

DEGRADABLE AND ENVIRONMENT-RESPONSIVE EXPLOSIVES

by

Benjamin Y. S. Lee
Energetic Materials Branch
Airframe, Ordnance, and Propulsion Division

and

Russell Reed, Jr.
Engineering Sciences Branch
Research and Technology Division

APRIL 1996

NAVAL AIR WARFARE CENTER WEAPONS DIVISION
CHINA LAKE, CA 93555-6001

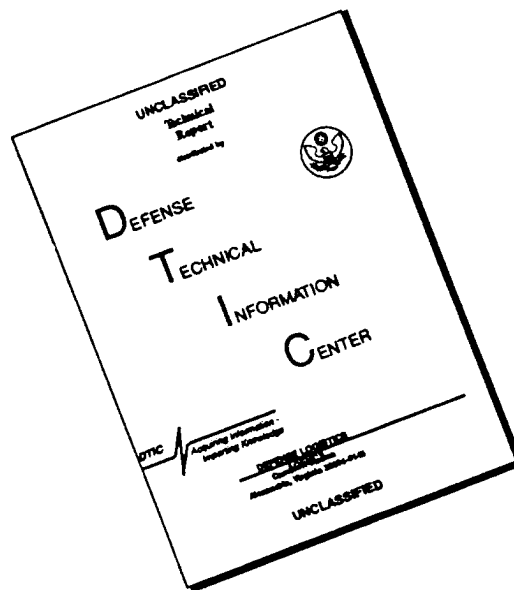


Approved for public release; distribution unlimited.

DTIC QUALITY INSPECTED 1

19960530 025

DISCLAIMER NOTICE



THIS DOCUMENT IS BEST QUALITY AVAILABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF PAGES WHICH DO NOT REPRODUCE LEGIBLY.

Naval Air Warfare Center Weapons Division

FOREWORD

This report describes the latest results of an exploratory explosive development effort based on a degradable and hydrolyzable binder system. The work described was conducted between October 1993 and December 1995. The effort was supported in part by in-house funding and by the Office of Naval Research under Program Element 0602234N; the technology principal was Steven L. Collignon, Naval Surface Warfare Center (Code 90H).

This report was reviewed for technical accuracy by Al Lopez.

Approved by
D. GOSS, *Head*
Airframe, Ordnance,
and Propulsion Division
30 April 1996

Under authority of
D. B. McKINNEY
RAdm., U.S. Navy
Commander

Released for publication by
S. HAALAND
Director for Research and Engineering

NAWCWPNS Technical Publication 8282

Published by Scientific and Technical Documentation
Collation Cover, 15 leaves
First printing 40 copies

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding the burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE	3. REPORT TYPE AND DATES COVERED	
		April 1996	Summary	
4. TITLE AND SUBTITLE			5. FUNDING NUMBERS	
DEGRADABLE AND ENVIRONMENT-RESPONSIVE EXPLOSIVES			Program Element 0602234N	
6. AUTHOR(S)				
B. Y. S. Lee and R. Reed, Jr.				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)			8. PERFORMING ORGANIZATION REPORT NUMBER	
Naval Air Warfare Center Weapons Division 1 Administration Circle China Lake, CA 93555-6001			NAWCWPNS TP 8282	
8. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
Office of Naval Research 800 North Quincy St. Arlington, VA 22217-5660				
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT			12b. DISTRIBUTION CODE	
Approved for public release; distribution unlimited.				
13. ABSTRACT (Maximum 200 words)				
<p>This report describes the latest results of an exploratory explosive development effort based on a degradable and hydrolyzable binder system. The work described was conducted between October 1993 and December 1995.</p> <p>The feasibility of cast energetic compositions as acceptable main charge explosives has been demonstrated. This investigation established that an easily degradable composite polyurethane/RDX system can contribute significantly to our nation's environmental pollution abatement efforts. The relatively high cost explosive solids can be separated and reused, and the harmless binder liquid by-products can be disposed of in a non-hazardous fashion. This unique feature fits well in the current military efforts directed toward safe ordnance disposal and demilitarization. Similar efforts would be feasible in the realm of solid propellant formulations and development.</p>				
14. SUBJECT TERMS			15. NUMBER OF PAGES	
Nitramines, RDX, HMX, Binder Hydrolysis, Pollution Abatement, Ordnance Demilitarization			28	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT	
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	SAR	

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

[Empty rectangular box for security classification data]

CONTENTS

Introduction and Background	3
Technical Objectives	3
Initial Start-up	4
Increased Solids Loading and Baseline Explosives Development	8
RDX Recovery and Recycling	9
DBX-12 Explosive Property Tests.....	11
The New Degradable Binder Replacement.....	12
Binder Degradation Mechanism	13
Explosives Product Development	15
Conclusions	16
References	17
Nomenclature	18

Appendix: Explosive Performance Test Results for DBX-12 and DBX-13	19
--	----

ACKNOWLEDGMENTS

The authors would like to thank the following people for their fine support and technical contributions to this effort: Gwen Allbright, Nancy Carey, Anita Paiz, and Dan Wooldridge of the Energetic Materials Characterization Section; and Henry John of the Applied Mechanics Research Section; grateful thanks also to Antonella Thompson for her untiring support and efforts in editing and assembling this final report.

INTRODUCTION AND BACKGROUND

Almost two decades ago, an effort to develop a practical plastic-bonded explosive (PBX) that could be easily demilitarized resulted in a promising system consisting of 82% cyclotrimethylene-trinitramine (RDX) and a readily hydrolyzable polyurethane binder. Bench-top experiments successfully demonstrated the quick disintegration of the binder in a very dilute aqueous ammonia medium. The subsequent recovery of the solids explosive component was also demonstrated. Water alone or a 100% relative humidity environment had little effect on the composition. A safe, rapid demilitarization procedure was also demonstrated in a high-pressure water washout facility.

The finalized RDX explosive composition, PBXC-125, underwent almost all the mandatory safety tests required for Navy interim qualification of main charge explosives. Small- and full-scale cookoff tests were also conducted; these showed mild thermal reactions. However, extensive explosive performance and mechanical testing as well as demonstrations of explosive demilitarization, reclamation, and recycling (final proof-of-concept) were not carried out, as funds were eventually depleted. The results of that earlier program conducted between 1976 and 1981 have been documented (References 1 and 2).

In more recent years, with the passage of additional stringent Environmental Protection Agency (EPA) regulations to govern the open-burn/open-detonation disposal methods of surplus or obsolete munitions, interest in continuing this program was rekindled. To address the issue of ordnance demilitarization, the effort was revitalized during fiscal year 1994, and some funding was provided to continue the study on degradable and environment-responsive explosives.

TECHNICAL OBJECTIVES

The technical objectives of this renewed effort were 1) to further develop and improve upon the main charge explosive formulation, PBXC-125, that had been proven to successfully meet the constraints imposed by pollution abatement and environmental control regulations; 2) to improve its explosive performance potential by increasing its RDX solids loading; and 3) to determine, when feasible, whether other more energetic nitramine explosives could be incorporated with this binder system.

In short, the resulting product of the new effort had to be a degradable and hydrolyzable binder system encompassing all the desirable features demonstrated years ago, in addition to comprehensive continued work on PBXs that are easily degradable, recoverable and recyclable, safe and insensitive, adequate in performance, and low in cost.

This report describes the efforts that went into accomplishing these objectives.

INITIAL START-UP

The two major chemical binder ingredients from the past exploratory explosive development program on pollution abatement were recalled from long-term storage and pressed back into service.

Initial gumstock formulations were prepared using the same ingredients after a 12-year hiatus. Remarkably, the binder combination of the hydroxyl-terminated polyester (Fomrez YA 23-4) with lysine diisocyanate methyl ester (LDIM-100) resulted in good, firm polyurethane cures, as occurred years ago.

Explosive formulations were then begun where they were left off at the end of fiscal year 1981. As a point of reference, formulation PBXC-125, together with its properties, is shown in Table 1.

Now, instead of employing the tetramodal blend of RDX as in PBXC-125, the largest particle size (Class 4) was eliminated, resulting in a trimodal blend. All this was done in an effort to help reduce the shock sensitivity of the explosive composition—the underlying theme for insensitive munitions.

The new formulations were called degradable binder explosives or DBXs. The three DBX formulations are shown in Table 2, with the corresponding safety data.

Generally, the compositions were stable and exhibited no voids, gassing, or swelling under 60°C cure. Curing was completed in three days and yielded flexible compositions that were easily degraded by either dilute aqueous ammonia or hydrochloric acid. This sequence of events occurring at room temperature in 5% dilute aqueous ammonia is shown in Figures 1 through 4, with the RDX settling out within a day following immersion of the explosive.

Nine small-scale cylinders (each 2 inches long and 0.5 inch inside diameter) were cast from the DBX-3 formulation. Following cure, the cylinders were stacked and assembled (three units making up an assembly), and then fired for detonation velocity and detonation pressure measurements. Test results obtained thus far seem to corroborate the values reported earlier for PBXC-125 full-scale detonation velocity. Values of 7.87 to 7.95 mm/ μ s were reported for PBXC-125; average values obtained from these DBX-3 small-scale tests indicated 7.78 mm/ μ s for detonation velocity and 260.24 kbars for detonation pressure, respectively. Higher values are expected with higher RDX solids levels.

TABLE 1. PBXC-125 Formulation and Properties.

Ingredient	Weight %
<u>Binder</u>	
Fomrez YA 23-4	16.56-16.60 ^a
LDIM-100	1.44-1.40
TPB (added)	(0.05)
<u>RDX</u>	
Class 1	6.56
Class 3	14.76
Class 4	38.54
Class 5	<u>22.14</u>
	100.00
<u>Mechanical properties</u>	
Tensile strength, kPa (psi)	552 (80)
Elongation at max. stress, %	3
Elongation at rupture, %	47
Modulus, kPa (psi)	27,187 (3,943)
<u>Hazard properties</u>	
Impact sensitivity, cm	23-26
Friction sensitivity, kN (lb)	4.057 (912)
Electrostatic sensitivity, 0.25 J	10/10 no fire
LSGT, inches	1.847 (at lower density of 1.390 g/cm ³)
Detonation velocity, mm/ μ s	7.87-7.95
<u>Thermal properties</u>	
VTS, ml/g/48 hrs	0.03 (100°C) 0.75 (120°C)
Heat of explosion, cal/g	898
Self-heating (critical temp.)	124°C for a 12-inch-diameter warhead or 118°C for an 18- inch-diameter, 2000-pound bomb (Mk 84)
<u>Physical properties</u>	
Shore A hardness	50-63
Measured density, g/cm ³	1.55-1.60
End-of-mix viscosity (55°C), kPa-s	0.7-1.2

^a NCO/OH equiv. ratio = 1.2.

TABLE 2. Degradable Binder Explosives and Their Safety Data.

	Formulations		
	DBX-1	DBX-2	DBX-3
<u>Binder</u>			
Fomrez YA 23-4	16.51	16.51	16.51
LDIM-100	1.49	1.49	1.49
TPB (added)	(0.05)	(0.05)	(0.04)
<u>RDX</u>			
Class 1	25	25	25
Class 3	35	27	25
Class 5	22	30	32
End-of-mix viscosity, kP (at temperature indicated)	6.0 (59°C)	9.0 (58°C)	13.0 (48°C)
Measured density, g/cm ³	1.617	-	-
<u>Safety hazard properties (@ 50% point)</u>			
Impact sensitivity, cm	32	27	27
Friction sensitivity, lb	708	19/20 NF	10/10 NF
Electrostatic sensitivity, 0.25 J	10/10 NF	10/10 NF	10/10 NF
VTS, ml/g/48 hrs	0.2261 (1) 0.2392 (2)	- -	- -
<u>DTA</u>			
Onset, °C	203	-	-
Peak, °C	238	-	-

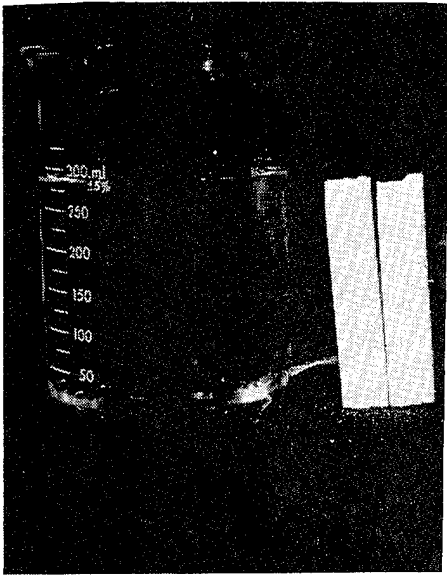


FIGURE 1. Explosive Sample Before Immersion in Dilute Aqueous Ammonia.

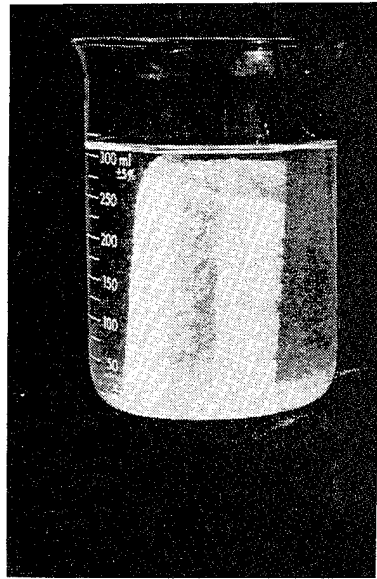


FIGURE 2. Explosive Sample After a Few Minutes Immersion.

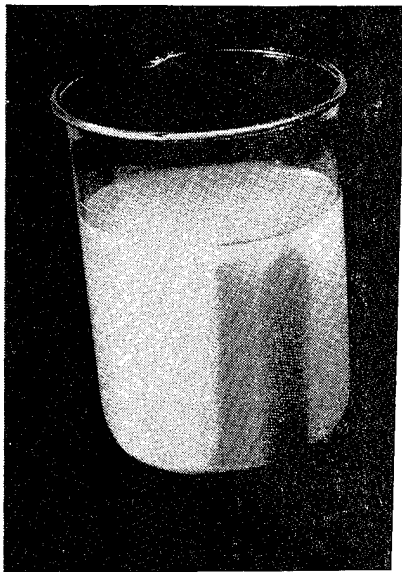


FIGURE 3. Explosive Sample After One Hour Immersion.

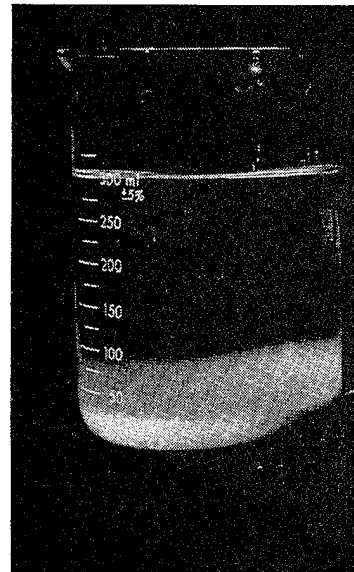


FIGURE 4. Explosive Sample After One Day Immersion.

INCREASED SOLIDS LOADING AND BASELINE EXPLOSIVES DEVELOPMENT

In pursuit of increased solids loading, three more compositions were prepared, each with 86% RDX, an increase from the initial 82% level. Because the resinous binder used in the formulation process requires some plasticizer as a processing aid, hand mixes established the plasticizer level at approximately 20% of the binder without exudation occurring. Two inert and one energetic plasticizer—dioctyl adipate (DOA), lecithin, and butanetriol trinitrate (BTTN)—were added to the basic formulation. The three new formulations are shown in Table 3, together with their safety and related properties.

Another series of plasticized binders with 86% RDX was prepared. Varying ratios and percentages of the three RDX classes (Classes 1, 3, and 5) were tried in order to obtain the lowest end-of-mix viscosity (EOMV) values consistent with good cure properties. EOMV values ranged from 48.0 down to 22.5 kP at 135°F.

The energetic plasticizer, BTTN, was dropped from further consideration because of its questionable volatility, long-term aging, and cost factors. Lecithin in these formulations did nothing to reduce mix viscosities and inhibited curing and cross-linking of the binder. The third plasticizer, DOA, was also dropped because of its insolubility in water. A plasticizer derived from natural products and more soluble in water was preferred.

Citroflex A-2, an inert plasticizer of relatively low toxicity, was also tried in these formulations. Comprising 20 to 25% of the binder, this ingredient worked well. Processing viscosities improved (were lowered) and the cured explosive compositions were quickly and easily degraded in very dilute (as low as 2%) aqueous ammonia. This new composition, DBX-12, containing 86% RDX, soon thereafter became the baseline explosive for further evaluation. Additional 1-pint mixes of this composition were made to provide enough explosive samples for the binder degradation and RDX solids recovery/recycling efforts. Other samples were used to attain physical, safety, thermal, and explosive performance data.

All other previously prepared formulations, which also contained 86% RDX in similar trimodal distributions, were collected for subsequent binder degradation/solids recovery operations and studies.

TABLE 3. Degradable Binder Explosives and Their Properties.

	Formulations		
	DBX-4	DBX-5	DBX-6
<u>Binder</u>			
Fomrez YA 23-4	10.3	10.3	10.3
LDIM-100	0.9	0.9	0.9
DOA	2.8	-	-
Lecithin	-	2.8	-
BTTN	-	-	2.8
TPB (added)	(0.03)	(0.03)	(0.03)
<u>RDX</u>			
Class 1	26	26	26
Class 3	37	37	37
Class 5	23	23	23
End-of-mix viscosity, kP (at temp indicated)	35 (58°C)	48 (58°C)	40 (58°C)
Measured density, g/cm ³	1.628	1.634	1.650
<u>Safety hazard properties (@ 50% point)</u>			
Impact sensitivity, cm	26	20	22
Friction sensitivity (@ 1000 lb max.)	10/10 NF	10/10 NF	10/10 NF
Electrostatic sensitivity, 0.25 J	10/10 NF	10/10 NF	10/10 NF
VTS, ml/g/48 hrs @ 100°C	0.0137 (1) 0.0198 (2)	0.2712 (1) 0.2558 (2)	0.0820 (1) 0.1054 (2)
<u>Mechanical properties @ 25°C</u>			
Shore A hardness	49	(soft)	42
Tensile strength, psi	19	13	40
Elongation at maximum stress, %	15	18	7
Elongation at rupture, %	152	31	71
Modulus, psi	568	233	1146

RDX RECOVERY AND RECYCLING

Cured slabs of DBX-12 were immersed in a 3% hydrochloric acid solution (dilute ammonia degradation having been demonstrated previously). Binder breakdown occurred within three days at room temperature without any rigorous mechanical agitation or stirring. The RDX that settled on the bottom of the beaker was then filtered, washed several times with water to a neutral pH value, and dried in an oven. RDX recovery from each original formulation (86% RDX) routinely exceeded 99%. The retention of all three classes of RDX was assumed.

The RDX blends that were recycled and dried were then incorporated into two other compositions, DBX-14 and DBX-15, respectively. What turned out was not expected. The mixes did not process well and resulted in unacceptably high EOMVs.

Photomicrographs of the original RDX blend of three classes compared with the recycled RDX components from both the dilute acid and dilute base treatments showed no appreciable differences in particle shape, as shown in Figure 5. The probability exists also that portions of recycled RDX weighed out to prepare the secondary mixes did not accurately represent the original particle size distribution of the successful DBX-12. Neither differential scanning calorimetry (DSC) nor Fourier transform infrared (FTIR) analysis techniques of the recycled RDX particles indicated any changes in purity or other contamination of the surfaces as compared to the original RDX used. However, when the recycled RDX crystals were converted into a "CXM" (coated explosive material) form before mixing, processing was again improved, resulting in a much lower EOMV (DBX-22). Prior coating of the RDX explosive with a fraction of the plasticizer used in the composition is considered the preferred and safer method for handling explosives in scale-up operations.

The DBX formulations described above are shown in Table 4. Physical and safety data are included.

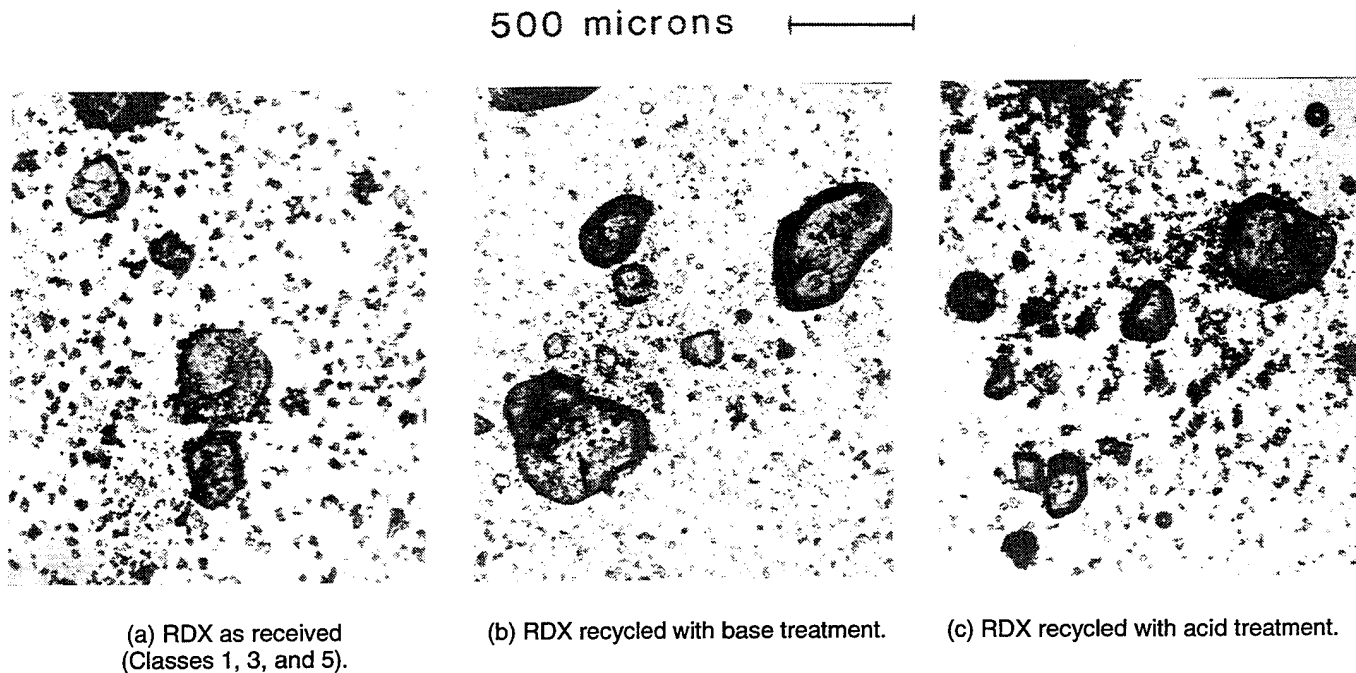


FIGURE 5. Photomicrographs of RDX Following Binder Degradation.

TABLE 4. Current Formulations.

Ingredients	Formulations			
	DBX-12	DBX-14	DBX-15	DBX-22
Binder				
Fomrez YA 23-4	9.64	9.64	9.64	-
Witco 10PE-37	-	-	-	10.51
LDIM-100	0.86	0.86	0.86	-
HMDI	-	-	-	0.69
Citroflex A-2	3.50	3.50	3.50	0.22 (+2.58)
TPB (added)	(0.02)	(0.02)	(0.02)	(0.02)
RDX				
Class 1	25.00	-	-	-
Class 3	40.00	86.00*	86.00**	86.00***
Class 5	21.00			
	100.00	100.00	100.00	100.00
EOMV, kPa-s (58°C)	2.3	>10.0	>10.0	3.0
Shore A-2 hardness	24	-	-	45
Measured density, g/cm ³	1.63	-	-	1.62
Impact sensitivity, cm	28	-	-	42
DTA, onset of exotherm, °C	210	-	-	210
VTS, ml gas/g/48 hrs @ 100°C	0.13	-	-	0.20

* Recycled from base treatment (five formulations).

** Recycled from acid treatment (two formulations).

*** RDX in CXM form (with a film-coat of plasticizer).

DBX-12 EXPLOSIVE PROPERTY TESTS

Formulation DBX-12 is considered a viable candidate for a main charge (warhead) explosive. Filled with 86% RDX, it can be compared with one of the Navy's current main charge explosives, PBXN-107. DBX-12, however, is designed to be degradable and recyclable, and therein lies its chief advantage over PBXN-107. For this reason, additional explosive property data were collected and compared with those of PBXN-107. Data comparisons are presented in Table 5. Complete gap sensitivity and detonation velocity values are included in the appendix. DBX-13, mentioned in the appendix, is identical to DBX-12 except for a slight 5% increase in plasticizer content.

TABLE 5. Explosive Properties Compared: DBX-12 vs. PBXN-107.

Properties	DBX-12	PBXN-107
Basic Safety Properties		
Impact sensitivity, cm	28	30
Friction sensitivity, lb	-	676
Electrostatic sensitivity, @ 0.25 J	-	20/20 no fires
Physical Properties		
Shore A-2 hardness	24	62
Measured density, g/cm ³	1.63	1.64
Thermal Properties		
DTA (onset of exotherm), °C	210	200
VTS, ml gas/g/48hrs @ 100°C	0.13	0.68
Gap Sensitivity		
Mean gap, in/mm	1.751/44.48	1.515/38.51
		1.611/40.92
		1.753/44.53*
kbar	28	38
		33
		28*
Standard deviation	2.595 x 10 ⁻²	8.475 x 10 ⁻³
		7.188 x 10 ⁻³
		4.807 x 10 ⁻³ *

* Values obtained from the Naval Ordnance Laboratory large-scale gap test.

THE NEW DEGRADABLE BINDER REPLACEMENT

Toward the end of fiscal year 1994, it became apparent that the two key chemical ingredients that comprised the original degradable and hydrolyzable binder, Fomrez YA 23-4 and the curative LDIM-100, would soon be depleted. To complicate the situation, it was also learned that they were no longer commercially available. It became imperative to find some substitutes.

Fortunately, after we provided the original vendor, Witco Chemical Corp., with information and polymer specifications from the first samples we received years ago, Witco Chemical was able to produce a new batch of hydroxyl-terminated polyester binder with specifications almost exactly matching those of Fomrez YA 23-4. The properties of the new replacement polyester are shown in Table 6.

TABLE 6. Properties of Hydroxyl-Terminated Polyethylene Glycol Adipate, 10PE-37.

Equivalent weight	1500
Hydroxyl no.	36.9
Acid no.	0.4
Functionality	2.33
Molecular weight	3500
Color, Gardner	3-4
Viscosity, cP, 25°C	8500
Moisture, %	<0.03

A substitute isocyanate curative for LDIM-100 was also found, one still commercially available and commonly used in solid propellant compositions.

Adequate binder cure was obtained with the replacement hexamethylene diisocyanate (HMDI). Binder degradation was also attained by hydrolysis in either 2% aqueous ammonium hydroxide or hydrochloric acid. This is the binder system currently in use. Note that these two new binder ingredients were utilized in formulation DBX-22 (see Table 4). A finalized explosive composition like DBX-22, containing the new plasticized binder (10PE-37/HMDI) and 86% RDX, has been assigned a PBXC number; it is PBXC-132.

BINDER DEGRADATION MECHANISM

As mentioned in the first section of this report, initial binder degradation studies using the original hydroxyl-terminated polyester diol, Fomrez YA 23-4, cured with the diisocyanate, LDIM-100, proved very successful. Binder hydrolysis occurred almost immediately and was completed within a day. The mechanism of binder degradation is depicted by the chemical diagram shown in Figure 6. The by-products of this hydrolysis reaction were considered to be relatively harmless and non-polluting to the environment, well within the scope of this program.

Subsequent explosive mixes with the more commercially available binder substitutes (10PE-37 and HMDI curative) again proved quite successful. Binder hydrolysis and degradation in dilute acid or dilute base now yields somewhat different by-products (which are still considered innocuous and relatively non-toxic), as depicted in Figure 7. Note that the first two hydrolysis products, adipic acid and 1,6-hexanediamine (or hexamethylenediamine), are marketable chemical ingredients used in the manufacture of nylon. Additional benefits would accrue if these key products could be recovered and recycled.

A more comprehensive, tutorial-type treatment of this subject concerning hydrolyzable binders for composite propellants and explosives has been published (Reference 3). In that paper the rationale for the selection of the hydrolyzable polyester binder and the effects of different binder chemical structures on the rates of hydrolysis are discussed in greater detail.

EXPLOSIVES PRODUCT DEVELOPMENT

All current mixes utilize Witco 10PE-37 and HMDI as binder ingredients. The level of Citroflex A-2 plasticizer remains at 20 to 25% (of the total binder). With 86% RDX solids loading, mixing and processing are quite satisfactory. EOMVs at 60°C mixing temperatures range from 2.3 to 2.8 kPa-s. Explosive binder degradation and hydrolysis procedures were again demonstrated in dilute acid and base, resulting in the complete recovery and recycling of the RDX solids filler. The new hydrolysis reaction products formed in the binder breakdown have not presented any problems in disposal thus far.

For a short period we applied this binder system to the more energetic explosive, HMX, and, on a small scale, to the new caged nitramine explosive compound designed for insensitive munitions, CL-20. A few mixes were made, more for binder compatibility checkout and ammonia/acid hydrolysis degradation studies than for obtaining optimized compositions. Both HMX (in DBX-23 and DBX-24) and CL-20 (in a 100-gram mix) were completely compatible with the new replacement binder, Witco 10PE-37/HMDI/Citroflex A-2. Following binder degradation in either dilute ammonium hydroxide or hydrochloric acid, almost 100% HMX and CL-20 recovery was attained. In the case of the CL-20 sample degrading in dilute ammonia, the solution turned to a tan-brown color. This, in turn, left a tan discoloration on the washed and dried CL-20 crystals. The white CL-20 crystals recovered from the dilute acid degradation reactions, however, were not affected that way.

One of the last 1-pint mixes made was based on the baseline composition, DBX-12 (86% RDX) (see Table 4). Following a firm cure in a few days, the cast slab was cut into two pieces and immersed in a beaker containing approximately 4% dilute ammonia solution. Binder solids separation was completed in a few days. Filtration-separation, washing, and oven-drying concluded the RDX recycling operations. Solids recovery was 99.87%. Again, the recovery of all three classes of RDX particles used in the mix was assumed.

The entire recycled batch of RDX was then used to prepare a final 1-pint mix (DBX-27). This time, unlike the disappointing experiences encountered in making DBX-14 and DBX-15 (see Table 4), the mix turned out successfully. With only a slight increase in plasticizer content, the EOMV was 33 kPa (3.3 kPa-s) at 58°C. This value is still within the range of explosive castability. These final degradable binder explosive compositions are shown in Table 7.

With the final testing of the formulations, this program came to a close.

TABLE 7. Current Formulations.

Ingredients	Formulation			
	DBX-23	DBX-24	DBX-27	100-gram CL-20 Mix
<u>Binder</u>	10.51	9.85	9.20	10.51
Witco 10PE-37	0.69	0.65	0.60	0.69
HMDI	2.80	3.50	4.20	2.80
Citroflex A-2	(0.02)	(0.02)	(0.02)	(0.02)
TPB (added)				
<u>HMX</u>	33.50	33.50	-	-
Class 1	26.25	26.25	-	-
200 µm	26.25	26.25	-	-
Class 5				
<u>RDX</u>	-	-	86.00	-
Entirely recycled from DBX-26				
<u>CL-20</u>	-	-	-	86.00
150 µm				
	100.00	100.00	100.00	100.00
EOMV, kPa-s (58°C)	3.4	3.4	3.3	*
Measured density, g/cm ³	1.71	-	-	1.60
Impact sensitivity, cm	35	-	-	17
DTA, onset of exotherm, °C	-	-	-	169
VTS, ml gas/g/48 hrs @ 100°C	-	-	-	0.59

* Too viscous and dry to measure.

CONCLUSIONS

The feasibility of cast energetic compositions, such as DBX-12 and PBXC-132, as acceptable main charge explosives has been demonstrated. This investigation established that an easily degradable composite polyurethane/RDX system can contribute significantly to our nation's environmental pollution abatement efforts. The relatively high-cost explosive solids can be separated and reused, and the harmless binder liquid by-products can be disposed of in a non-hazardous fashion. This unique feature fits well in the current military efforts directed toward safe ordnance disposal and demilitarization. Similar efforts would be feasible in the realm of solid propellant formulations and development. An illustration of this final proof-of-concept is shown in Figure 8.

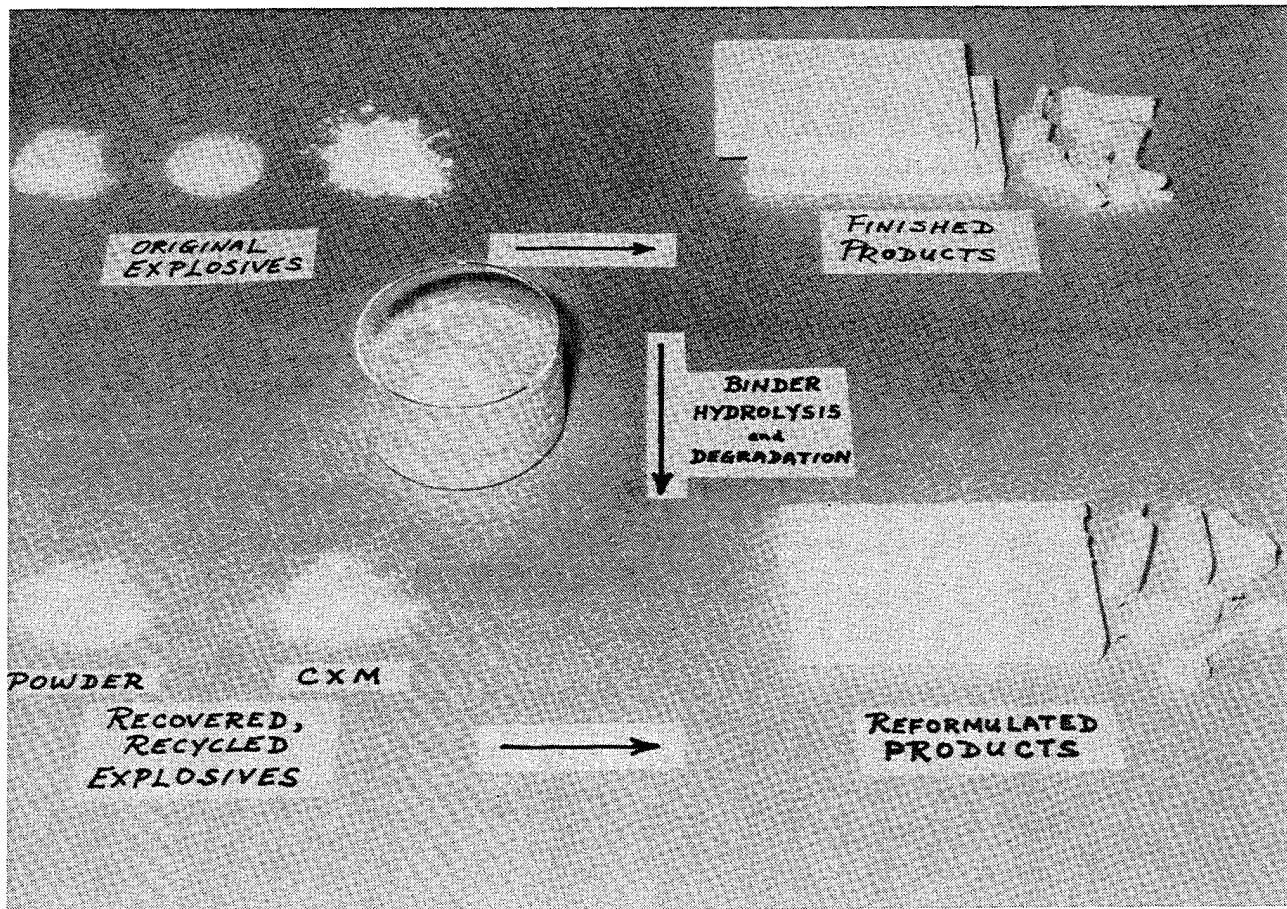


FIGURE 8. Proof-of-Concept—A Degradable and Environmentally Responsive Explosive.

REFERENCES

1. Naval Weapons Center. *Water Soluble and Hydrolyzable Binder Explosives*, by B. Y. S. Lee. China Lake, Calif., NWC, February 1982. (NWC TP 6313, publication UNCLASSIFIED.)
2. Benjamin Y. S. Lee, Russell Reed, Jr., and Roger L. Miller. *Degradable Binder Explosives*, U. S. Patent No. 4,293,352, 6 October 1981. Patent UNCLASSIFIED.
3. R. Reed, Jr., B. Y. S. Lee, and V. L. Brady. "Hydrolyzable Binders for Composite Propellants and Explosives," *Proceedings of the 1995 JANNAF Propellant Development and Characterization Subcommittee Meeting*, April 1995, Jet Propulsion Laboratory, Pasadena, Calif. (CPIA Pub. 625, p. 161, April 1996, publication UNCLASSIFIED.)

NOMENCLATURE

BTTN	1,2,4-butanetriol trinitrate
Citroflex A-2	acetyl triethyl citrate (Morflex Chemical Co., Inc.)
CL-20	hexanitrohexaazaisowurtzitane (HNIW)
cP	centipoise
CXM	coated explosive material
DBX	degradable binder explosive (series)
DOA	dioctyl adipate
DSC	differential scanning calorimetry
DTA	differential thermal analysis
EOMV	end-of-mix viscosity
f	functionality
Fomrez YA 23-4	hydroxyl-terminated polyester diol with 79% poly(ethylene glycol) content: $f = 2.33$; $MW = 3500$ (Witco Chemical Corp.)
FTIR	Fourier transform infrared
HMDI	hexamethylene diisocyanate (Mobay Chemical Corp.)
HMX	cyclotetramethylenetetranitramine
J	joule
kPa-s	kilopascal-seconds
kP	kilopoise
LDIM-100	lysine diisocyanate methyl ester (Toray Industries)
LSGT	large-scale gap test
MW	molecular weight
NCO/OH	ratio of isocyanate to hydroxyl
NF	no fire
PBXC	plastic-bonded explosive, China Lake
PBXN	plastic-bonded explosive, Navy qualified
RDX	cyclotrimethylenetrinitramine
TPB	triphenyl bismuth
VTS	vacuum thermal stability
Witco 10PE-37	hydroxyl-terminated polyethylene glycol adipate (Witco Chemical Corp.)

Appendix A
EXPLOSIVE PERFORMANCE TEST RESULTS FOR DBX-12 AND DBX-13

8010
 C2713/054
 11 Aug 94

MEMORANDUM

From: Henry John, Energetic Materials Characterization Branch (C2713)
 To: Ben Lee, Propellant and Explosives Branch (C2711)

Subj: IHE GAP TESTING TESTING ON DEGRADABLE BINDER EXPLOSIVE DBX-12-2

Ref: (a) NSWC TR 86-58, 12 Jul 86
 (b) NAVORD OD 44811, Vol.1, 1 Jan 72
 (c) NAVWPNCEN memo 8010 Reg 2713/4778 of 2 Jun 94
 (d) NAVWPNCEN memo 8010 Reg 3213-030-91 of 6 Jun 91
 (e) NAVWPNCEN memo 8010 Reg 2713-045-93 of 16 Sep 93
 (f) NAVWPNCEN memo 8010 Reg 4541-158-74 of 28 Feb 74
 (g) NAVWPNCEN memo 8010 Reg 3241-6-77 of 19 Oct 76
 (h) NAVWPNCEN memo 8010 Reg 3247-004-77 of 26 Oct 76
 (i) NAVWPNCEN memo 8010 Reg 3262-2-80 of 1 Oct 79
 (j) NOLTR 70-25, 17 Mar 70

Encl: (1) Statistics of Go/No-Go Results
 (2) Go/No-Go Plot of IHE DBX-12-2

1. IHE gap testing have been conducted on 25 charges of Degradable Binder Explosive DBX-12-2 in accordance to reference (a). The Theoretical Maximum Density (TMD) for DBX-12-2 is 1.675 g/cm³. Assistance on this test series was provided by Danny Wooldridge at the 254 test area.
2. The average density of the samples was calculated by obtaining the explosives volume and weight, then dividing the mass by volume. This method does not take into consideration the possibility of voids in the sample and assumes a void-free sample. Using this method the average density was 1.575 g/cm³ with a standard deviation of 0.0299 g/cm³. The densities varied from 1.515 to 1.625 g/cm³ which is 90.4% to 97.0% TMD in the 25 tubes.
3. The test results are shown in Table 1.

Shot Number	Tube Number	Gap (# Cards/ in)	Density (g/cm ³)	Go/ No-Go
1	1	150/ 1.507	1.556	Go
2	2	175/ 1.752	1.574	No-Go
3	3	160/ 1.603	1.571	Go
4	4	166/ 1.657	1.551	Go
5	5	170/ 1.702	1.610	Go
6	6	174/ 1.742	1.595	Go

Subj: IHE GAP TESTING TESTING ON DEGRADABLE BINDER EXPLOSIVE DBX-12-2

Shot Number	Tube Number	Gap (# Cards/ in)	Density (g/cm ³)	Go/No-Go
7	7	177/ 1.767	1.601	No-Go
8	8	176/ 1.762	1.595	No-Go
9	9	174/ 1.739	1.601	Go
10	10	175/ 1.753	1.554	Go
11	11	176/ 1.763	1.625	No-Go
12	12	174/ 1.740	1.594	No-Go
13	13	173/ 1.728	1.585	Go
14	14	175/ 1.752	1.530	Go
15	15	177/ 1.768	1.595	No-Go
16	16	176/ 1.757	1.561	Go
17	17	178/ 1.780	1.520	No-Go
18	18	174/ 1.740	1.515	Go
19	19	175/ 1.754	1.613	No-Go
20	20	172/ 1.723	1.582	Go
21	21	174/ 1.742	1.603	Go
22	22	175/ 1.751	1.615	No-Go
23	23	174/ 1.741	1.604	No-Go
24	24	173/ 1.729	1.555	Go
25	25	176/ 1.764	1.562	Go

Table 1. IHE Gap Test Results for DBX-12-2.

4. The mean gap value for the 50% fire point is estimated to be 44.48 mm (1.751") with a standard deviation of 0.66 mm (0.026") and a 95% confidence interval of 43.74 mm (1.722" to 1.645"), the results are shown in enclosure (1). This value corresponds to a input pressure of 28.0 kbar (2.80 GPa) for the 50% fire point and a 95% confidence interval of input pressure of 29.1 kbar to 32.2 kbar (2.91 GPa to 3.22 GPa). The plot of the test results are shown in enclosure (2).

5. This material had the same sensitive compared to an earlier NOL Large Scale Gap Test (LSGT) reference (b), from NSWC Yorktown, comparing different batch process for PBXN-107, (mix JHY 1-18-94. Mix IHY 1-18-94 used batch processed RDX and mix JHY 18 January 1994 used continuous process RDX), reference (c). Comparing this test series to PBXN-107, type II, reference (d). This PBXN-107 was more sensitive than the DBX-12-2. This material however, was more sensitive than earlier IHE Gap testing discussed in reference (e). A table comparing and summarizing the mean gap, input pressure, and standard deviation for DBX-12-2 to PBXN-107 all the test results are shown below in Table 2.

Subj: IHE GAP TESTING TESTING ON DEGRADABLE BINDER EXPLOSIVE DBX-12-2

Sample Tested	Type Test Conducted	Mean Gap (In./mm)	Kbar Of Pressure	Standard Deviation
DBX-12-2	IHE GAP	1.751/44.48	28.0	2.595 X 10 ⁻²
IHY 1-18-94	NOL/LSGT	1.753/44.53	28	4.807 X 10 ⁻²
JHY 1-18-94	NOL/LSGT	1.71/43.43	29.5	2.066 X 10 ⁻²
PBXN-107(II)	NOL/LSGT	2.034/51.66	20	1.840 X 10 ⁻²
PBXN-107	IHE GAP	1.516/38.51	38	8.475 X 10 ⁻³
PBXN-107	IHE GAP	1.611/40.92	33	7.188 X 10 ⁻³


Table 2. Comparing Gap Test Results of DBX-12-2 to PBXN-107


6. Another comparison of results with previous data are shown in Table 3 below, (references (d), (f), (g), (h), and (i)) for PBXN-107. The first test used Tetryl pellets as a donor, but all subsequent tests used Pentolite pellets as the donor. In the range of gaps of interest in these data (>35 mm) the shock amplitude delivered to the sample is the same for either donor (reference (j)).

Date Tested	Type	Density g/cm ³	Mean Gap Sensitivity 50% Pt., in.	95% C. L. Range, in.
Feb. 1974	PBXC-116(I)	1.65	1.411	
Apr. 1976	PBXC-116(I)	1.63	1.783	1.775-1.790
Sep. 1976	PBXC-116(I)	1.64	1.870	1.855-1.886
May 1979	PBXC-116(M)	1.63	1.666	1.657-1.675
May 1991	PBXN-107, type II	1.64	2.034	2.033-1.971

Table 3. Comparing Gap Test Results of DBX-12-2 to PBXN-107

NOTE: PBXC-116(M) is the same as PBXN-107, type II. The difference between PBXC-116(I) and PBXN-107, type II is a small change in the binder ingredients, they have equivalent weight percentages of RDX. From all the data that is available on PBXN-107 type II, the mean gap sensitivity for DBX-12-2 is very similiar to that PBXN-107. Should you have any questions, I can be reached at 939-7528/7588.


HENRY JOHN

Copy to:
271
2713 (Burchett , John, Wooldridge, files)

Writer: H. J. John, C2713, x7528
Typist: Same

TEST IDENTIFICATION

SHOT NUMBER: 2874

DATE: 8-4-94

TEST CONDUCTOR: John - Wooldridge

TEST TYPE: IHE Gap Test

EXPLOSIVE: RDX-Degradable Binder

SIZE OF SAMPLE: STD

TEST LEVEL	#FIRES	#NO FIRES
1.7800	0	1
1.7700	0	1
1.7600	2	2
1.7500	2	3
1.7400	4	2
1.7300	2	0
1.7200	1	0

PRECISION OF SDM .001 PRECISION OF SDS .001

OUTPUT

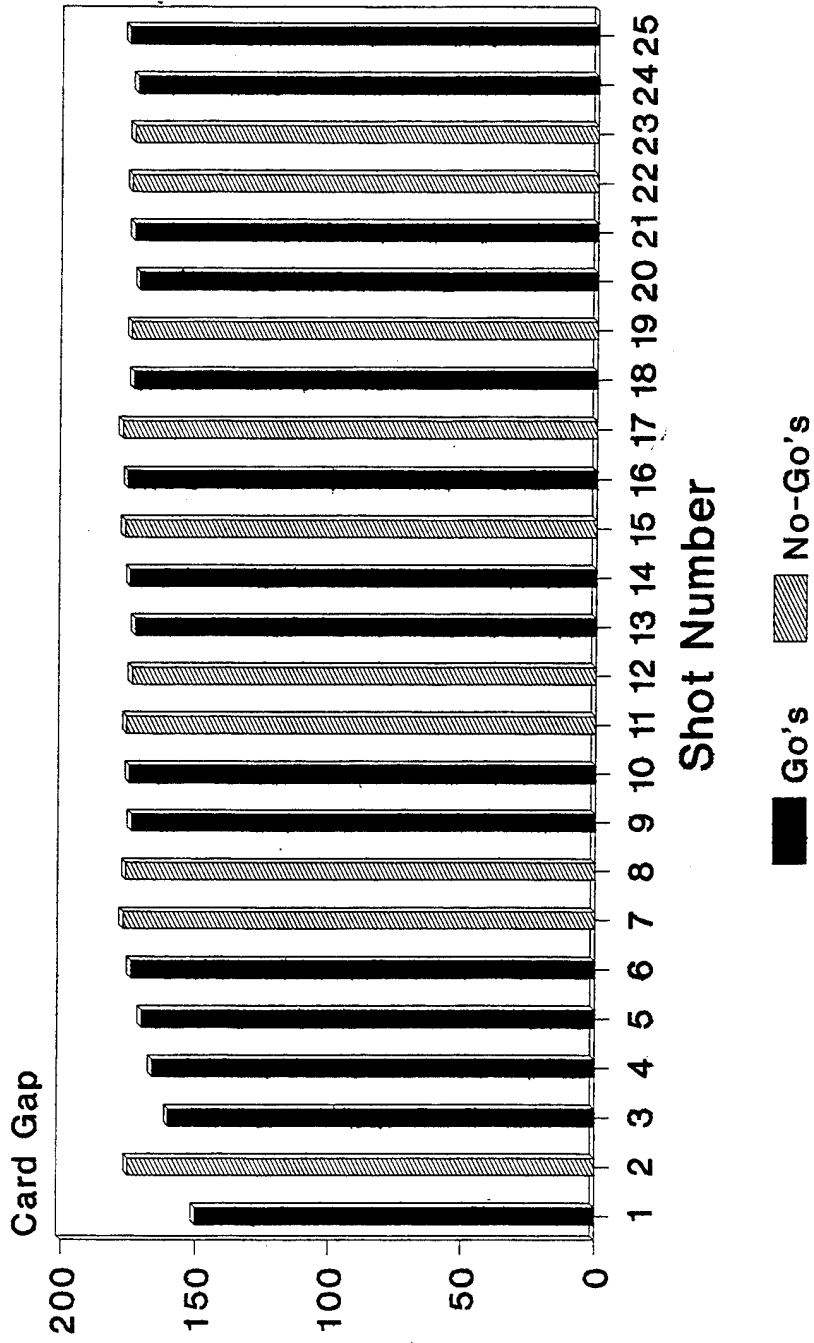
MEAN	1.751D+00
STD DEV	2.595D-02
SMALL TEST ANALYSIS	
ITERATIONS	4
CORRECTION TO THE MEAN	3.6293D-05
CORRECTION TO STD DEV	4.8237D-04
AVERAGE	1.7506D+00
STANDARD DEVIATION	1.7444D-02
S SUB M	5.4774D-03
S SUB S	8.4133D-03

TABULATION OF THE MOST LIKELY RESPONSE
AND SINGLE SIDED CONFIDENCE ESTIMATE

PERCENT	VARIABLE	MOST LIKELY RESPONSE	.90 CONFIDENCE UPPER	.90 CONFIDENCE LOWER	.95 CONFIDENCE UPPER	.95 CONFIDENCE LOWER
99.98	3.5000	1.6896	1.731	1.648	1.744	1.635
99.90	3.0900	1.6967	1.733	1.660	1.745	1.648
99.00	2.3260	1.7101	1.738	1.682	1.747	1.673
95.00	1.6450	1.7219	1.743	1.701	1.749	1.695
90.00	1.2820	1.7283	1.745	1.712	1.750	1.706
75.00	0.6750	1.7389	1.750	1.728	1.753	1.724
50.00	0.0000	1.7506	1.758	1.743	1.761	1.741
25.00	-0.6750	1.7624	1.773	1.752	1.777	1.748
10.00	-1.2820	1.7730	1.790	1.756	1.795	1.751
5.00	-1.6450	1.7793	1.800	1.759	1.807	1.752
1.00	-2.3260	1.7912	1.819	1.763	1.828	1.754
0.10	-3.0900	1.8045	1.841	1.768	1.853	1.756
0.02	-3.5000	1.8117	1.853	1.770	1.867	1.757

Encl. (1)

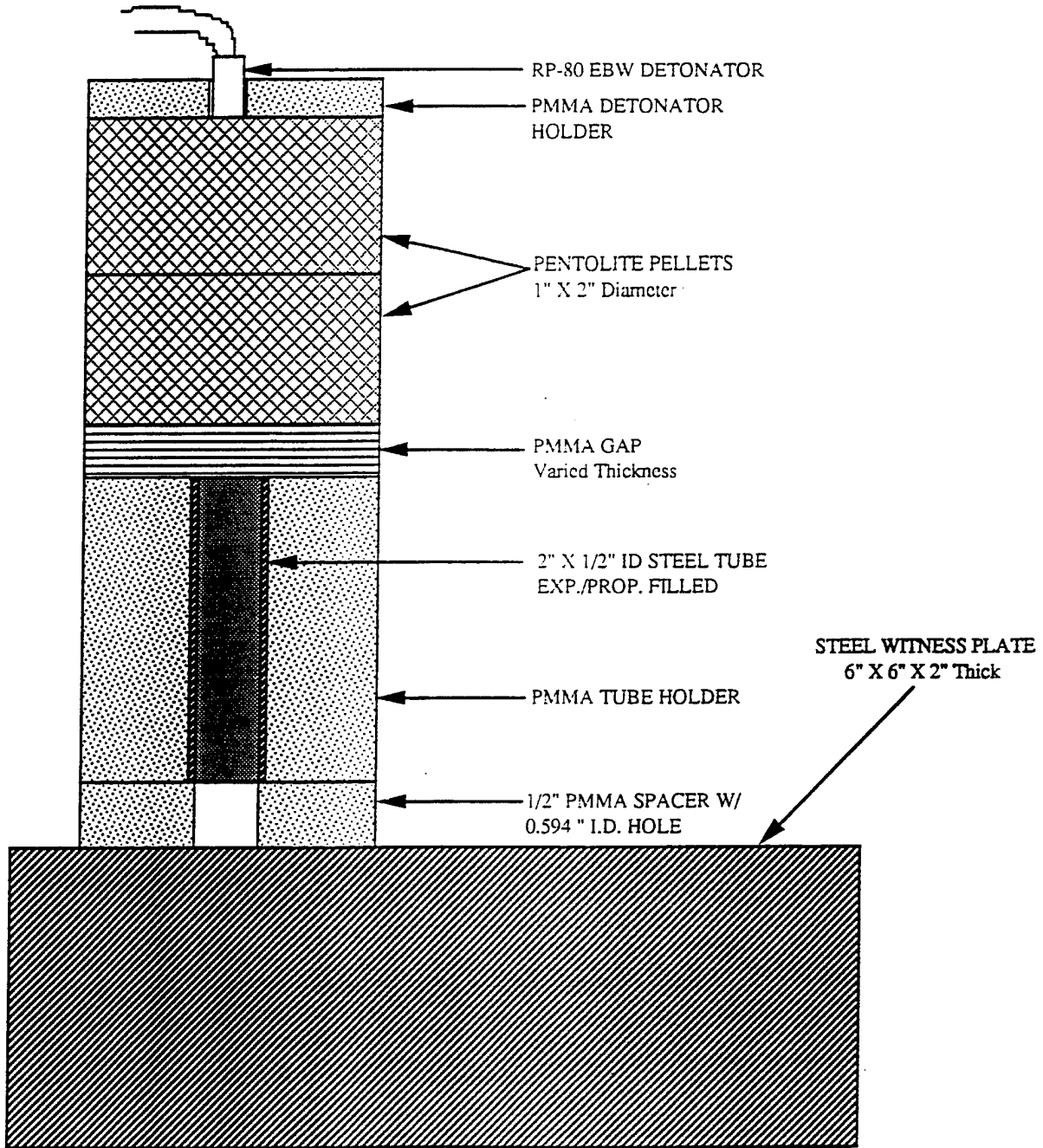
IHE GAP TEST RDX-Degradable Binder



8-4-94

Encl. (2)

IHE GAP TEST



8010
C2713/045
8 Aug 94

MEMORANDUM

From: Henry John, Energetic Materials Characterization Branch(C2713)
To: Ben Lee, Propellant and Explosives Branch(C2711)

Subj: PERFORMANCE TESTING ON DEGRADABLE BINDER EXPLOSIVE

Encl: (1) PLOT OF CALIBRATION TEST FOR PRESSURE VS. DENT DEPTH

1. Detonation velocity and extrapolation of detonation pressure testing has been conducted on 3 charges of RDX/Binder mix number DBX-13 in a series of steel tubes 6" long with a inside diameter of 0.500". The Theoretical Maximum Density (TMD) is 1.675 g/cm³. Assistance on this test series was provided by Danny Wooldridge and Mark Swett at the 254 test area.

2. The test charge was positioned on a 6" x 6" x 2" mild steel witness plate with a Rockwell hardness of B-83 and four piezoelectric pins were positioned in the steel tube for detonation velocity. A detonator holder was positioned on the steel tube with a 1/2" x 1/2" RDX booster charge. Then a RP-501 detonator was placed in contact with booster charge, and the test was fired.

3. A calibration constant of detonation pressure versus plate dent depth was produced by measuring the dent depth for a series of well characterized explosives, and plotting these values against known detonation pressures. The explosives used in the calibration series were PBXN-5, Tetryl, PBXN-7, HMX, and RDX. The calibration plot is shown in enclosure (1). Each explosive except for HMX and RDX was tested in triplicate. The resulting data was fit with a linear equation using the least squares method. The derived equation,

$$P_{cj} = md + b$$

where P_{cj} is detonation pressure, "d" is the dent depth, "m" is the slope of the line, and "b" is the y-intercept, was used to determine the detonation pressure of the RDX/Binder material. The equation for the best linear fit to the data was:

$$P_{cj} = 2649d - 109.317$$

The dent depth was measured for each test of RDX/Binder and is recorded in Table 1 with the extrapolated detonation pressure in Kbars.

Shot Number	Density (g/cm ³)	Dent Depth (in./mm)	Detonation Pressure (Kbars)
1	1.574	0.135/3.43	248.3
2	1.562	0.141/3.58	264.2
3	1.581	0.136/3.45	250.9

Table 1. RDX/Binder Dent Depth and Detonation Pressure.

4. The detonation velocity was measured with four piezoelectric pins. The average separation of the four pins was 25.4 mm. The measured detonation velocity is shown in Table 2.

Shot Number	Detonation Velocity (mm/μs)
1	7.920
2	7.735
3	7.892

Table 2. Detonation Velocity of RDX/Binder.


5. The average detonation velocity was 7.849 mm/μs with standard deviation of 0.081 mm/μs for all three shots. The average detonation pressure was 254.5 Kbars with a standard deviation of 7.057 Kbars for all three tests. Comparison with an early test series of degradable binder explosive DBX-12, we see about the same detonation pressure and 4% increase in the detonation velocity. This early test series had a 86% loading of RDX compared to 86% on this series. The variations in densities are show in table 3. The densities varied from 1.553 to 1.585 g/cm³ in the nine tubes that

Shot Number	Density (g/cm ³)	Average Density (g/cm ³)	Standard Deviation
1	Tube # 4-1.577 Tube # 5-1.574 Tube # 7-1.571	1.574	0.002
2	Tube # 1-1.567 Tube # 2-1.553 Tube # 9-1.566	1.565	0.006
3	Tube # 3-1.585 Tube # 6-1.582 Tube # 8-1.576	1.581	0.004

Table 3. RDX/Binder Density Comparisons.

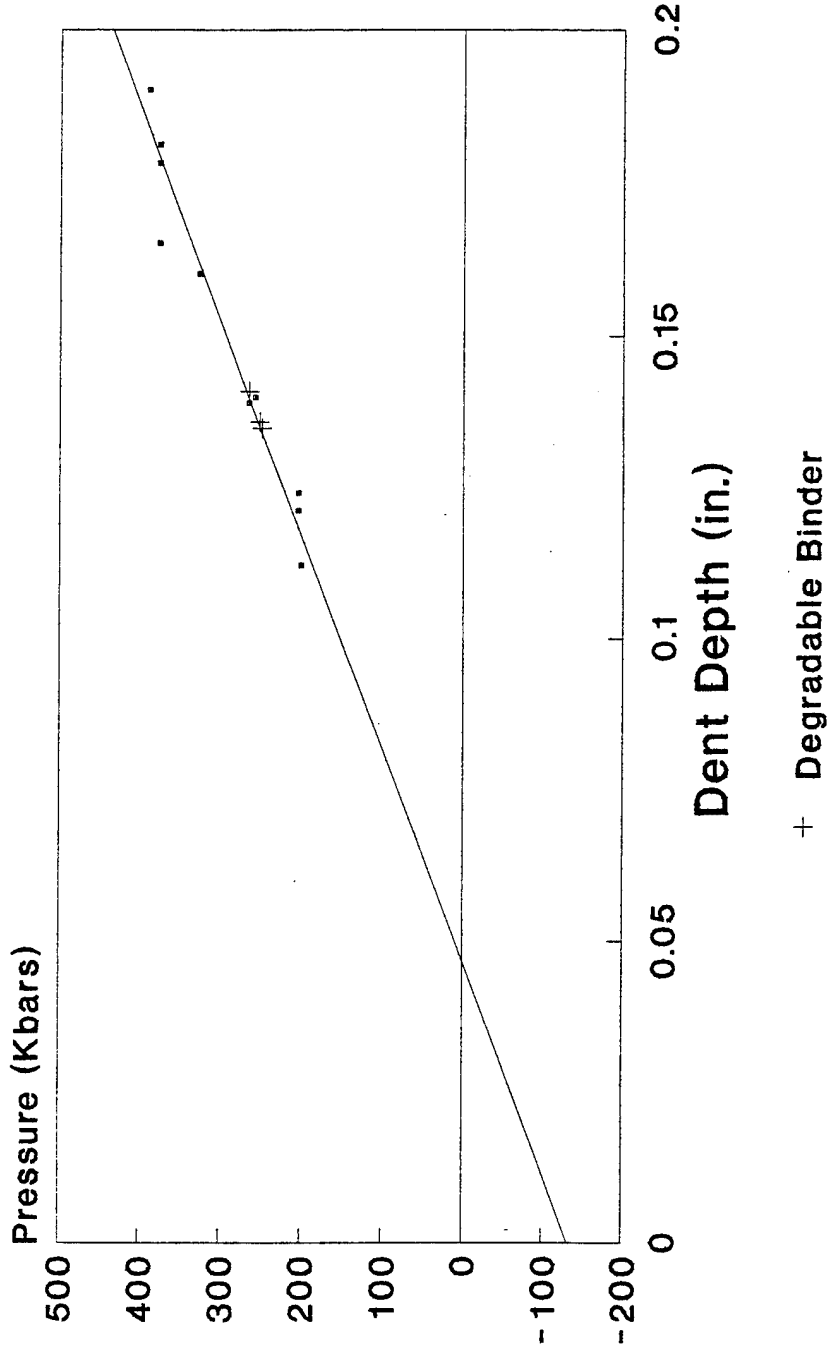
were tested with an average density of 1.572 g/cm³ and a standard deviation of 0.009 g/cm³, which is 92.7 to 94.6% TMD. The densities of the tubes in this test series were very consistant compared to the early test series DBX-12. Should you have any questions, I can be reached at 939-7528/7588.


HENRY JOHN

Copy to:
271
2713 (Burchett , John, Wooldridge, files)

Writer: H. J. John, C2713, x7528

Pressure vs Dent Depth Calibration Testing



Confined Charges

Encl. (1)

INITIAL DISTRIBUTION

- 1 Office of Chief of Naval Research, Arlington (Code 033, Dr. D. Miller)
- 2 Naval Surface Warfare Center, Indian Head Division, Indian Head
 - Code 9110, Dr. A. Stern (1)
 - Code 9110N, L. Nock (1)
- 5 Naval Surface Warfare Center, Indian Head Division, White Oak Laboratory, Silver Spring
 - Code 90H, S. Collignon (1)
 - Code 920, Dr. R. Doherty (1)
 - C. Gotzmer (1)
 - C. Peletski (1)
 - Dr. L. Roslund (1)
- 1 Army Missile Command, Redstone Arsenal (AMSMI-RD-PR-T, L. Asaoka)
- 1 Aberdeen Proving Ground (Dr. W. Hillstrom)
- 1 Army Armament Research Development and Engineering Center, Picatinny Arsenal (G. Chesnov)
- 1 Army Defense Ammunition Center and School, Demil Technology Office, Savannah (SMCAC-TD, J. G. Wheeler)
- 2 Defense Technical Information Center, Alexandria
- 1 Lawrence Livermore National Laboratory, Livermore, CA (C. O. Pruneda)
- 1 Los Alamos National Laboratory, Los Alamos, NM (J. A. Sanchez)
- 1 Attenuation Technology, Incorporated, La Plata, MD (R. L. Dow)
- 1 Alliant Techsystems, Incorporated, Hopkins, MN (G. G. Wittmer)
- 1 Thiokol Corporation, Propellant Research Section, Brigham City, UT (Dr. R. B. Wardle)