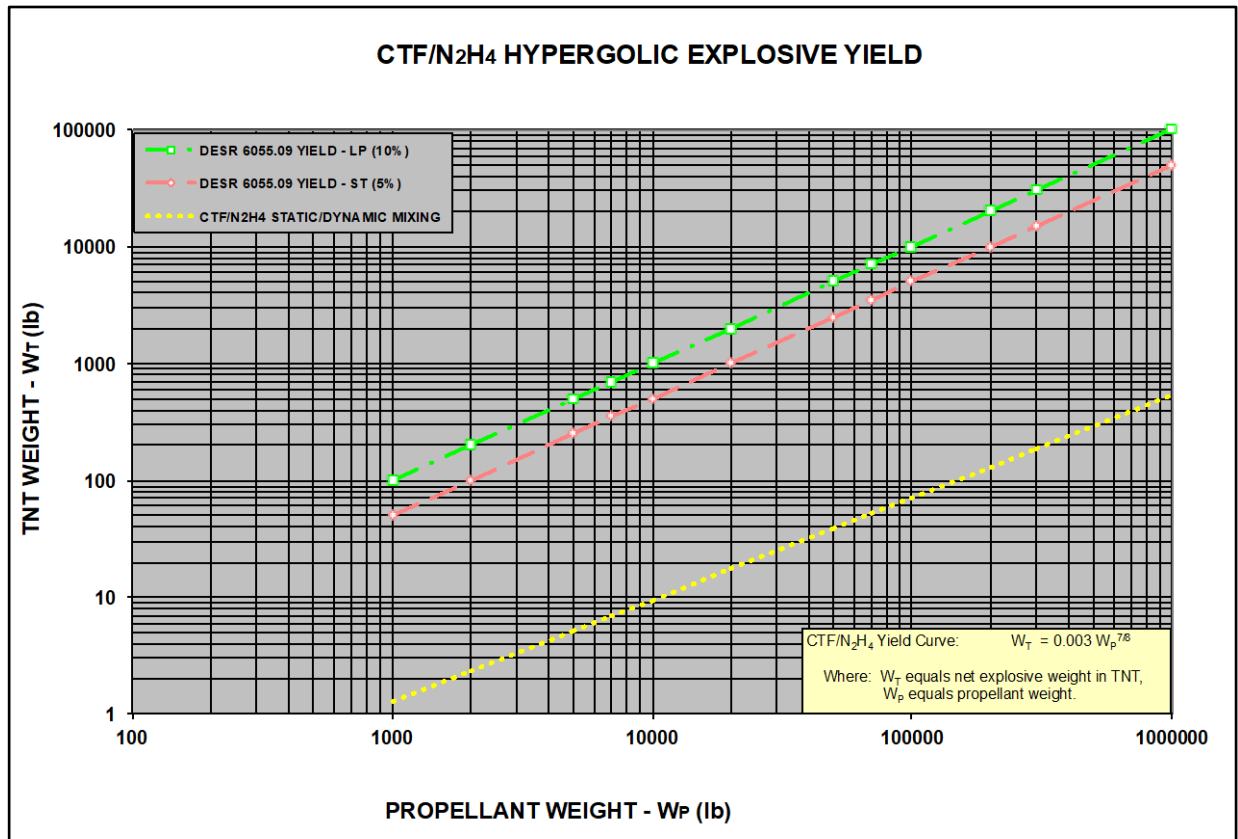


Figure 6. CTF/N₂H₄ proposed explosive Yield Curve.

2.7 Application

Use of the N₂O₄/A-50 and IRFNA/UDMH propellant combinations dates to the early days of the missile and launch vehicle programs. With the recent retirement of the Delta II, it is highly unlikely that either will ever be used again in large quantities. However, they remain as options to use on test programs or space vehicles along with N₂O₄/N₂H₄ and N₂O₄/MMH. Current uses of CTF and CPF are unknown, but ClF₃/N₂H₄ and ClF₅/N₂H₄ remain available as bipropellants in missile applications. In fact, ClF₅/N₂H₄ remains an attractive hypergolic combination due to its performance. Research into use of PB as a propellant has been discontinued; however, although the PB and CTF/CPF values are considered appropriate, due to the nature of the limited data used to establish the above yield values it is recommended that this information be retained in an appropriate database and a note added that these values could be used in lieu of a new comprehensive explosive test program, which would be required to establish an appropriate EEW pending any plans for reuse.

Other hypergolic combinations have recently been proposed, such as WFNA/turpentine and WFNA/furfuryl alcohol, but no operational systems have been developed. Use of such combinations in launch vehicle quantities must be analyzed using the appropriate data in this report or undergo specific explosive testing. In addition, other hypergolic propellants remain in use for engine starting circuits (e.g., furfuryl alcohol); however, such usage is in small quantities that are not governed by the requirements of DESR 6055.09 [1].

3. Background

Per [6], the current launch pad explosive factor of 10% for $\text{N}_2\text{O}_4/\text{A-50}$ found in [7] (and prior versions) was based on hazard analysis estimates in advance of obtaining definitive test results. The 10% factor for $\text{N}_2\text{O}_4/\text{A-50}$ appears initially in [9]. This hazard analysis was performed for a large theoretical vehicle using $\text{N}_2\text{O}_4/\text{A-50}$ and $\text{LO}_2/\text{RP-1}$. The 10% value used was conservatively applied to the entire vehicle and was based principally on $\text{LO}_2/\text{RP-1}$ information. The derivation of the 5% explosive factor used for static test stands, however, has not been found.

In the very early days of the missile and sounding rocket programs, nitric acid (red fuming nitric acid (RFNA), white fuming nitric acid (WFNA), IRFNA, etc.) and UDMH were popular hypergolic propellant combinations. Explosive testing of these combinations appears limited to specialized testing by the Bureau of Mines during the 1940s and 1950s. Then in the early 1960s, attention was placed on the new storable hypergolic propellants planned for the Titan missile. This testing and the results are discussed in detail in [6]. The primary testing was done by Rocketdyne and involved the hypergolic combinations $\text{N}_2\text{O}_4/\text{N}_2\text{H}_4$, $\text{ClF}_3/\text{N}_2\text{H}_4$, $\text{ClF}_3/\text{B}_5\text{H}_9$, $\text{B}_5\text{H}_9/\text{N}_2\text{H}_4$, $\text{N}_2\text{O}_4/\text{B}_5\text{H}_9$, and $\text{N}_2\text{O}_4/\text{A-50}$. This test program is discussed below.

Other than Aerojet-General testing for NASA's Gemini and Apollo test programs, the only other significant testing done with $\text{N}_2\text{O}_4/\text{A-50}$ was performed by Project PYRO. It is evident that the PYRO data were not used to re-evaluate the $\text{N}_2\text{O}_4/\text{A-50}$ criteria, and it is unknown whether any additional discussions took place in this time frame. This report is the first known effort to re-assess the explosive potential and appropriate yield values for the various hypergolic combinations since the mid-1960s.

3.1 Propellant Test Programs Overview

Table 1 shows a matrix of liquid propellant test programs that have been reviewed [10]–[57]. The table gives the experimenter, program, date, propellant combinations (cryogenic LO_2/LH_2 , various hypergolic pairs, $\text{LO}_2/\text{hydrocarbons}$ (HCs), $\text{LO}_2/\text{LH}_2/\text{RP-1}$ tri-propellants, and $\text{H}_2\text{O}_2/\text{hydrocarbon}$), and mixing method.

Table 1. Liquid Propellant Test Programs

Agency/Test Program	Propellants				
	LO_2/LH_2	Hyper	LO_2/HC	Tri	$\text{H}_2\text{O}_2/\text{HC}$
NAVY/PUSHOVER (1948) Vehicle toppling			X		
NAVY/NRL TESTS (1949) Propellant mixing			X		
BUREAU OF MINES (1949) Ballistic mortar test Detonability test		X X			
AEROJET GENERAL (1952) TBD		X			
ROCKETDYNE/FIELD TESTS (1954-1956) Propellant mixing Ground spill Impinging streams			X X X		

Table 1. Liquid Propellant Test Programs (continued)

Agency/Test Program	Propellants				
	LO ₂ /LH ₂	Hyper	LO ₂ /HC	Tri	H ₂ O ₂ /HC
ARMY/REDSTONE (1956) Vehicle destruct			X		
NAVY/JUPITER (1956) Propellant mixing Ground spill Vehicle destruct Tank fallback Tank fallback–water Underwater			X X X X X		
BROADVIEW/ATLAS (1957-1961) Ground spill Tank rupture–ground Tank fallback Tank rupture–in silo			X X X X		
BUREAU OF MINES/NAVY (1959-1960) Propellant mixing		X			
A. D. LITTLE/CENTAUR (1960) Gas phase Intertank mixing Ground spill	X X X		X X	X X	
A. D. LITTLE/SATURN (1961) Ground spill	X		X	X	
ROCKETDYNE/STORABLE (1961) Ground spill Tank rupture		X X			
ROCKETDYNE/TITAN II (1961) Ground spill Tank rupture–ground Tank rupture–in silo Propellant mixing		X X X X			
ATLANTIC RESEARCH/LAB TESTS (1962) Ground spill Falling droplet Liquid I/F injection Gas/liquid		X X X X			
MARTIN MARIETTA/TITAN II (1962) Vehicle destruct		X			
NASA MSFC/SATURN I (1963) Vehicle destruct			X		
AEROJET/GEMINI (1963-1964) Distributed mixing* Intertank mixing Tank fallback		X X X	X X X		
URS/PYRO (1963-1968) Confined-by-missile mixing Confined-by-ground mixing Tank fallback High velocity impact Vehicle destruct Donor	X X X X	X X X X X X	X X X X	X	

Table 1. Liquid Propellant Test Programs (continued)

Agency/Test Program	Propellants				
	LO ₂ /LH ₂	Hyper	LO ₂ /HC	Tri	H ₂ O ₂ /HC
AEROJET (1964) Distributed mixing*		X			
AEROJET/APOLLO (1965) Distributed mixing*	X	X	X		
NASA MSFC/SATURN (1965) Ground spill	X		X		
Intertank mixing	X		X		
Vehicle destruct	X		X		
BUREAU OF MINES/GEMINI (1966) Ballistic mortar test		X			
Distributed mixing*	X				
NASA WSTF/CASSINI-PRC (1994-1995) Distributed mixing*		X	X		X
NASA WSTF/HOVI (1996) Tank fallback	X				

*Distributed mixing is also referred to as immersion mixing elsewhere.

3.2 Failure History Overview

Data were obtained and analyzed [58]–[73] from the near-pad failures of 33 liquid-propellant launch vehicles. These included the vehicle types shown in Table 2. Of the 33 failures studied, 2 were static test stand failures, 30 failed on or near the launch pad/silo, 1 occurred in flight, 6 occurred prior to engine ignition, 13 were instrumented, 7 were destruct cases, and for 4 events, explosive data have not been obtained.

Table 2. Liquid Propellant Launch Vehicle Failure History

Vehicle	Failures	Propellants
ANTARES	1	LO ₂ /RP-1/HTPB
ATLAS	5	LO ₂ /RP-1
ATLAS-CENTAUR	1	LO ₂ /RP-1/LH ₂
DELTA II	1	HTPB/LO ₂ /RP-1
FALCON 9	1	LO ₂ /RP-1
JUPITER/JUNO	3	LO ₂ /RP-1
LONG MARCH	1	N ₂ O ₄ /UDMH/LO ₂ /LH ₂
N-1	1	LO ₂ /Kerosene
NAVAHO	1	LO ₂ /Ethanol/JP-4
REDSTONE	1	LO ₂ /Ethanol
SATURN S-IV	2	LO ₂ /LH ₂
SPACE SHUTTLE	1	LO ₂ /LH ₂
THOR	4	LO ₂ /RP-1
TITAN I	3	LO ₂ /RP-1
TITAN II	4	N ₂ O ₄ /A-50
TITAN 34D	1	PBAN/N ₂ O ₄ /A-50
VANGUARD	1	LO ₂ /RP-1
V-2	1	LO ₂ /Ethanol

4. Review of Past Hypergolic Liquid Test Projects

Following is a brief discussion of the hypergolic explosive test projects. The discussions are organized according to the experimenter.

4.1 Bureau of Mines (BoM)

Testing of hypergolic propellants by the BoM dates to 1949 with the investigation of the explosive properties of hydrazine. Hypergolic propellant testing was performed by the BoM Explosive Research Laboratory. After the monopropellant hydrazine tests, the BoM began testing hypergolic bipropellant combinations under contract to the Navy Bureau of Ships and the Air Force Aeronautical Systems Division from 1959 through 1964. Additional testing was performed for NASA/Manned Spacecraft Center in 1966.

4.1.1 Hydrazine Explosive Tests

In order to understand the hazards associated with employing N_2H_4 and hydrazine hydrate ($\text{N}_2\text{H}_4\text{-H}_2\text{O}$) as fuels, the Department of the Interior (DoI) BoM Explosives Research Branch investigated the properties and explosive hazards associated with manufacture, storage, transportation, and use [11]. Explosive hazard tests included sensitivity to impact, friction, and electrostatic discharge; ballistic mortar TNT equivalence tests; and “Mettegang recorder” detonability tests. The ballistic mortar tests (4 tests) were conducted using 10 g (0.02 lb) of propellant. The BoM reported an N_2H_4 TNT equivalence of 135%. When testing for detonability using 0.46 lb of propellant, no detonations were recorded (4 tests).

4.1.2 New Liquid Propellant

Research was conducted for the Office of Naval Research to investigate the explosion hazards associated with a variety of new liquid propellants and propellant combinations [28][30]. Testing was defined in three phases: ignition, flame propagation and detonability, and burning. Hypergolic propellants tested include Report No. 7 [30] - N_2H_4 , MMH, UDMH, MAF-1, MAF-3, methanol, and benzene. Air, N_2O_4 , and O_2 /air were used as oxidants. Results are to be supplied (TBS).

4.1.3 Flight Vehicle Hazards

Research was conducted for the Air Force Systems Command to investigate the aircraft and missile explosion hazards associated with a variety of combustible propellants and propellant combinations [31][32][36]. Results are TBS.

4.1.4 Damage Assessments

In 1966, following the failure of the Gemini IV Agena (IRFNA/UDMH) target vehicle engine and Apollo reaction control system (RCS) thrusters (N_2O_4 /A-50) during altitude firing, NASA/Manned Spacecraft Center requested that the BoM’s Explosives Research Center investigate the combustion characteristics of N_2O_4 /A-50 [49]. In addition to damage assessments, the objective included determining the explosive potential of the oxidizer and fuel both individually and in combination. The BoM used their ballistic mortar test approach to determine the TNT equivalence of the propellants. The ballistic mortar test measures the energy imparted to a 36.6 lb projectile fired from a 500 lb mortar and compares the explosive energy to TNT. Claimed resolution is within $\pm 1\%$ TNT equivalence. Two types of tests were conducted using 5 g (0.01 lb) of propellant: (1) individual propellants (N_2H_4 , UDMH, MMH, N_2O_4) were fired in various atmospheres using a no. 8 detonator, and (2) liquid fuel and N_2O_4 stoichiometric combinations were explosively combined in a nitrogen atmosphere. In both cases, the liquids were

contained in glass vessels and the detonator encapsulated in glass under the liquid. The kinetic energy delivered to the mortar is presumed to be proportional to the energy released in the reaction. The test apparatus was calibrated using TNT. The 5 g (0.01 lb) bipropellant tests performed (6 tests each) resulted in 90% to 187% TNT explosive yields. The $\text{N}_2\text{O}_4/\text{A-50}$ and $\text{N}_2\text{O}_4/\text{N}_2\text{H}_4$ tests gave similar results (average 160%), while the $\text{N}_2\text{O}_4/\text{MMH}$ and $\text{N}_2\text{O}_4/\text{UDMH}$ tests were on the order of 115% (approximately 70% less). However, the $\text{N}_2\text{O}_4/\text{A-50}$ values were believed to be greater than expected due to the test configuration.

4.2 Aerojet-General

4.2.1 Aerojet-General (Aerobee)

A test program was performed [16] to develop safety and design criteria for storable liquid propellants. Results are TBS.

4.2.2 Aerojet-General (Gemini)

In 1963, Aerojet-General conducted experiments that supported NASA/Manned Spacecraft Center hazard assessments for the Gemini program [42][43]. The tests were conducted to obtain better estimates of the blast hazards associated with using new (i.e., other than $\text{LO}_2/\text{RP-1}$) propellant combinations on manned programs. The test approach was to mix constant 300 lb total weights of fuel/oxidizer combinations at varying mixture ratios and contact area ratios. Propellants used were $\text{N}_2\text{O}_4/\text{A-50}$ for the Gemini-Titan launch vehicle and $\text{LO}_2/\text{RP-1}$ for comparison. Mixing energy was achieved by dropping oxidizer-filled glass dewars, which were immersed in an aluminum pan filled with fuel, from a height of 20 feet. The purpose of the initial test program was to quantify the $\text{N}_2\text{O}_4/\text{A-50}$ blast hazard potential compared to the $\text{LO}_2/\text{RP-1}$ propellant combination. A second test phase was conducted which simulated propellant mixing during launch vehicle booster failures. However, no conclusions were made or inferred relative to full-scale failure modes or effects.

4.2.2.1 Propellant Mixing Tests

Test data were obtained for peak overpressure, positive impulse, and fireball history [42]. The overpressure impulse data were referenced to TNT equivalent yields. The farthest sensor was taken as the comparison value but may not have represented the terminal yield value for the highest-energy tests. It was reported that the test results demonstrated that explosive yield varied with contact area. The 300 lb test series (9 each) varied the oxidizer-to-fuel mixture ratios in order to observe the effect on explosive yield. The mixture ratios chosen for $\text{N}_2\text{O}_4/\text{A-50}$ were 1:1, 2:1, and 3:1. $\text{N}_2\text{O}_4/\text{A-50}$ yields varied from 0.4% to 36% TNT as a function of contact area.

4.2.2.2 Simulated Tankage Tests

A separate follow-up test series was conducted at the conclusion of the 300 lb maximum yield tests [43]. The follow-up program was intended to investigate the blast and fireball characteristics of hypergolic versus cryogenic propellants under simulated space booster launch conditions. The test setup involved using scaled propellant tankage configurations with failure modes caused by loss of thrust (two each) or a powered fallback (two each). The propellant tanks were loaded with 300 lbs of total weight for each test to compare test results directly with the previous mixing tests. The tankage L/D chosen was 1.6 for $\text{N}_2\text{O}_4/\text{A-50}$ and 1.8 for $\text{LO}_2/\text{RP-1}$. Propellant mixture ratios were also fixed at 2:1 for $\text{N}_2\text{O}_4/\text{A-50}$ and 2.5:1 for $\text{LO}_2/\text{RP-1}$. The static failure mode was accomplished by cutting a common tank bulkhead using a linear-shaped charge. Fuel was in the upper tank, and oxidizer was contained in the lower. In the fallback mode, the tankage was dropped from a 15 ft height and the inter-tank bulkhead ruptured by a ram. For

this test, the oxidizer was in the upper tank, fuel in the lower. An explosive charge with time delay was used to initiate detonation. Two time delays were used (0.1 sec and 0.4 sec) to test the effect of time delay on yield. As in the previous tests, data were obtained for peak overpressure, positive impulse, and fireball history with results referenced to TNT. Instrumentation location was also similar to the previous tests. It was reported that typical blast pressure-time histories were obtained for all cryogenic tests; however, the hypergolic yields were so low that no pressure trace was discernable in two of the static tests. $\text{N}_2\text{O}_4/\text{A-50}$ yields varied from $\ll 1\%$ to 1% TNT as a function of contact area.

4.2.3 Aerojet-General (Detonation Tests)

In 1964, Aerojet-General conducted experiments to determine whether, under ideal conditions of vigorous mixing, the hypergolic propellant combination of N_2O_4 and A-50 could detonate. It was postulated that if a failure mode could be found such that rapid mixing occurred prior to the finite ignition time delay of the hypergolic components, then a mass detonation of the liquid mixture would result [44]. To test this hypothesis, a technique was devised to intimately disperse one of the hypergolic propellants rapidly within the other. Various mixing techniques were studied experimentally to establish an optimum configuration. The mixing method that was determined to give the best results was the concentric vessel technique in which a glass cylinder was filled with one liquid propellant, then placed concentrically within a larger cylindrical vessel containing the other propellant. The inner vessel was shattered by initiating a pair of primacord strips 180° apart. Following a preplanned time delay, a second pair of primacord strips, located 90° from the first, were initiated to provide the detonating stimulus for the mixed propellants. The tests were conducted in an oxidizer vat containing eleven 4 ft plexiglass tubes containing fuel. The tubes were shattered using a mild detonating fuse prior to initiating a planar booster at the base of the vat. Propellant quantities varied from 100 lbs to 140 lbs at a mixture ratio of 2.4:1. Twelve tests were performed with initiation delay time varied from 0.1 msec to infinity. No evidence of propagating detonation was noted with the yields varying from 14% TNT to 52% TNT.

4.2.4 Aerojet-General (Apollo)

In 1965, Aerojet-General conducted experiments that supported NASA/Manned Spacecraft Center hazard assessments for the Apollo program [48]. The objective was to reduce the uncertainty in quantifying the explosive potential by controlling/minimizing the propellant mixture. Previous tests were performed by Aerojet-General in 1963 and 1964 for the Gemini program using $\text{LO}_2/\text{RP-1}$ and $\text{N}_2\text{O}_4/\text{A-50}$, and additional $\text{LO}_2/\text{RP-1}$ and $\text{N}_2\text{O}_4/\text{A-50}$ tests were performed during this Apollo test series. In these experiments, an external shock was transmitted through the metal pan to rupture the glass dewars, resulting in instantaneous mixing of the propellants. A single $\text{N}_2\text{O}_4/\text{A-50}$ test was performed at 230 lbs that resulted in a 42% to 52% TNT explosive yield.

4.3 Rocketdyne

A test program was performed [33][34] to develop safety and design criteria for five storable liquid propellants. The propellants involved in the investigation were N_2O_4 , ClF_3 , N_2H_4 , pentaborane (B_5H_9), and Aerozine-50 (50% N_2H_4 + 50% UDMH). The hazards program in [33] consisted of both small- and large-scale spill tests of various mono- and bipropellant combinations to investigate both explosive and toxic hazards. The intent of the hazard evaluation effort was to determine the hazards involved in storage and handling of these propellants in quantities up to 5,000,000 lbs. Small-scale tests were intended to simulate failures, such as line leakage or failure, and large-scale tests were intended to simulate tank rupture. Safe-distance storage assessments were also made for the four propellant types. Additional investigations included evaluation of meteorological influence and biological hazards relative to toxic effects. The test project in [34] also performed a series of sub-scale tests of the Titan II missile to determine the hazard potential of the new hypergolic propellants $\text{N}_2\text{O}_4/\text{A-50}$. Missile failures were

simulated above ground and in-silo, as well as small-scale and large-scale spill tests of up to 1,600 lbs. The test program was performed in 1960 and 1961.

4.3.1 Small-Scale Spill Tests

There were 23 $\text{N}_2\text{O}_4/\text{N}_2\text{H}_4$, 13 $\text{B}_5\text{H}_9/\text{N}_2\text{H}_4$, 13 $\text{ClF}_3/\text{N}_2\text{H}_4$, 12 $\text{ClF}_3/\text{B}_5\text{H}_9$, 5 $\text{N}_2\text{O}_4/\text{ClF}_3$, and 5 $\text{N}_2\text{O}_4/\text{B}_5\text{H}_9$ small-scale tests ranging from 1.7 lbs to 19 lbs. Several tests were conducted without instrumentation. The largest explosions that were recorded during the small-scale test program were caused by combined spills of $\text{B}_5\text{H}_9/\text{N}_2\text{H}_4$ on concrete, dirt, and asphalt. The explosions occurred as a single shock wave with reflections and were originated at times varying from slightly after ignition to the start of the post-test purge. Strong overpressures were recorded on five of seven instrumented spills and were observed on four of six un-instrumented tests. $\text{N}_2\text{O}_4/\text{B}_5\text{H}_9$ spills were conducted without blast instrumentation; therefore, no TNT equivalents were calculated. However, it was concluded that this combination was potentially the most hazardous of the combinations tested. The $\text{N}_2\text{O}_4/\text{ClF}_3$ combination was not hypergolic as would be expected.

4.3.2 Large-Scale Spill Tests

The magnitude of the hazards involved during leakage or rupture of propellant systems containing pentaborane, hydrazine, chlorine trifluoride, and nitrogen tetroxide was determined by performing controlled spills of large quantities of propellants. A total of nine tests were conducted: five singular and three multiple spill tests and one propellant heating test. The propellants were spilled into a 20 ft $\times$ 20 ft $\times$ 2 ft steel tray from 150- or 165-gallon tanks. The propellants were rapidly expelled from the tanks through 6-inch ports in less than 2 seconds. The oxidizer/fuel tests were conducted using 1,600 lbs of $\text{N}_2\text{O}_4/\text{N}_2\text{H}_4$ at a mixture ratio of 1.29:1 and 1,000 lbs of $\text{ClF}_3/\text{N}_2\text{H}_4$ at a mixture ratio of 1:1. A singular spill test of 500 lbs of pentaborane resulted in ignition upon contact with air, resulting in an intense fire lasting several minutes. A combined spill test was also conducted using 275 lbs of pentaborane and 100 lbs of N_2H_4 . Several large explosions were recorded during this spill test. In the heating test, 135 lbs of hydrazine were heated inside a stainless-steel tank with 90% ullage for 5 minutes, resulting in a hydrazine explosion that fragmented the tank and scattered pieces over a radius of 1,100 feet.

4.3.3 Titan II Tests

The Titan II test program involved 9 small-scale (2.5 lbs), 20 sub-scale model (50 lbs and 300 lbs), and 2 large-scale (1,300 lbs and 1,600 lbs) $\text{N}_2\text{O}_4/\text{A-50}$ tests. The small-scale tests used propellant feed lines to inject the liquids into a reaction basin, whereas the model tests used 1/18- and 1/10-scale propellant tanks stacked vertically. The model tests were initiated by removing the bottoms from both tanks either simultaneously or sequentially above ground into a reaction basin or below ground into an open silo. The two large-scale tests used dump tanks and did not simulate a vehicle configuration. The 1,600 lb test was conducted in the presence of deluge water and no overpressure was registered. All data were in terms of TNT equivalence. Only peak overpressure data were recorded. The Titan II model tests varied the spill sequence and surface, including water-covered surfaces in some cases.

4.4 Atlantic Research Corporation

In 1961 and 1962, Atlantic Research Corporation investigated the explosive mechanism from hydrazine-type liquids when in contact with liquid nitrogen tetroxide during testing performed for the Air Force Flight Accessories Laboratory at the Aeronautical Systems Division [40]. All testing was done using $\text{N}_2\text{O}_4/\text{N}_2\text{H}_4$ at laboratory scale (1 cc to 10 cc) and included falling droplet, liquid interface injection, and gas-liquid experiments. The tests yielded only qualitative data in terms of explosive effects since only photographic instrumentation was used. A series of dump tests were also reported using up to 700 ml

(2 lbs) of reactants. Data from the dump tests were not reported; however, information in the report implies yields on the order of less than 0.1% TNT equivalency. Although of interest from a reaction-mechanism perspective, these tests were not found useful in assessing vehicle-scale explosive risks and are not included in the data assessment. However, findings included explosive correlations with contact-sequence and drop-height dynamic interaction. The investigators also concluded that, contrary to the Rocketdyne test report discussed in section 4.3, the $\text{N}_2\text{O}_4/\text{N}_2\text{H}_4$ explosions did not result from vapor-phase hydrazine/air reaction but rather from the presence of the more reactive oxidizer, even though a final conclusion regarding reaction mechanics at the interface could not be defined.

4.5 The Martin Marietta Corporation

The Martin Marietta Corporation conducted a series of Titan vehicle destruct tests in support of the Titan II/Dyna-Soar Program [39]. The tests were performed under contract to the Air Force Space Systems Division and used $\text{N}_2\text{O}_4/\text{A-50}$. Small-scale tests used propellant weights up to 292 lbs. Two large-scale tests were also conducted with propellant weights of 32,700 lbs and 15,800 lbs, which simulated half-scale Titan Stages 1 and 2, respectively. The test project took place in 1961 and 1962. Since the test program was intended to develop a destruct system for the Titan vehicle, emphasis was not placed on maximizing and measuring explosive effects. Instead, the tests principally concentrated on destruct charge placement, configuration, and mixing phenomenon. Small-scale test configurations included vertical and horizontal vehicle simulations with destruct charges located along the tank barrels, on the tank hemispherical bulkheads, or at both locations. The half-scale test simulated the Titan II vehicle tank configurations and was oriented vertically. The stage 1 length/diameter (L/D) was 6, while the stage 2 L/D was 3.4. The half-scale test destruct charges were placed on both hemispherical tank domes in the intertank area and represent a confined-by-missile (CBM) type of mixing mode. The small-scale tests yielded only qualitative data in terms of explosive effects because no instrumentation was used. Post-test observations were visual. The half-scale tests were instrumented with pressure and temperature sensors. Due to a test malfunction, no data were obtained for the stage 2 test; therefore, the only usable data from this test series applicable to propellant explosive hazards were obtained from the stage 1 test. The stage 1 destruct test resulted in two detonations with yields that did not exceed 2% TNT equivalency.

4.6 URS Corporation (Project PYRO)

Project PYRO was the largest of the liquid-propellant explosion studies. This was an extensive experimental project conducted in the early- and mid-1960s to establish the blast environment for the three common liquid propellant combinations ($\text{LO}_2/\text{RP-1}$, LO_2/LH_2 , and $\text{N}_2\text{O}_4/\text{A-50}$). The PYRO $\text{N}_2\text{O}_4/\text{A-50}$ experiments were conducted in two phases [46][47][50]. Propellant quantities ranged from small (200 lbs) to medium-scale (1,000 lbs) at 1.9:1 mixture ratio. In total, 32 successful $\text{N}_2\text{O}_4/\text{A-50}$ tests were performed. The test series for the hypergolic tests were subdivided by configuration and failure mode. The configurations were defined as static test stand, launch pad (pre-launch and launch), and post-launch (in-flight and ground impact). The series of postulated failure modes were identified as CBM (3 tests), confined-by-ground surface (CBGS) (2 tests), tower drop (11 tests), explosive donor (2 tests), command destruct (2 tests), and high-velocity impact (HVI) (10 tests). Three additional tests were attempted using chilled propellants. The PYRO CBM apparatus was similar to the Marshall Space Flight Center (MSFC) CBM apparatus, consisting of a single tank separated by a glass diaphragm. However, in the PYRO tests, the diaphragm was broken using a cutter ram driven by an explosive charge. In the CBGS experiments, the glass diaphragm in the tank was broken by dropping the tank from a tower onto a cutter ram. An additional special cold-propellant test case was added in [49] to determine whether a mixing technique could be used to increase the explosive yield of hypergolic propellants.

4.6.1 Static Test Stand Case

Failure mode tests included CBM, CBGS, small explosive donor, and 100 ft tower drop. The range of estimated upper limit yield was determined to be from 0.5% TNT (CBGS) to 1.5% TNT (CBM) to 2% TNT (small donor).

4.6.2 Launch Pad Case

Failure mode tests included CBM, CBGS, small and large explosive donor, command destruct, and 300 ft (~140 ft/sec) fallback. The range of estimated upper-limit yield was determined to be from 0.5% TNT (CBGS and command destruct) to 3% TNT (fallback) to 5% TNT (large donor). As reported in Project PYRO, for the launch pad case, the highest yields were obtained from the large explosive-donor case. However, an explosive donor weighing two or three times the effective weight of the exploding propellant mass was required to achieve this large a yield. Thus, in any case where this situation occurs, there would be more concern about the blast from the donor than that from the resulting propellant explosion. Therefore, it seemed reasonable to present two yield values for this case: one with a large explosive donor and one without.

4.6.3 Post-Launch Case

Failures after launch are divided into two subcategories: in-flight and HVI ground impact. In-flight failure modes included CBM, small and large explosive donor, and command destruct. Ground impact modes included flat-surface and soft-surface impact cases. The worst credible failure mode for the post-launch case is the high-velocity ground impact. This failure mode would occur from high-altitude fallback or powered impact. The data from the experimental tests indicate that at the maximum impact velocity investigated (~570 ft/sec), the mean of the explosive yields varied from 14% (for impact on a flat surface) to $\geq 80\%$, depending on the degree of cratering and therefore containment provided by the target surface. The estimated upper limit for these two failure modes is 24% for the flat-surface case and 96% for the cratering case.

4.6.4 Cold-Propellant Case

The oxidizer and fuel were cooled in separate containers, using LN₂ to chill the propellants before mixing. Three tests were attempted using 200 lbs of N₂O₄/A-50 with yields of 6.1% TNT to 13% TNT from 2 of the tests.

4.7 NASA White Sands Test Facility (WSTF)

Beginning in the early 1990s, a series of propellant tests was performed at the NASA WSTF. The tests were separated into three programs. The first was the Large-Scale Hydrogen/Oxygen Explosion (LSHOE) test program, the second was the Propellant Reaction Characterization (PRC) test program, and the third was the Hydrogen/Oxygen Vertical Impact (HOVI) test program. PRC testing was an extension of the LO₂/LH₂ distributed mixing tests performed by LSHOE to characterize the maximum yield from other possible propellant mixtures resulting from a Titan IVA/Centaur failure. The test programs included development of hydrodynamic mixing and reaction models. LSHOE conducted a series of distributed mixing tests of medium scale (150 lbs and 500 lbs). The PRC tests included immersion testing of 150 lb mixtures of LO₂/MMH, N₂O₄/MMH, N₂O₄/LH₂, LO₂/RP-1, and H₂O₂/Jet-A. Three N₂O₄/MMH tests were performed at 150 lbs [54] and a weight ratio of 2.8:1. The N₂O₄/MMH PRC tests yielded TNT equivalences of 34% to 66%.

5. Hypergolic Explosive Assessment

5.1 Assessment Methodology

Due to observed differences in explosive yield assessment methods used by the various experimenters and analysts, as part of the original study [6], all liquid-propellant explosion data were analyzed using a consistent methodology. The approach used was as follows:

- Data values were corrected as needed where calibration data were available
- Identified instrumentation faults were discarded
- Yields were calculated in terms of overpressure
- Far-field measurements were averaged
- All data were recalculated using Kingery's surface-burst factors to establish TNT percent yields

The TNT percent yields derived for all tests and failures were then compiled by mass and mixing scenario. To accomplish this, the following mixing scenarios were defined:

STATIC MIXING

- Propellant spills from tank rupture/leakage
- Inter-tank bulkhead rupture
- Vehicle destruct test cases included
- Static conditions ≤ 10 ft/sec

DYNAMIC MIXING

- Vertical fallback impact
- Horizontal fallback impact (toppling)
- Vehicle destruct flight failures not included
- Dynamic conditions ≤ 150 ft/sec

HIGH-VELOCITY IMPACT MIXING

- Powered impact
- HVI conditions > 150 ft/sec

DISTRIBUTED (IMMERSION) MIXING

- Matrix of propellant immersed within a bath

DONOR MIXING

- Secondary reaction resulting from initial (smaller) explosion
- Data included in dynamic mixing

5.2 Hypergolic Vehicle Failures

Results of the independently performed explosive yield analyses from data obtained from [58]–[73] for the hypergolic liquid-propellant launch vehicle failures are tabulated in Table 3 by vehicle. Included are the propellant type and quantity, failure mode, and estimated explosive yield resulting from the failure reaction. The Long March failure was analyzed as total vehicle yield based on the reconstruction of the accident scenario ([6], Addendum 1).

Table 3. Hypergolic Launch Vehicle Failures

VEHICLE	MODE	PROPELLANTS	K lb	YIELD
LONG MARCH CZ-3B ¹	Impact	N ₂ O ₄ /UDMH LO ₂ /LH ₂	776 39	12.5%
TITAN II				
Titan II B-54	Fallback	N ₂ O ₄ /A-50	230	1.0%
Titan II B-22	Fallback	N ₂ O ₄ /A-50	230	2.0%
Titan II B-57	Donor	N ₂ O ₄ /A-50	230	UNK
Titan II M68B-25	Donor	N ₂ O ₄ /A-50	230	3.0%
TITAN III				
Titan 34D-9	Destruct	N ₂ O ₄ /A-50	384	1.5%
¹ Combined yield				

5.3 Hypergolic Propellant Data Assessment

The plots in Figure 7 through Figure 16 are the results of this assessment. Figure 7 and Figure 8 include all hypergolic propellant data points (N₂O₄/A-50, N₂O₄/N₂H₄, N₂O₄/MMH, N₂O₄/UDMH, PB/N₂H₄, CTF/N₂H₄, and CTF/PB) whether from tests or failures. Each dataset is identified by mixing mode. The data were then assessed for large-scale (≥ 100 lb) conditions and the 95% upper limits established for each dataset (i.e., static or dynamic mixing) for each propellant combination.

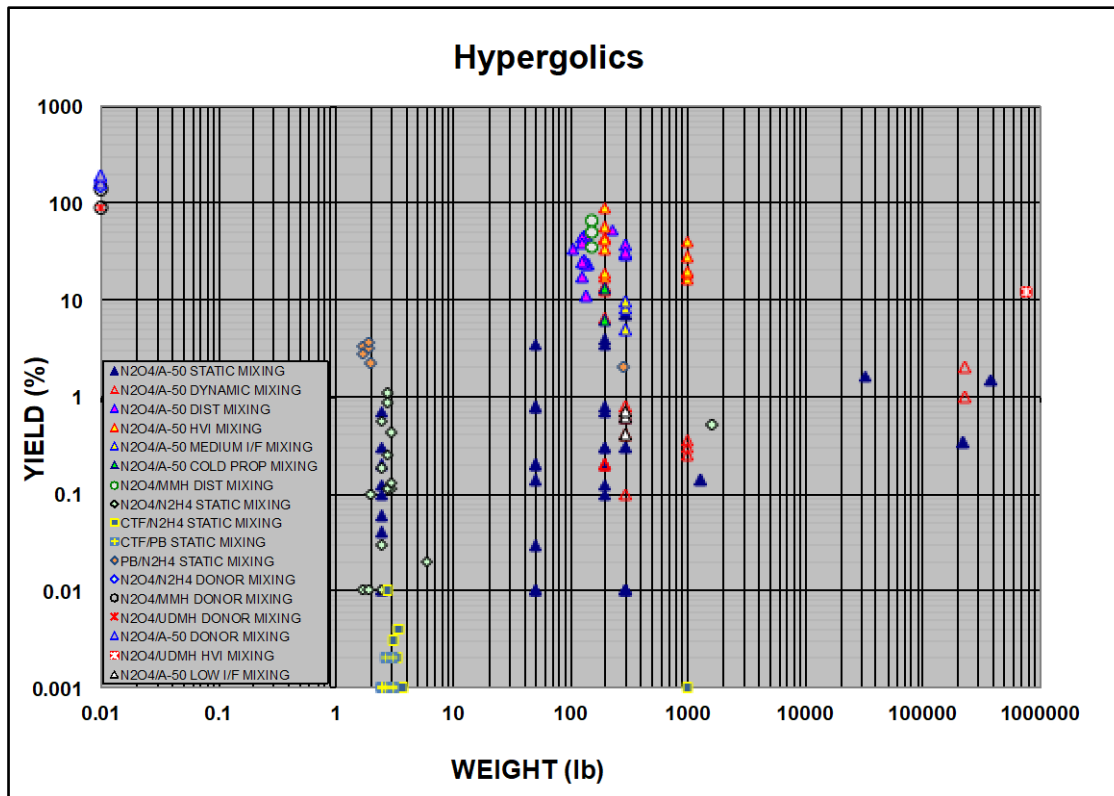


Figure 7. EEW yields for hypergolic propellants.

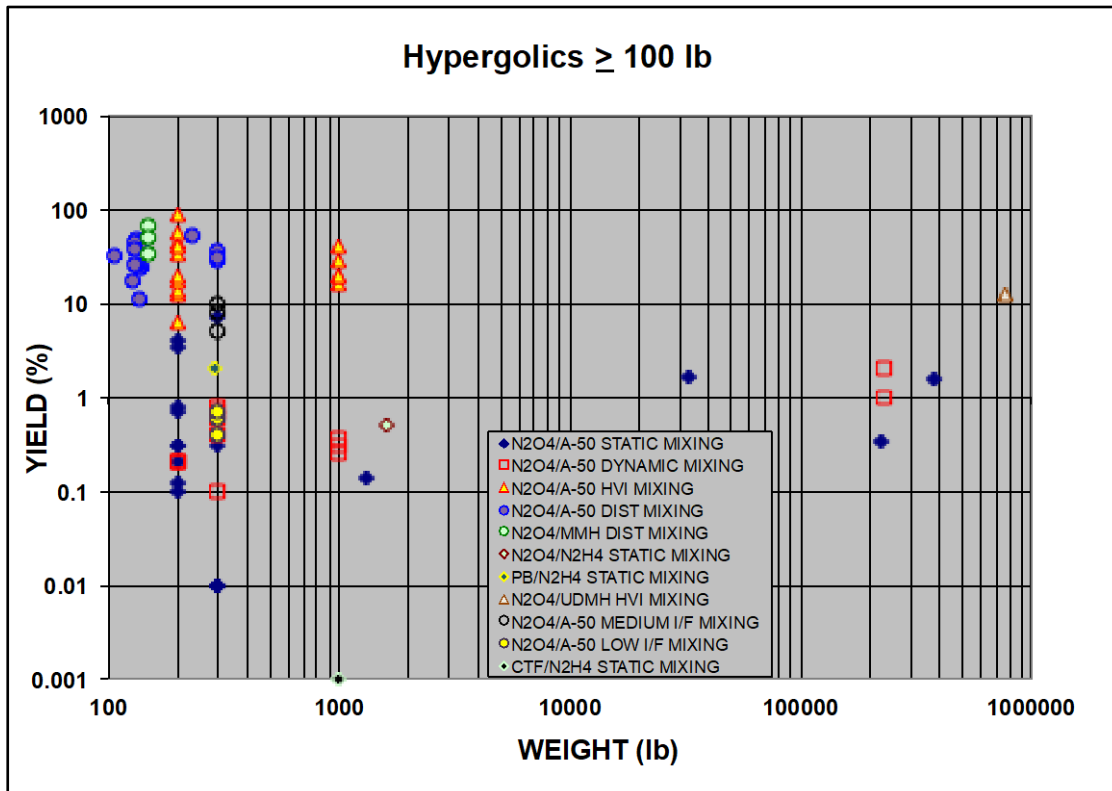


Figure 8. EEW yields for hypergolic propellants ≥ 100 lbs.

5.3.1 N₂O₄/A-50 Data

Figure 9 shows all N₂O₄/A-50 data, and Figure 10 includes the 95% upper-limit level for static and dynamic mixing modes for the data ≥ 100 lbs.

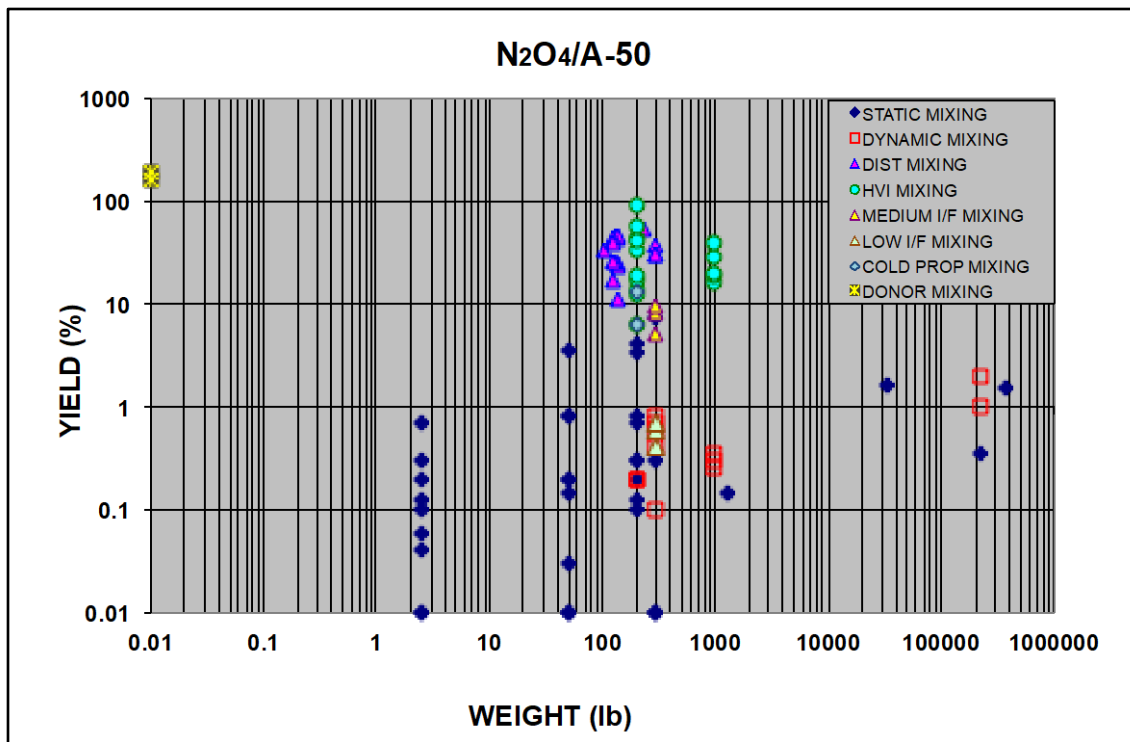


Figure 9. EEW yields for all N₂O₄/A-50 tests/failures.

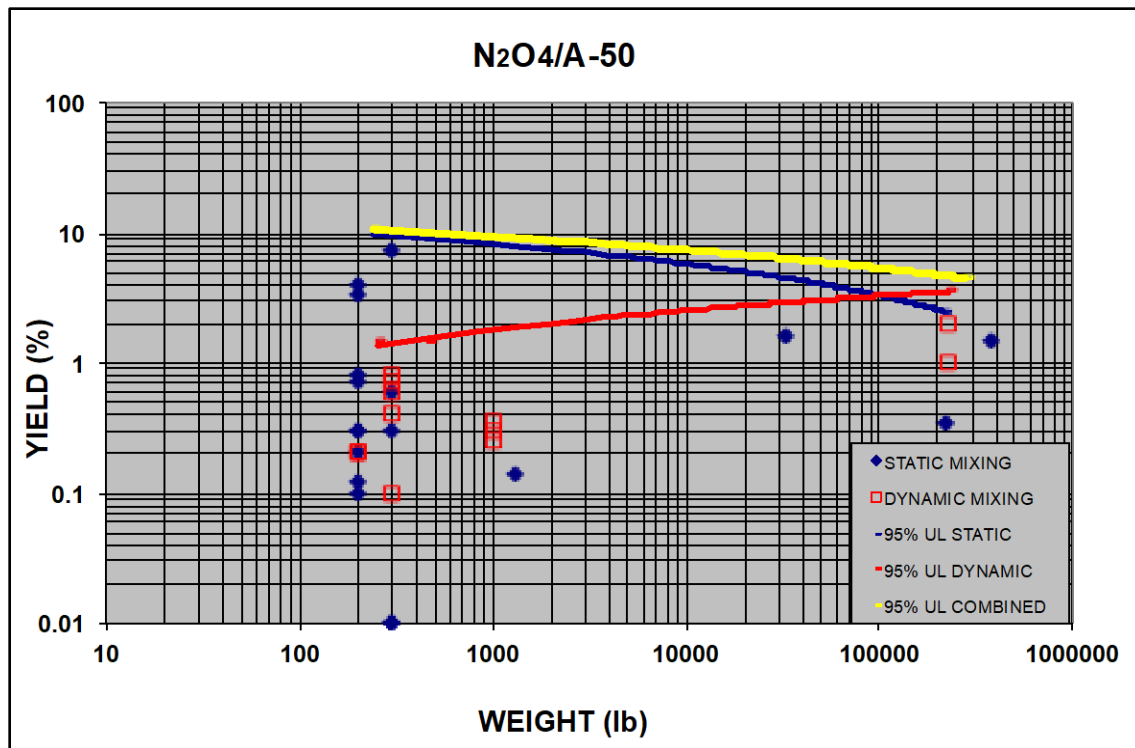


Figure 10. 95% upper limit for N₂O₄/A-50 EEW yields.

5.3.2 N₂O₄/N₂H₄ Data

Figure 11 shows all N₂O₄/N₂H₄ data obtained to date along with the N₂O₄/A-50 data. Figure 12 compares the ≤ 5 lb N₂O₄/N₂H₄ data 95% upper-limit values to similar N₂O₄/A-50 data in conjunction with the N₂O₄/A-50 ≥ 100 lb data and 95% upper-limit plots.

5.3.3 N₂O₄/MMH and N₂O₄/UDMH Data

Figure 13 shows all N₂O₄/MMH and UDMH data obtained to date along with the N₂O₄/A-50 data. Figure 14 compares the ≥ 100 lb N₂O₄/MMH DMT data 95% upper-limit values to similar N₂O₄/A-50 data in conjunction with the N₂O₄/A-50 ≥ 100 lb data and 95% upper-limit plots.

5.3.4 PB and CTF Data

Figure 15 shows all PB/N₂H₄, CTF/N₂H₄, and CTF/PB data obtained to date along with the N₂O₄/A-50 data. Figure 16 compares the ≤ 5 lb PB and CTF data 95% upper-limit values to similar N₂O₄/A-50 data in conjunction with the N₂O₄/A-50 ≥ 100 lb data and 95% upper-limit plots.

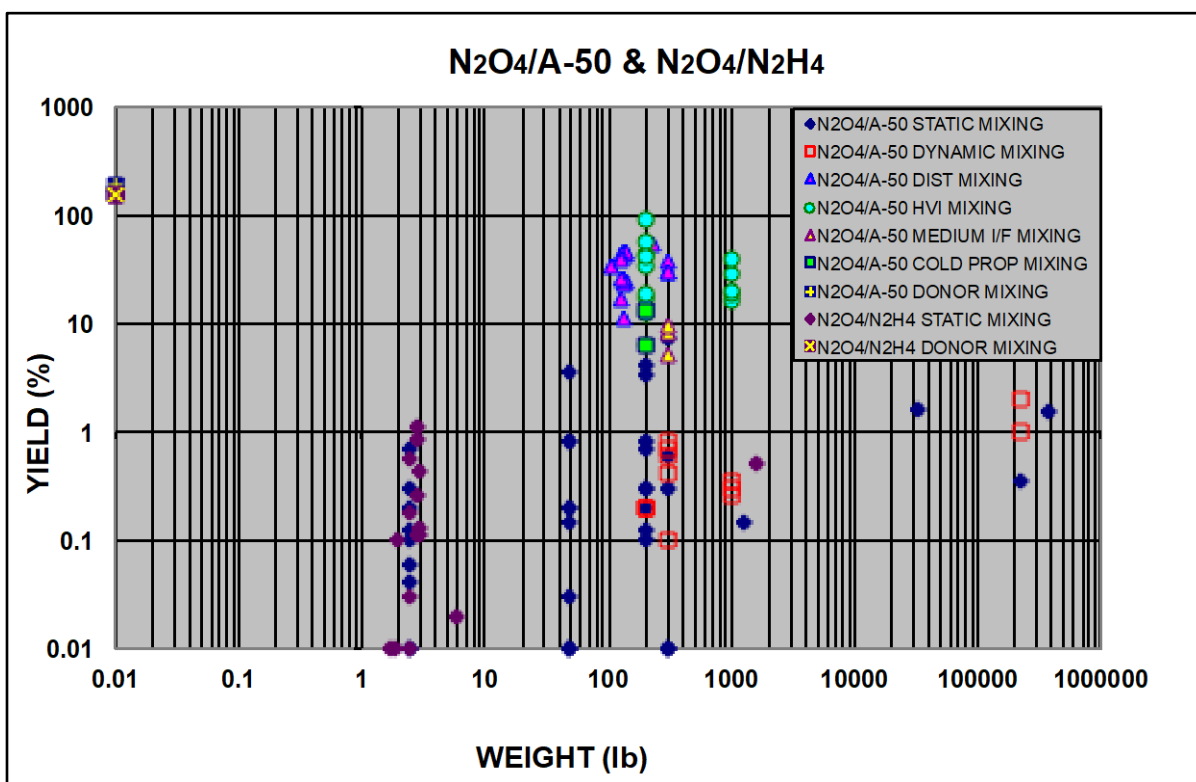


Figure 11. EEW yields for all N₂O₄/N₂H₄ tests.

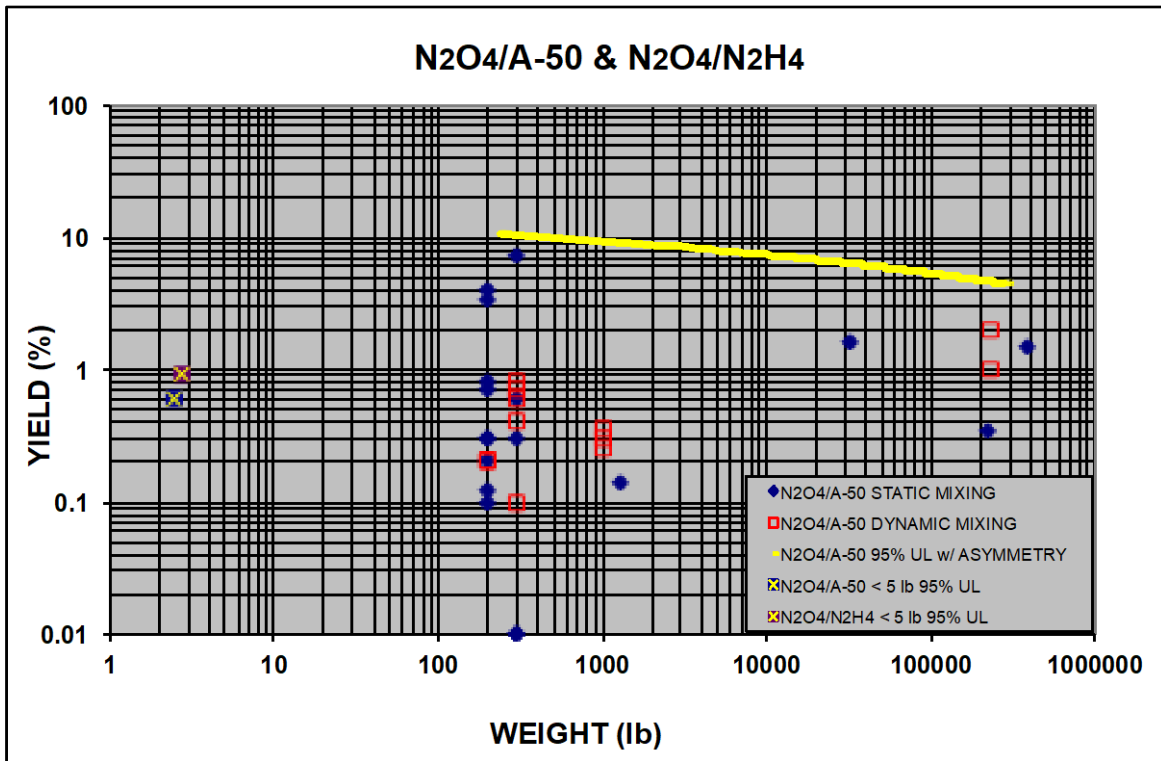


Figure 12. 95% upper limit for N₂O₄/A-50 and comparable N₂O₄/N₂H₄ EEW yields.

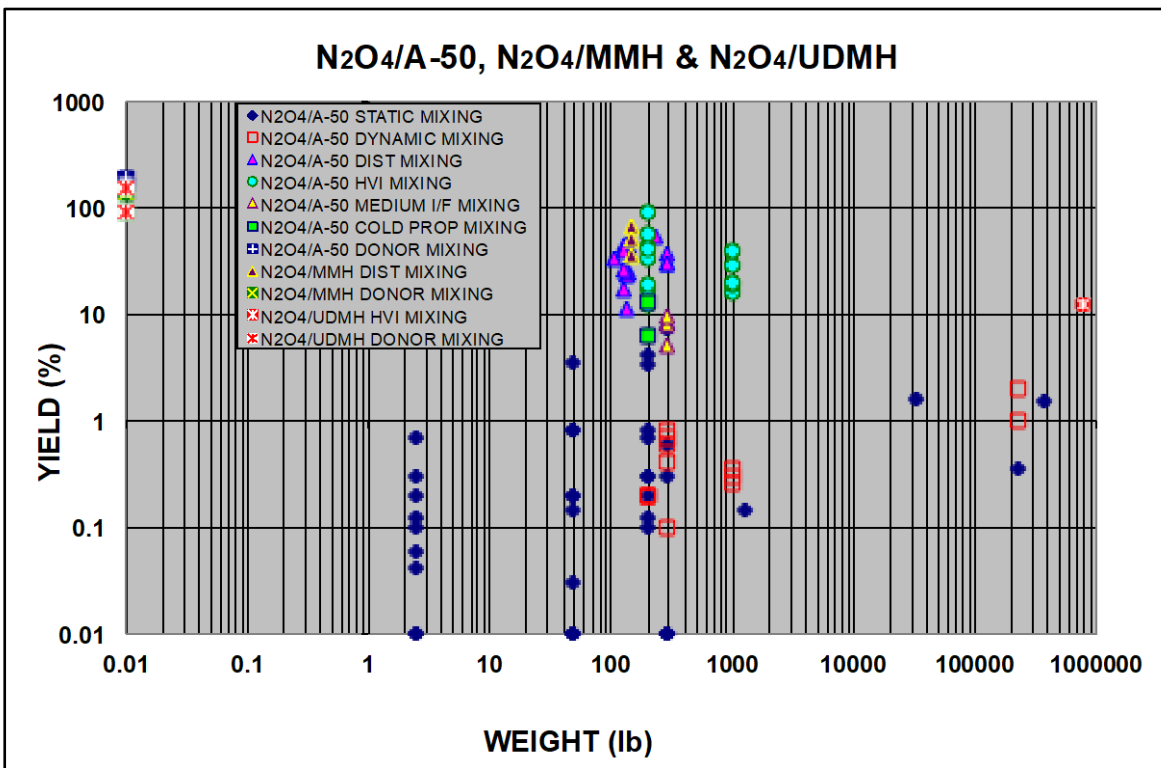


Figure 13. EEW yields for all N₂O₄/MMH and N₂O₄/UDMH tests/failures.

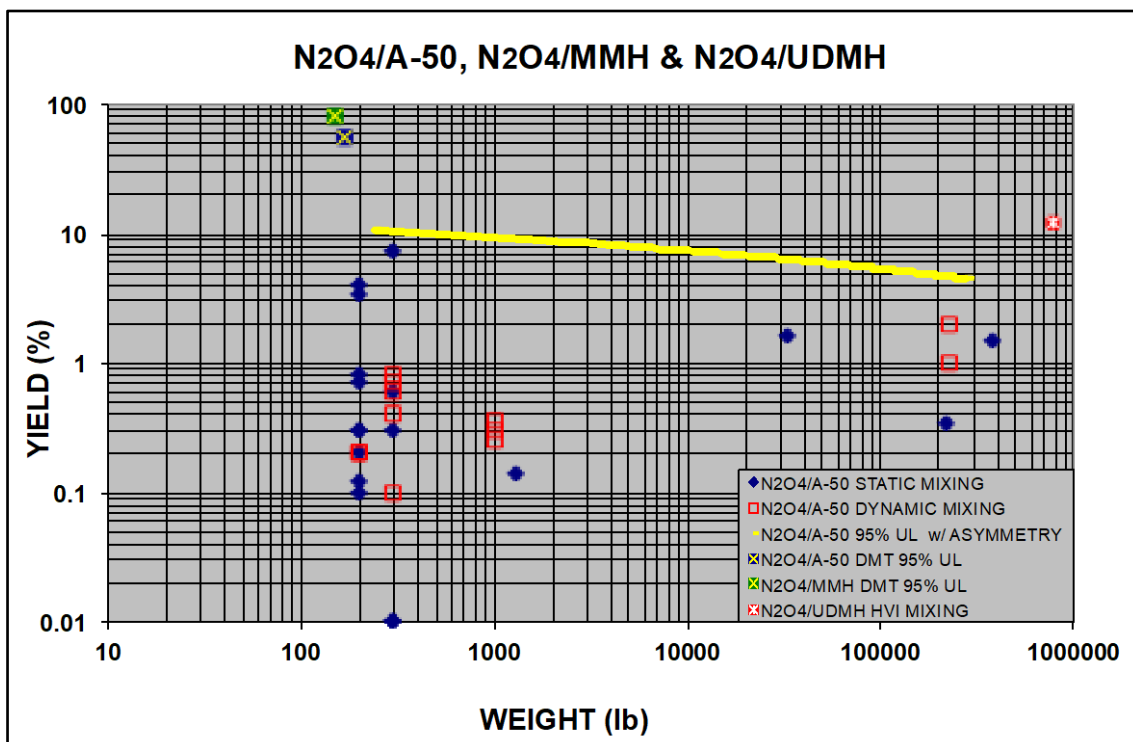


Figure 14. 95% upper limit for N₂O₄/A-50 and comparable N₂O₄/MMH EEW yields.

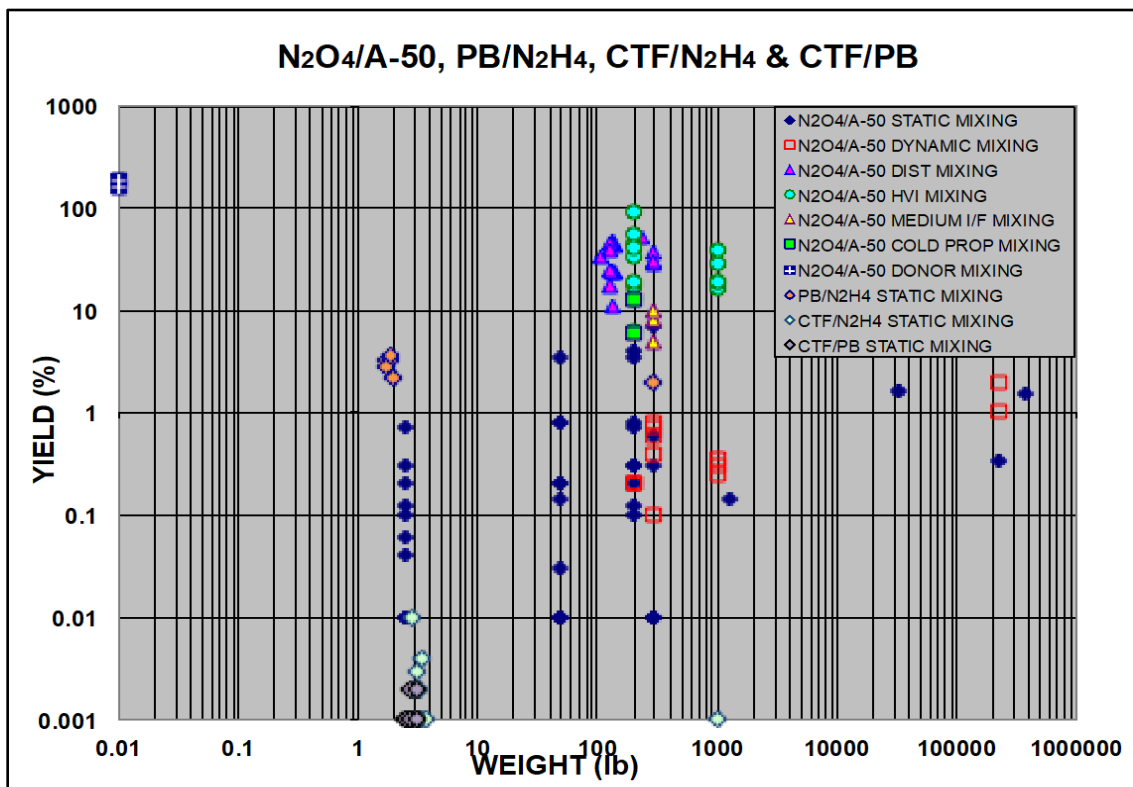


Figure 15. EEW yields for all PB and CTF tests.

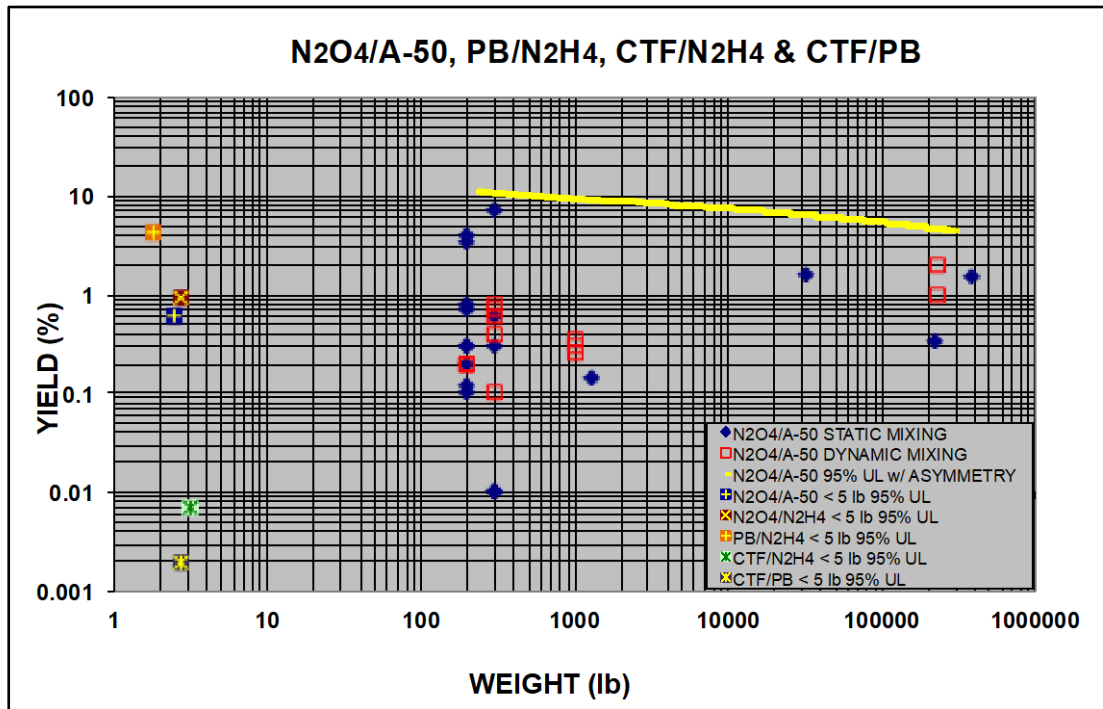


Figure 16. 95% upper limits for PB and CTF and comparable N_2O_4/N_2H_4 EEW yields.

5.4 Discussion

As mentioned above, since the initial assessments presented in [3], several adjustments have been included in this analysis. One modification was to include additional propellant combinations rather than addressing the $N_2O_4/A-50$ propellant combination as a single assessment. Most of this data were initially included in [6] but not assessed in [3]. Additional test reports and failure data were obtained and incorporated as well. The plots shown in previous sections reflect this revised assessment.

5.4.1 $N_2O_4/A-50$ Results

In this report, $N_2O_4/A-50$ Yield Curves were created using the dataset shown in Figure 9. Each yield curve was created by converting the percent yield versus propellant weight plots shown in Figure 10 into TNT weight (W_T) versus propellant weight (W_P) plots for both the static and dynamic 95% upper-limit cases and performing curve fits.

The resulting yield curves, shown in Figure 17, are $W_T = 0.20 W_P^{7/8}$ for static and $W_T = 0.25 W_P^{7/8}$ for dynamic conditions. The yield curves are shown along with the current DESR 6055.09 Table V5.E4.T5 [1] values. The results are conclusive in that the vehicle-scale quantity dynamic yields are significantly less than the current values.

A-50 was developed for use in the Titan II missile and was widely used in all Titan III, Titan IV, and Delta launch vehicles, the Apollo program, and other spacecraft. A-50's 50/50 mixture of N_2H_4 and UDMH added the extra performance of hydrazine with the stable characteristics of UDMH.

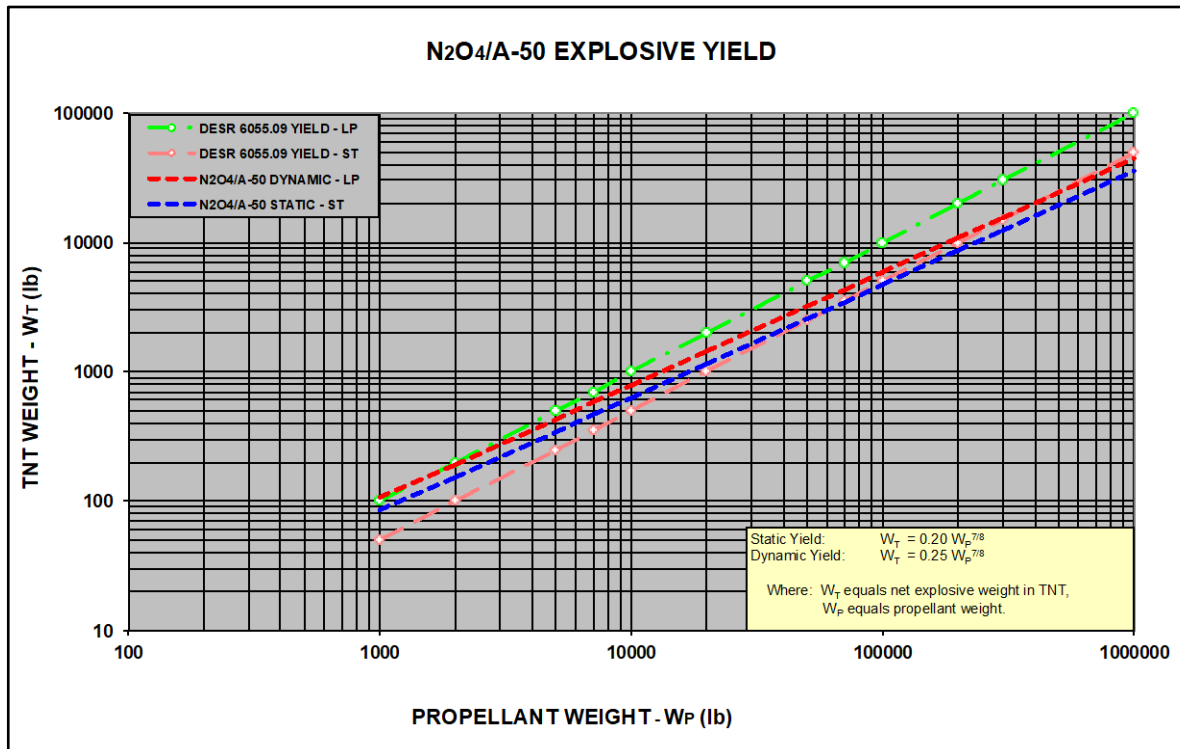


Figure 17. Proposed N₂O₄/A-50 Yield Curves and current DESR 6055.09 [1] values

The explosive nature of hypergolic propellant combinations is fundamentally different from any other combination type. Since the explosive yield is directly proportional to the initial contact area, the yields do not correspond to available or mixed volumes or mass. Therefore, the term “mixing” is not relevant to these liquids. This phenomenon can be readily observed in Figure 10 by noting the slight decrease in yield under static conditions as available weight increases while the initial contact area remains relatively fixed. Whereas a moderate yield increase is noted under dynamic conditions as the prompt interface area is instantaneously increased prior to initial reaction. These propellants also exhibit multiple pressure pulses (as opposed to a single reaction) as separate ignition events occur at various locations throughout the “mixing” domain.

While the static yields remain on the order of the current 5%, the dynamic yields are nearly half (~6%) the current 10% at the same vehicle scale. Although large-scale failure data are limited, a reasonable difference in yield factor was found between the static and dynamic cases. This factor was then applied to the overall results to determine static and dynamic ranges. In addition, significant asymmetry was noted in all hypergolic explosive data and an appropriate factor was applied as described in [2], [3], and Appendix A. This asymmetry can be attributed to the distributed nature of the multiple reactions noted in the data. At lower mass-scale conditions, however, both the static and dynamic yields are on the order of the current 10% used only for dynamic launch pad conditions. Therefore, it is believed that the N₂O₄/A-50 Yield Curve equations proposed here realistically represent the mass/yield function and are appropriate for use as a new standard.

Another observation regarding N₂O₄/A-50 data—and hypergolic combinations in general—is that the yield associated with the DMTs does not reflect consistency with the overall yield equation as they do for the cryogenic (LO₂/LH₂) and hydrocarbon (LO₂/RP-1) combinations (see [2] and [3]). This disparity can be seen in Figure 18, which shows the dynamic yield curves and DMT results for LO₂/LH₂ and LO₂/RP-1 along with the data and N₂O₄/A-50 Yield Curves. The small-scale (< 5 lb) data points are also included.

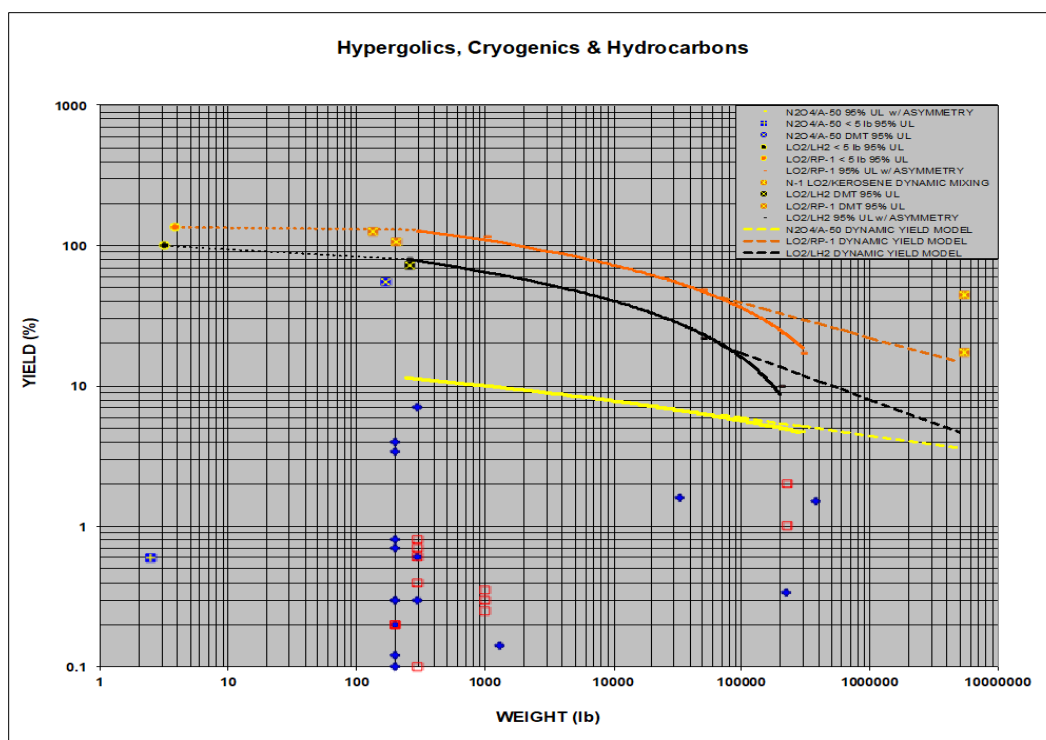


Figure 18. Yield curves, DMT, and < 5 lb data for LO₂/RP-1, LO₂/LH₂, and N₂O₄/A-50.

Figure 19 highlights the differences observed in the cryogenic/hydrocarbon versus the hypergolic explosive data. The DMT observation can be explained by the same reaction phenomenon discussed above regarding the disparity in static and dynamic trends. In the DMT tests, the immediate surface contact areas were varied from low- to high-contact area/lb of propellant. The high-contact area data are plotted here. Variance with yield can be seen in all combinations; however, the increased yield effect due to surface area is most pronounced in the hypergolic reaction. Both the LO₂/RP-1 and LO₂/LH₂ DMT results correspond to the lower weight range of their respective yield curves. This allows a smooth transition from the static test and launch facility yield functions to a fixed maximum value for quantities below 1,000 lbs at other types of facilities (designated as “other PES” in the criteria).

However, in the N₂O₄/A-50 case, this does not occur. A five-fold increase is seen between the lower weights of the yield function and the DMT data. For example, while the yield curve indicates the maximum explosive factor below 1,000 lbs should be on the order of 15%, the DMT data suggest 55% is appropriate. Since it is virtually impossible to create the DMT conditions in any accidental explosion scenario due to the reactive nature of the participants, the DMT results are useful for understanding the hypergolic reaction mechanisms but should not be applied as criteria for any combination. Therefore, in terms of explosive potential, it is proposed that a maximum of 14% TNT should be used for N₂O₄/A-50 combinations below 1,000 lbs.

Another contrary result seen in the N₂O₄/A-50 comparison is the increased yield with mass that is evident with hypergolics under static mixing conditions. This again is a function of the surface area/lb of propellant increasing significantly under static conditions up to an optimum that may occur on the order of 500 lbs total weight at typical mixture ratios. This is because even at small scale, most hypergolic combinations exhibit random multiple reaction events, whereas for the other propellant combinations (hydrocarbon and cryogenic), most cases result in single explosive reactions as propellant mixing is observed in all other propellant combinations of these types at this scale.

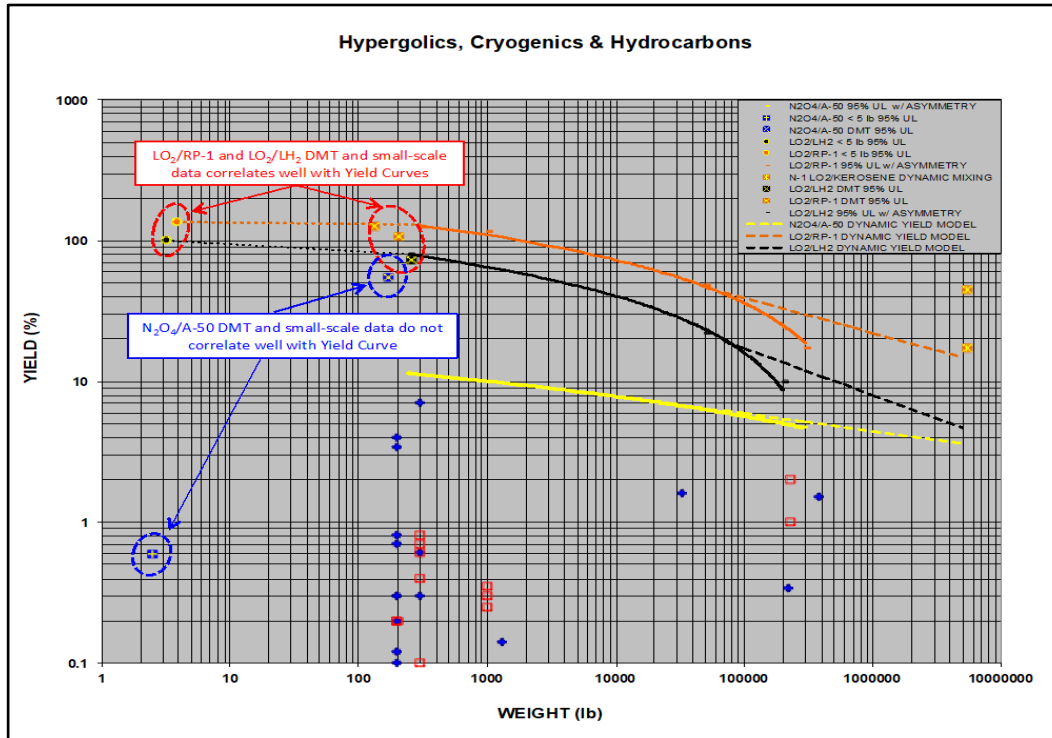


Figure 19. Yield curves, DMT, and < 5 lb data for LO₂/RP-1, LO₂/LH₂, and N₂O₄/A-50 with DMT annotation.

An additional observation can be made from the data shown in Figure 20, where the HVI test results for each combination were added to Figure 18. For consistency, the HVI data included in Figure 20 for all cases was from the confined impact case. It can be clearly seen that the N₂O₄/A-50 hypergolic combination under these HVI conditions shows a dramatic (~175%) increase over the DMT results. This is attributable to the prompt increase in surface area prior to hypergolic reaction. This increase is similar to that of the cryogenic LO₂/LH₂ combination, which increases ~208% over the DMT case under HVI dispersion due to the prompt release of the gaseous mixture prior to vapor phase autoignition. In the case of LO₂/RP-1, however, the HVI yields actually decrease on the order of 36% when compared to DMT results as mixing is in fact reduced. In this case, the reactants are dispersed under HVI conditions, resulting in a lesser contribution from the available propellants. These impact sensitivity results are discussed in Appendix A and in [2] and [3].

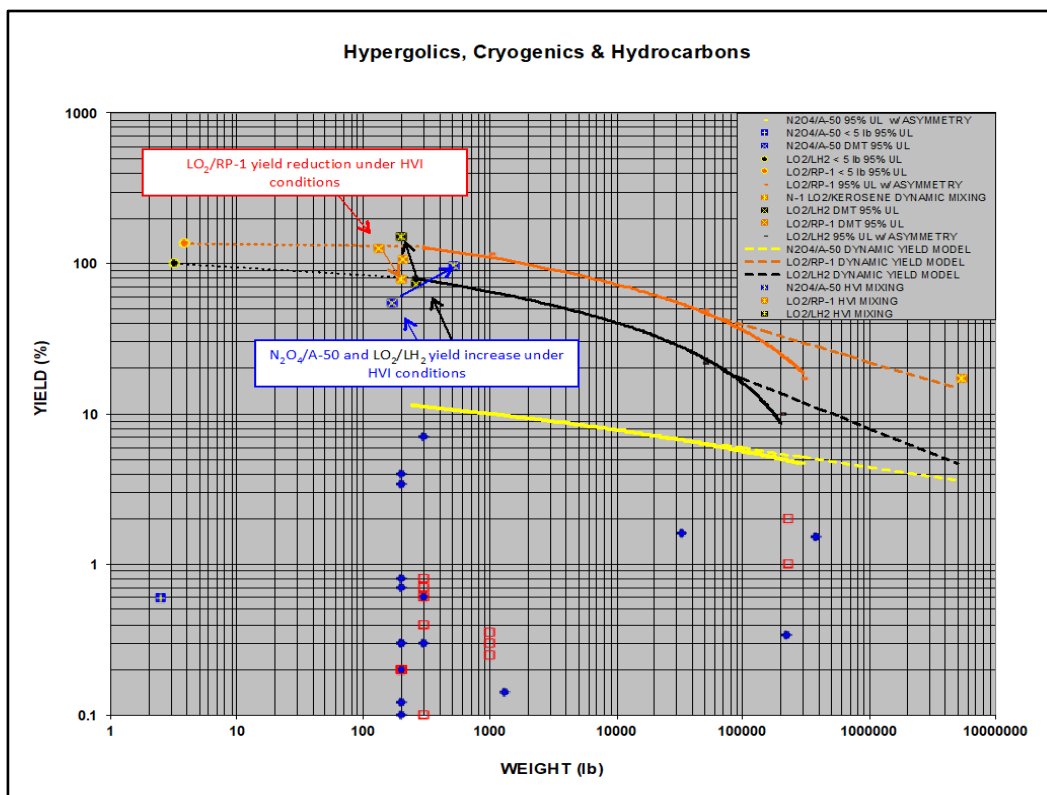


Figure 20. Yield curves, DMT, < 5 lb, and HVI data for LO₂/RP-1, LO₂/LH₂, and N₂O₄/A-50 with HVI annotation.

During Project PYRO, an attempt was made to induce N₂O₄/A-50 mixing by first chilling the propellants using LN₂. This test data are included in Figure 9. Although the test conditions limit the ability to extract much more than comparative conclusions from the results, it is interesting to note that the yields from these tests were on the order of the DMT medium contact area/lb of propellant results.

5.4.2 N₂O₄/N₂H₄ Results

N₂H₄ saw early use as a hypergolic fuel but was later replaced largely by UDMH. Due to limited test data, a common scale assessment was performed for the N₂O₄/N₂H₄ hypergolic combination. Available data are also insufficient to determine any variation between static and dynamic conditions. Hydrazine has been well established as having explosive characteristics in the vapor state [8]. Therefore, the presence of N₂H₄ in a bipropellant combination (including the above N₂O₄/A-50 combination) enhances the explosive characteristics.

The available data indicate that the N₂O₄/N₂H₄ reaction is estimated to be on the order of 25% to 50% more energetic than N₂O₄/A-50 due to the additional hydrazine available in the reaction. Using similarity and the data in Figure 11 and Figure 12, a yield curve was created for N₂O₄/N₂H₄ that resulted in $W_T = 0.30W_P^{7/8}$ (see Figure 21). It is proposed that this value be used for both static and dynamic cases. In terms of explosive potential, however, it is proposed that a maximum of 18% TNT should be used for this combination below 1,000 lbs.

N₂H₄ remains widely used as a monopropellant but is also used in select spacecraft as an N₂O₄/N₂H₄ bipropellant.

5.4.3 N₂O₄/MMH Results

MMH was developed in the early 1950s at the same time as UDMH. Although MMH had higher performance than UDMH, MMH became less widely used due to production and stability questions. Due to limited test data, a common scale assessment was performed for the N₂O₄/MMH hypergolic combination. Although N₂O₄/MMH does not have small-scale comparative data, it was also subjected to DMT testing of similar scale to N₂O₄/A-50. This combination is observed to be of lower yield than N₂O₄/N₂H₄ but slightly greater than N₂O₄/A-50. It is acknowledged that this conclusion is limited by data availability and may be somewhat conservative but not significantly so. Using similarity and the data in Figure 13 and Figure 14, a yield curve was created for N₂O₄/MMH that resulted in $W_T = 0.28 W_P^{7/8}$ (see Figure 21). Similar to N₂O₄/N₂H₄, it is proposed that this value be used for both static and dynamic cases. In terms of explosive potential, however, it is proposed that a maximum of 16% TNT should be used for these combinations below 1,000 lbs.

MMH was used by NASA on the Gemini program and was also used on Apollo and on the Space Shuttle. It is currently used on many spacecraft and has largely replaced UDMH due to its higher performance.

5.4.4 N₂O₄/UDMH and IRFNA/UDMH Results

UDMH was developed in the early 1950s as one of the hydrazine derivatives (MMH, symmetrical dimethyl hydrazine (SDMH), and UDMH). SDMH was discarded, but by 1955, UDMH became the hypergolic fuel of choice throughout the space industry. It was replaced by A-50 or MMH in the U.S. Nitric acid in the form of RFNA, stable fuming nitric acid (SFNA), IRFNA, WFNA, inhibited white fuming nitric acid (IWFNA), etc. was the hypergolic oxidizer of choice in the early missile and launch vehicle programs of the 1940s and 1950s. Nitric acid was replaced by N₂O₄ in the 1960s. Due to limited test data, a common scale assessment was performed for the N₂O₄/UDMH hypergolic combination; however, no explosive data could be found for IRFNA/UDMH and there is one vehicle failure using N₂O₄/UDMH. Although both combinations are observed to be of lower yield than N₂O₄/N₂H₄ and N₂O₄/A-50, it is acknowledged that this conclusion is limited by data availability. Using similarity and the data in Figure 13 and Figure 14, a yield curve was created for N₂O₄/UDMH that resulted in $W_T = 0.19 W_P^{7/8}$ (see Figure 21). Similar to N₂O₄/MMH, it is proposed that this value be used for both static and dynamic cases. In terms of explosive potential, however, it is proposed that a maximum of 12% TNT should be used for these combinations below 1,000 lbs.

In the case of IRFNA/UDMH, no test or failure data could be found, although the current yield criteria specifies 10% TNT equivalence for both static (test facility) and dynamic (launch facility) conditions in [1], Table V5.E4.T5. However, from a purely reaction chemistry consideration, a difference can be calculated between the yields of N₂O₄/UDMH and IRFNA/UDMH. Using relative specific energies, a yield curve was created for IRFNA/UDMH that resulted in $W_T = 0.26 W_P^{7/8}$ (see Figure 21). Similar to N₂O₄/UDMH, it is proposed that this value be used for both static and dynamic cases. In terms of explosive potential, however, it is proposed that a maximum of 15% TNT should be used for these combinations below 1,000 lbs.

IRFNA/UDMH found continued in use on the Delta and Agena upper stages into the 1970s but is no longer in operational use. There is currently no operational use of N₂O₄/UDMH in the U.S., but future use is possible. It remains in use in many non-U.S. hypergolic systems.

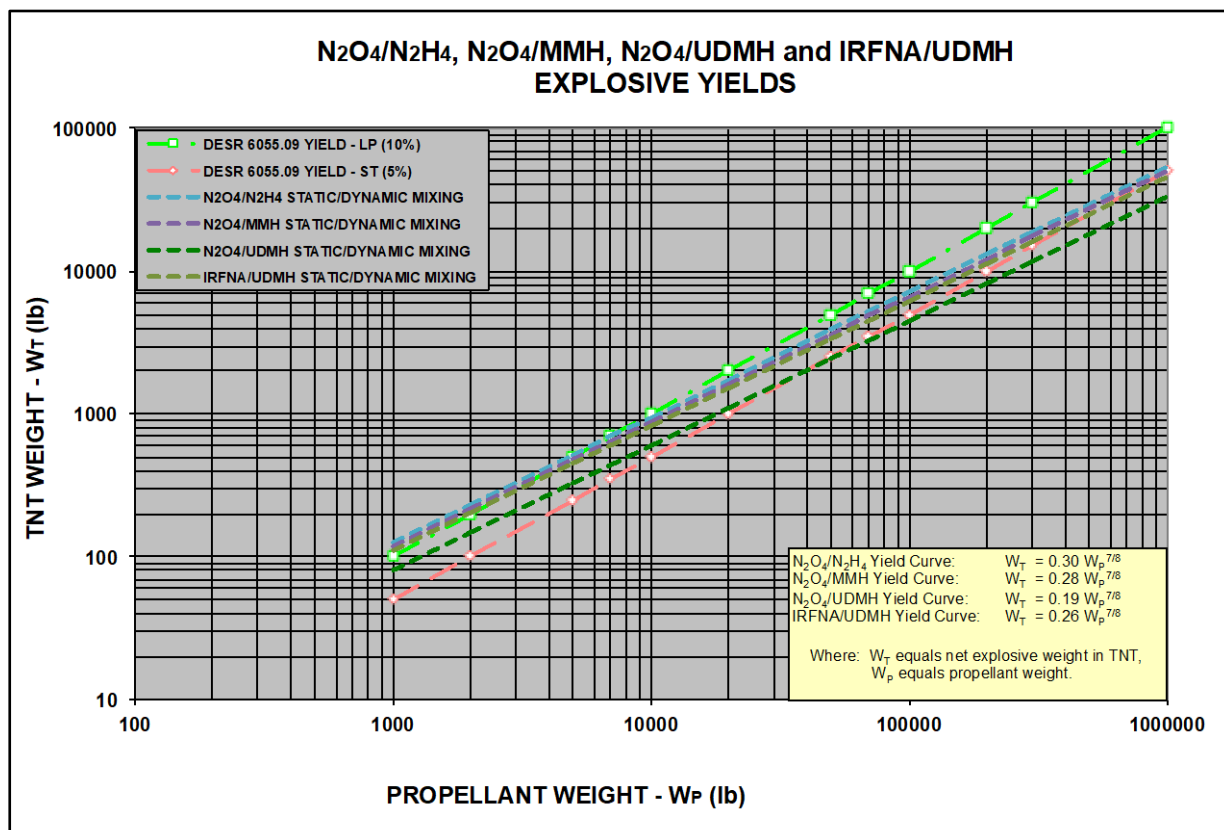


Figure 21. Combined $\text{N}_2\text{O}_4/\text{N}_2\text{H}_4$, $\text{N}_2\text{O}_4/\text{MMH}$, $\text{N}_2\text{O}_4/\text{UDMH}$, and IRFNA/UDMH proposed explosive yield curves and current DESR 6055.09 [1] values.

5.4.5 Pentaborane (PB) Hypergolic Combination Results

During the late 1950s and 1960s, pentaborane (B_5H_9) was investigated as a potential rocket propellant in both the U.S. and the Soviet Union. Pentaborane (PB) is a high-energy, pyrophoric compound that was extensively investigated during development of the missile programs. Applications included both monopropellant and bipropellant jet and rocket engine use. Its highly reactive nature resulted in hypergolic reactions with any oxidizer and high specific impulse performance. Due to its toxicity and acute reactivity, including tendency to react in air, its applicability research was curtailed; however, explosive data were obtained during testing in various combinations and it is appropriate that this information be included here.

The hypergolic bipropellant testing involved combinations of PB with N_2H_4 , N_2O_4 , and CTF. Most bipropellant testing was small scale (< 5 lb), although one spill test using 275 lbs of PB and 100 lbs of N_2H_4 was attempted. The PB hypergolic reactions differed significantly from the typical N_2O_4 /hydrazine-based combinations. In the case of PB and either N_2H_4 or N_2O_4 , rather than multiple distributed reactions, the PB combinations exhibited single explosive reactions with reasonable overpressures. Although the PB/ N_2O_4 tests were not instrumented, the observations indicated that this combination resulted in a greater yield than that of N_2H_4 /PB. Using similarity and the data in Figure 15 and Figure 16, yield curves were created for both PB/ N_2H_4 and N_2O_4 /PB that resulted in $W_T = 0.65 W_P^{7/8}$ for PB/ N_2H_4 and $W_T = 1.30 W_P^{7/8}$ for N_2O_4 /PB (see Figure 22). Similar to $\text{N}_2\text{O}_4/\text{N}_2\text{H}_4$, it is proposed that this value be used for both static and dynamic cases. In terms of explosive potential, however, it is proposed that a maximum of 40% TNT should be used for PB/ N_2H_4 and 75% for N_2O_4 /PB combinations below 1,000 lbs.

Although tested extensively, pentaborane was never used in an operational system. In fact, PB is no longer available; however, due to its past interest as a hypergolic propellant, its data should be retained for the historical record.

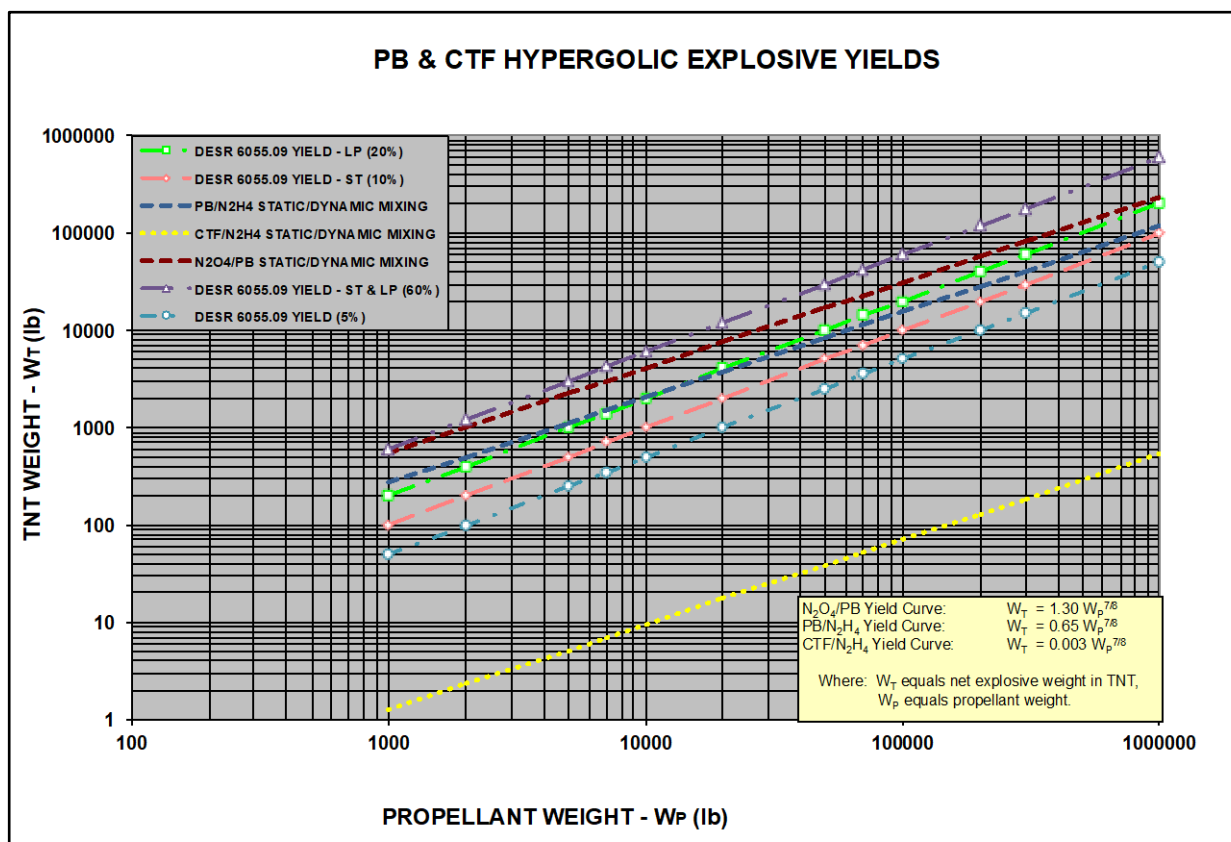


Figure 22. Combined N_2O_4/PB , PB/N_2H_4 , and CTF/N_2H_4 proposed explosive yield curves and current DESR 6055.09 values.

5.4.6 Chlorine Trifluoride/Pentafluoride (CTF/CPF) Hypergolic Combination Results

CTF (ClF_3) is an extremely reactive compound that was pursued as a hypergolic oxidizer for missile systems in the late 1950s. Initially identified in Germany in 1930, use as a rocket propellant began in the late 1940s and early 1950s [75]. Although not adopted in wide use it has been applied to smaller systems and remains an option for packaged systems today.

CTF is a halogenated compound whose hypergolic reactions were found to be the most reactive of any tested but produced the lowest explosive results. This is due to the prompt instantaneous burning encountered when combined, as CTF is reactive with nearly everything but can be stored. CTF's reactivity is surpassed only by elemental fluorine itself. Although toxic and difficult to handle, CTF propellant research continued well into the 1960s.

The CTF hypergolic bipropellant testing involved combinations of ClF_3 with N_2H_4 , and B_5H_9 . Most bipropellant testing was small scale (< 5 lb), although one spill test using 500 lb of ClF_3 and 500 lb of N_2H_4 was performed. The CTF hypergolic reactions differed significantly from the typical N_2O_4 /hydrazine-based combinations. In the case of CTF and either N_2H_4 or PB, rather than multiple distributed reactions, the CTF combinations exhibited prompt burning reactions with minimal

overpressures. Contrary to expectations, the data indicated that the CTF/N₂H₄ combination resulted in a slightly greater yield than that of CTF/PB. Using similarity and the data in Figure 15 and Figure 16, a common yield curve was created for CTF/N₂H₄ that resulted in $W_T = 0.003 W_P^{7/8}$ (see Figure 22). Similar to N₂O₄/N₂H₄, it is proposed that this value be used for both static and dynamic cases. In terms of explosive potential, however, it is proposed that a maximum of 1% TNT could be used for CTF/N₂H₄ below 1,000 lb. An alternative approach could use the individual commodity criteria for CTF and hydrazine, respectively. CTF continues to be used for various purposes and considering past applications of CTF/N₂H₄ as a hypergolic propellant in missile systems, this data should be retained, as future use is possible.

Chlorine pentafluoride (ClF₅) was discovered by accident in the early 1960s. It was originally identified as “Compound A”: one of two unidentified compounds encountered during chemical experiments. Later identified as ClF₅, it retained the Compound A name for many years as a classification measure. Once identified, however, its potential as a hypergolic oxidizer was obvious and production research continued. Although its hypergolic reaction and other attributes are similar to that of ClF₃, it results in approximately 20 sec I_{sp} improvement in engine performance [75]. Therefore, although no explosive test data have been found involving CPF, its reaction physics appear to duplicate that of CTF, meaning the CTF/N₂H₄ results noted above likely apply to CPF/N₂H₄ as well.

6. Findings and Recommendations

The findings and recommendations discussed in this section encompass the results of both the prior analyses along with the specific results of this latest hypergolic propellant assessment.

6.1 Findings

- Although explosions produced by liquid propellants are significantly different from TNT, the explosive yield in the far-field approximates that of TNT (see Figure 27)
 - Therefore, TNT equivalence is an acceptable criterion for test stand and launch pad siting
- Hypergolic liquid propellant yields are less susceptible to the influence of mixing conditions
- Liquid propellant combination sensitivity to physical environment varies
 - Hypergolic propellants are much different due to their reaction mechanism
- All liquid propellant percent yields decrease as mass increases
 - Therefore, yield curves rather than constant percentage of TNT equivalence is a more appropriate criterion
- Hypergolic reactions inherently display yield asymmetry
- Limited or biased test conditions can result in significant under- or over-prediction of explosive yields under vehicle failure conditions
- Hypergolic static versus dynamic yields differ by a factor of 1.25
- Hypergolic propellant yields are governed by a spontaneous surface area reaction mechanism
- Hypergolic propellants inherently do not represent a significant explosive hazard
 - Surface area generation and contact governs net explosive yield
 - However, this phenomenon should not be generalized for all combinations
 - The presence of N_2H_4 in any combination enhances the explosive potential due to its vapor phase reaction
- Liquid propellant combinations tested to date do not act like HD 1.1 explosives
 - Only mixed quantities explode as rapid deflagration
 - Far-field effects are due to significant afterburning
 - Near-field effects analysis requires propellant-specific explosive data
 - Pressure fields do not emulate TNT

- Reaction mass detonation not observed
- Interface generation time determines participation
- Explosive hazards must be validated by comprehensive (distributed, static, and dynamic) test programs
 - Dynamic modes include:
 - Fallback, toppling, impact, donor
 - Static modes include:
 - Tank rupture, inter-tank rupture, line leakage, fire
- Explosive yields of launch vehicles are affected by their configuration and accident sequence
 - For large vehicle quantities, mixing time prior to ignition is the primary contributor to explosive yield

6.2 Recommendations

As a result of this assessment, several recommendations and selected options are included regarding the explosive yield values for the hypergolic combinations.

- Recommend replacing the explosive criteria in [1], Table V5.E4.T5 for each hypergolic bipropellant combination as noted
 - Combinations include $\text{N}_2\text{O}_4/\text{A-50}$, $\text{N}_2\text{O}_4/\text{N}_2\text{H}_4$, $\text{N}_2\text{O}_4/\text{MMH}$, $\text{N}_2\text{O}_4/\text{UDMH}$, and IRFNA/UDMH
- Recommend retaining explosive data as tentative criteria options for PB and CTF/CPF combinations in a database in DESR 6055.09

6.2.1 Recommendation for $\text{N}_2\text{O}_4/\text{A-50}$

Launch facility:	$W_T = 0.25 W_P^{7/8}$ for all $W_P \geq W_{Pmin}$
Test or processing facility:	$W_T = 0.20 W_P^{7/8}$ for all $W_P \geq W_{Pmin}$
Other PES:	$W_T = 14\% W_P$

6.2.2 Recommendation for $\text{N}_2\text{O}_4/\text{N}_2\text{H}_4$

Launch facility:	$W_T = 0.30 W_P^{7/8}$ for all $W_P \geq W_{Pmin}$
Test or processing facility:	$W_T = 0.30 W_P^{7/8}$ for all $W_P \geq W_{Pmin}$
Other PES:	$W_T = 18\% W_P$

6.2.3 Recommendation for N₂O₄/MMH

Launch facility:	$W_T = 0.28 W_P^{7/8}$ for all $W_P \geq W_{Pmin}$
Test or processing facility:	$W_T = 0.28 W_P^{7/8}$ for all $W_P \geq W_{Pmin}$
Other PES:	$W_T = 16\% W_P$

6.2.4 Recommendation for N₂O₄/UDMH

Launch facility:	$W_T = 0.19 W_P^{7/8}$ for all $W_P \geq W_{Pmin}$
Test or processing facility:	$W_T = 0.19 W_P^{7/8}$ for all $W_P \geq W_{Pmin}$
Other PES:	$W_T = 12\% W_P$

6.2.5 Recommendation for IRFNA/UDMH

Launch facility:	$W_T = 0.26 W_P^{7/8}$ for all $W_P \geq W_{Pmin}$
Test or processing facility:	$W_T = 0.26 W_P^{7/8}$ for all $W_P \geq W_{Pmin}$
Other PES:	$W_T = 15\% W_P$

6.2.6 Option for PB/N₂H₄

Launch facility:	$W_T = 0.65 W_P^{7/8}$ for all $W_P \geq W_{Pmin}$
Test or processing facility:	$W_T = 0.65 W_P^{7/8}$ for all $W_P \geq W_{Pmin}$
Other PES:	$W_T = 40\% W_P$

6.2.7 Option for N₂O₄/PB

Launch facility:	$W_T = 1.30 W_P^{7/8}$ for all $W_P \geq W_{Pmin}$
Test or processing facility:	$W_T = 1.30 W_P^{7/8}$ for all $W_P \geq W_{Pmin}$
Other PES:	$W_T = 75\% W_P$

6.2.8 Option for CTF/N₂H₄ and CPF/N₂H₄

Launch facility:	$W_T = 0.003 W_P^{7/8}$ for all $W_P \geq W_{Pmin}$
Test or processing facility:	$W_T = 0.003 W_P^{7/8}$ for all $W_P \geq W_{Pmin}$
Other PES:	$W_T = 1\% W_P$

or use individual commodity siting criteria in [1], Table V5.E4.T3.

Where:

W_T = net explosive weight in lb of TNT

W_P = propellant weight in lb as defined in [1], V5.E4.5.6.1, and V5.E4.5.6.2

W_{Pmin} = 1,000 lb is the minimum value applicable to the yield curves

MON can be substituted for N₂O₄

7. Acronyms and Abbreviations

A-50	Aerozine-50
BoM	Bureau of Mines
CBGS	confined-by-ground surface
CBM	confined-by-missile
cc	cubic centimeter
CPF	chlorine pentafluoride
CTF	chlorine trifluoride
DDESB	DOD Explosive Safety Board
DESR	Defense Explosives Safety Regulation 6055.09
DMT	distributed mixing test
DoD	Department of Defense
DoI	Department of Interior
EEW	equivalent explosive weight
ELWG	Energetic Liquids Working Group
ft	feet
g	gram(s)
HC	hydrocarbon
HD	hazard class/division
HOVI	hydrogen/oxygen vertical impact
HVI	high-velocity impact
IBD	inhabited building distance
IRFNA	inhibited red fuming nitric acid
I_{sp}	specific impulse
IWFNA	inhibited white fuming nitric acid
lb	pound(s)
L/D	length/diameter
LP	launch pad
LPWG	Liquid Propellant Working Group
LSHOE	large-scale hydrogen/oxygen explosion
MAF	mixed amine fuel
MCE	maximum credible event
ml	milliliter
MMH	monomethylhydrazine
MON	mixed oxides of nitrogen
msec	millisecond(s)
MSFC	Marshall Space Flight Center
NASA	National Aeronautics and Space Administration

NEW	net explosive weight
PB	pentaborane
PES	potential explosive site
PRC	Propellant Reaction Characterization
PTRD	public transportation route distance
RCS	reaction control system
RFNA	red fuming nitric acid
SDMH	symmetrical dimethyl hydrazine
sec	second(s)
SFNA	stable fuming nitric acid
ST	static test (stand)
TBS	to be supplied
TNT	trinitrotoluene
UDMH	unsymmetrical dimethyl hydrazine
UoF	University of Florida
U.S.	United States
W_T	TNT weight
WFNA	white fuming nitric acid
W_p	propellant weight
WSTF	White Sands Test Facility

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Appendix A. Methods and Observations

A.1 N₂O₄/A-50 Explosive Yield Prediction Methods

Few prediction methods have been developed to estimate the yield for hypergolic bipropellants. These methods are:

1. Farber/UoF (1965-1973) - Mixing/Yield Model and Critical Mass Method
2. URS Corp (1968) - Model Based on PYRO Test Data

Prediction methods were compared to 95% upper-limit values from the above data assessment and are shown in Figure 23. These prediction methods give dissimilar results although Farber appears to be a blend of the three PYRO predictions that are independent of weight. In comparison to the 95% upper-limit curves, our N₂O₄/A-50 data assessment is in good agreement with the predictions of PYRO around 300,000 lb.

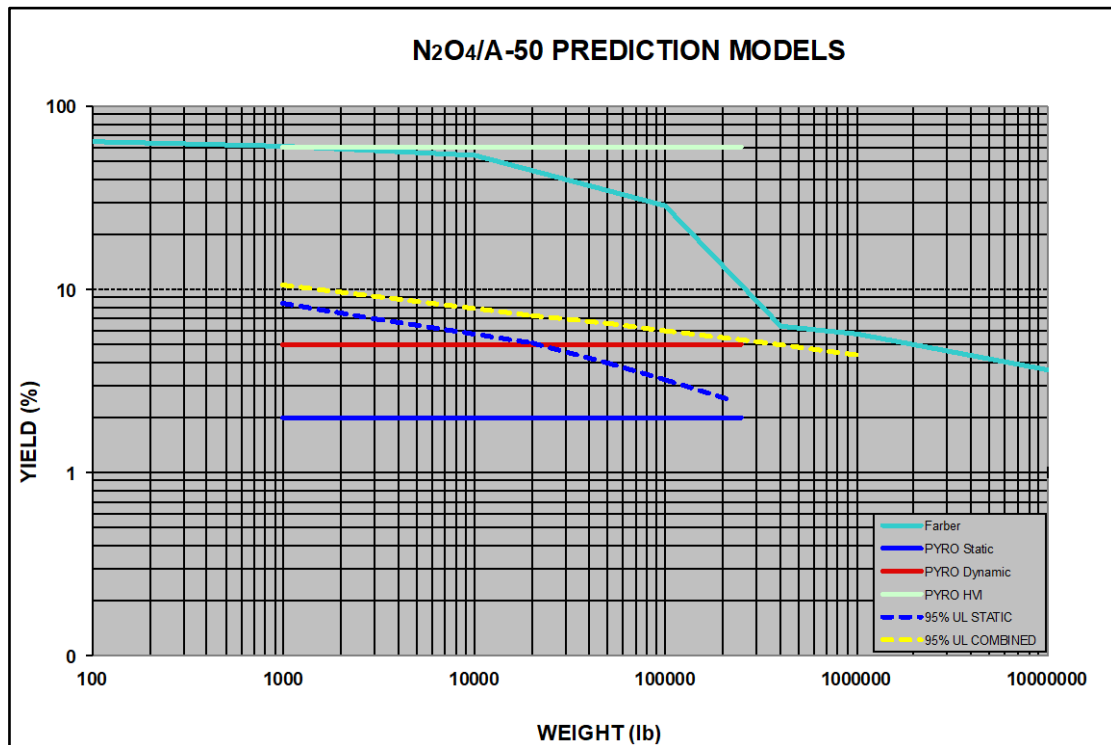


Figure 23. Comparison of N₂O₄/A-50 explosive prediction methods.

Figure 24 includes the above prediction methods, our proposed yield curves, the DMT and HVI data, the DESR 6055.09 criteria, and the explosive yield estimate from the Long March CZ-3B failure described in [6], Addendum 1. Figure 24 shows consistency between the Long March failure and the corresponding HVI/DMT data. The HVI and DMT results are not incorporated in our proposed N₂O₄/A-50 Yield Curves, as this failure mode does not apply to the DESR criteria. However, our proposed N₂O₄/A-50 static and dynamic yield curves approximate the upper criteria (10%) at the lower weights and the lower criteria (5%) at higher weights and are consistent with the shape of the HVI plot.

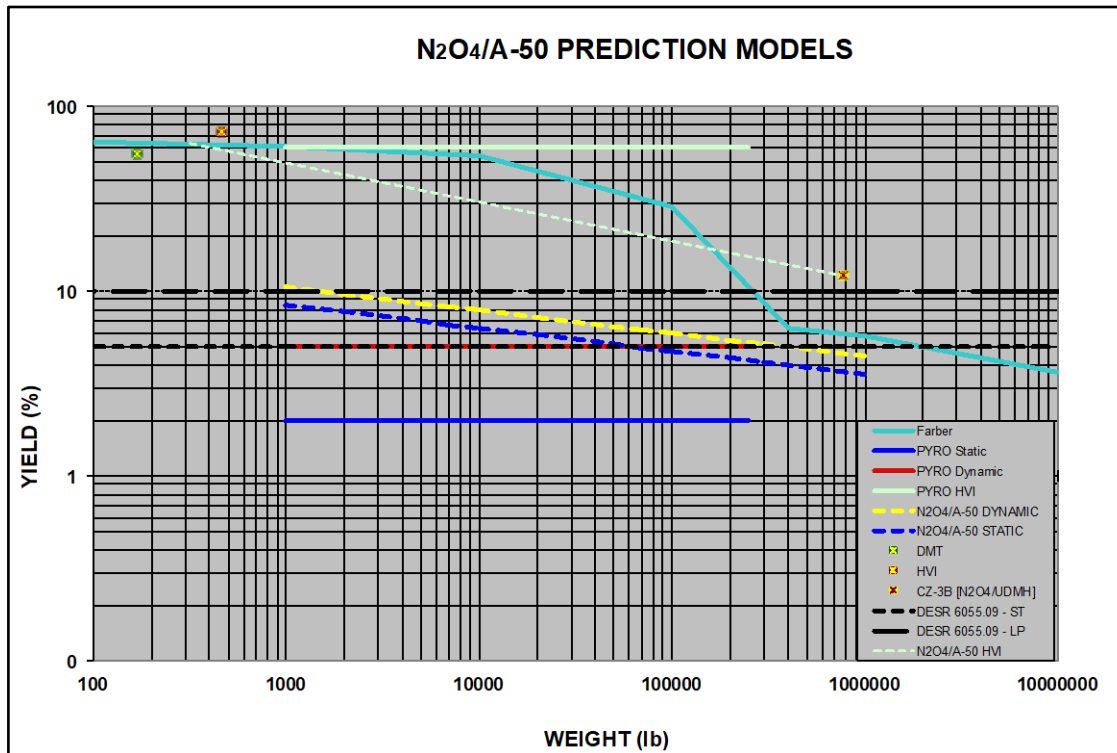


Figure 24. Comparison of N₂O₄/A-50 explosive prediction methods with CZ-3B failure.

A.2 Blast Asymmetry of Hypergolic Propellants

Liquid propellant explosions are often asymmetric and all vehicle failures that have been studied exhibited some degree of asymmetry as the explosive pressure fields exhibit a hemi-ellipsoidal rather than hemispherical form. Review of the test and failure data indicates that this is more prevalent in dynamic mixing modes. This is likely due to a variety of conditions related to launch vehicles such as failure dynamics, rupture and spill mechanics, vehicle orientation, and propellant tank configuration, which are all probable contributing factors. This means that using average yield data (as is done by most experimenters and analysts) underestimates the hazard potential for a given explosion direction, however, using only maximum values risks basing the safety criteria on spurious data. In addition, it was found that the LO₂/LH₂ reactions exhibited more severe asymmetry in comparison to LO₂/RP-1 due to the inherent differences in the manner in which the propellants are released and mixed.

In the case of these hypergolic mixtures a similar increase in asymmetry was noted due to the lack of a consistent geometry of the reacting products. Therefore, for this assessment, all large-scale ($\geq 1,000$ lb) test and failure cases were assessed for asymmetry. For LO₂/RP-1, the ratio of maximum/average yield was found to range on average from 1.1 to 1.26 where the lowest values correspond to pre-ignition static failure events, while the LO₂/LH₂ reactions exhibited as high as a 1.8 factor. Therefore, it was concluded that the higher asymmetry factor should be applied to the results of the hypergolic N₂O₄/A-50 combination data assessment in deriving the final recommended yield values. These factors were applied to the 95% upper-limit curves (see Figure 25) and are inherent in the yield curves of all hypergolic combinations based on similarity.

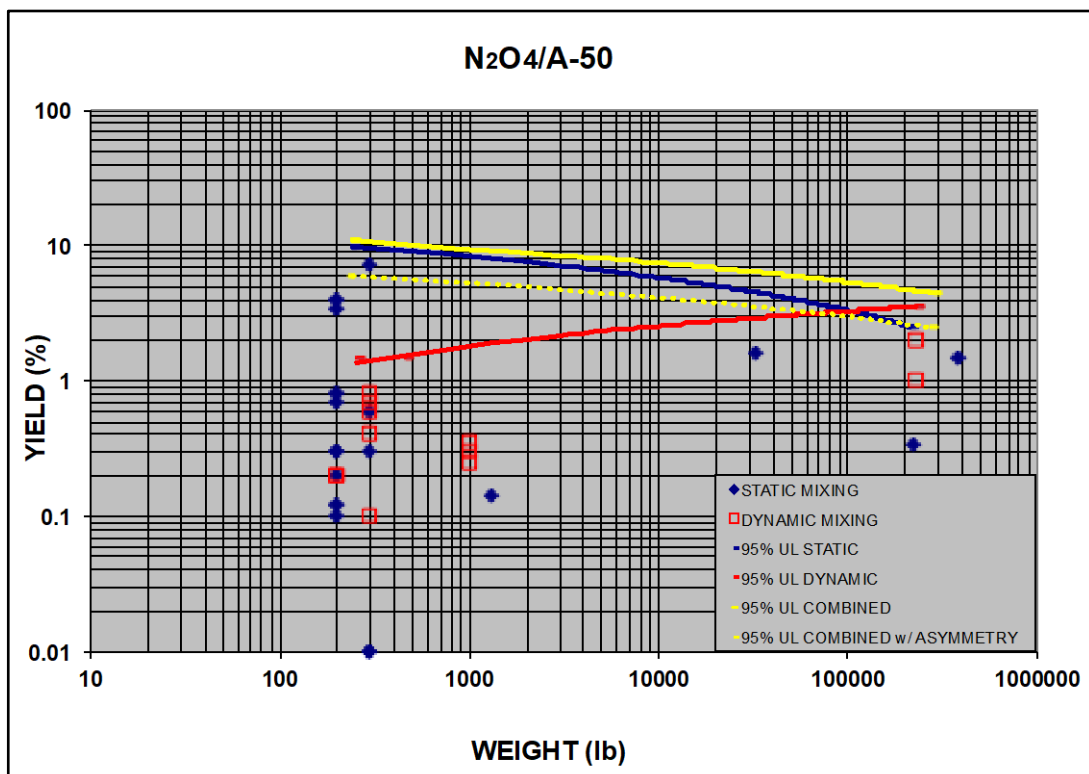


Figure 25. Effect of asymmetry factors on yield estimate.

A.3 Impact Sensitivity of Hypergolic Propellants

This assessment found a factor of 25% difference in $N_2O_4/A-50$ yields between static and dynamic (≤ 150 ft/sec) conditions. This difference is minimal when compared to the four-times difference of $LO_2/RP-1$. The hypergolic large-scale test and failure data are also very limited compared to the hydrocarbon and cryogenic database. However, a significant influence on yield from high-velocity impact is clearly evident in the data.

This can be readily explained by the inherent nature of the various hypergolic bipropellant combinations. The hypergolic propellants in fact do not mix, as prompt reaction occurs at the interface. As discussed above, the $N_2O_4/A-50$ explosive reaction is a function of the combination of liquid/liquid and vapor droplet products that react spontaneously when they come together. When released separately or at high velocity, larger surface areas and hence reactions can occur (see Figure 26).

The PYRO and Rocketdyne CBGS tests demonstrated that low kinetic energy imparted to the mixing process does not significantly promote increased yield and, in fact, often retards it due to the minimal contact area needed to initiate the reaction sequence. This sequence then results in multiple distributed reactions as the surface contact expands and disperses. This is an inherent probability with any hypergolic combination since the reaction tendency is so pronounced. However, there are optimum conditions of both contact surface generation time and confinement that influence the final reaction yield under high-kinetic-energy conditions.

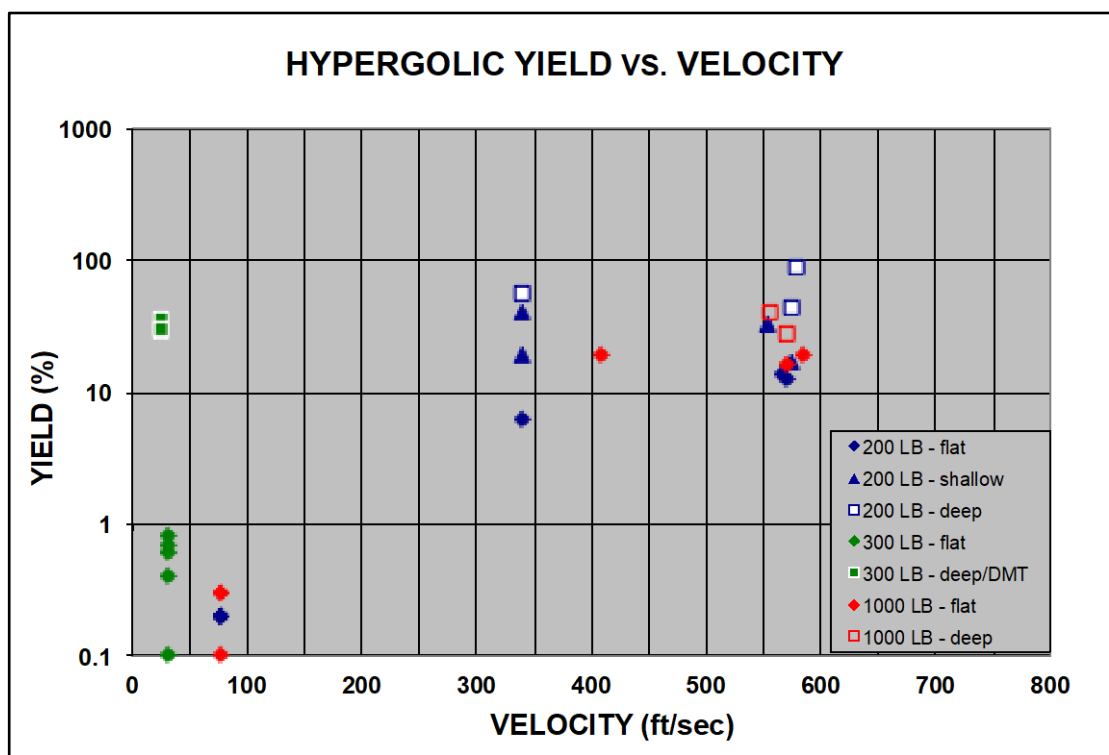


Figure 26. Effect of impact velocity on hypergolic yield.

A.4 Past Hypergolic Propellant Combinations

There have been literally thousands of hypergolic propellant combinations tested in the laboratories during the 1940s and 1950s beyond the group contained in this report, but explosive test data have not been found for any of them, although detonations were observed in many cases. However, in addition to the hypergolic combinations discussed above ($\text{N}_2\text{O}_4/\text{A-50}$, $\text{N}_2\text{O}_4/\text{N}_2\text{H}_4$, $\text{N}_2\text{O}_4/\text{MMH}$, $\text{N}_2\text{O}_4/\text{UDMH}$, IRFNA/UDMH , $\text{B}_5\text{H}_9/\text{N}_2\text{H}_4$, $\text{N}_2\text{O}_4/\text{B}_5\text{H}_9$, $\text{ClF}_3/\text{N}_2\text{H}_4$ and $\text{ClF}_5/\text{N}_2\text{H}_4$), other combinations have been used operationally in the past in the U.S. These include RFNA/Aniline on the Aerobee, Corporal, WAC Corporal, and Bumper; SFNA/Aniline on Corporal II; IWFNA/UDMH on Vanguard and Thor Able; and IRFNA/JP-X on the SNORT rocket. Although no explosive test data have yet been found (pending search for [16] and others), their explosive attributes are likely no greater than the combinations studied in this report.

A.5 TNT Equivalence of Liquid Propellants

It has been well established by many analysts—including the authors—that energetic liquids, particularly liquid propellants, do not replicate TNT explosions. For example:

- Near-field overpressures are at least an order of magnitude less than TNT
- Liquid propellant TNT equivalence increases with distance
- Liquid propellant TNT equivalence decreases with increasing propellant weight
- Near-field liquid propellant impulse percent yield is greater than pressure yield
- Liquid propellant impulse yield decreases with distance

However, it has also been shown that these liquid propellant blast environments do approach TNT in the far-field. This is generally attributed to the propensity of the reactants to continue to supply energy to a

blast wave for a much longer time than that which influences the initial shock interaction with air. Figure 27, taken from J. Taylor analysis of LSHOE LO₂/LH₂ distributed mixing tests (DMT), demonstrates this phenomenon [74]. Although analysts often take issue with the equivalence approach, this is primarily related to the near-field pressure field interactions with other components within the blast environment. However, relative to the use of this method in DESR 6055.09, facility siting using this method is surprisingly appropriate. The difference between the overpressure range of interest for inhabited building (IBD) and public transportation route (PTRD) siting using TNT and liquid propellants is seen to be negligible.

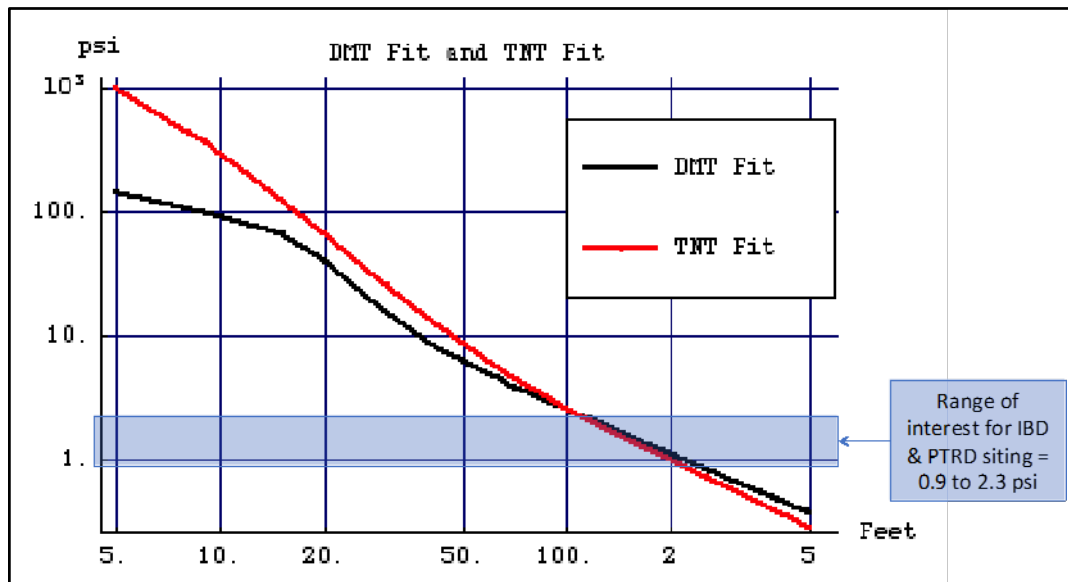


Figure 27. TNT vs. liquid propellant explosive yield [74].

Explosive Equivalence of Hypergolic Propellants

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