

CONF-94255-5

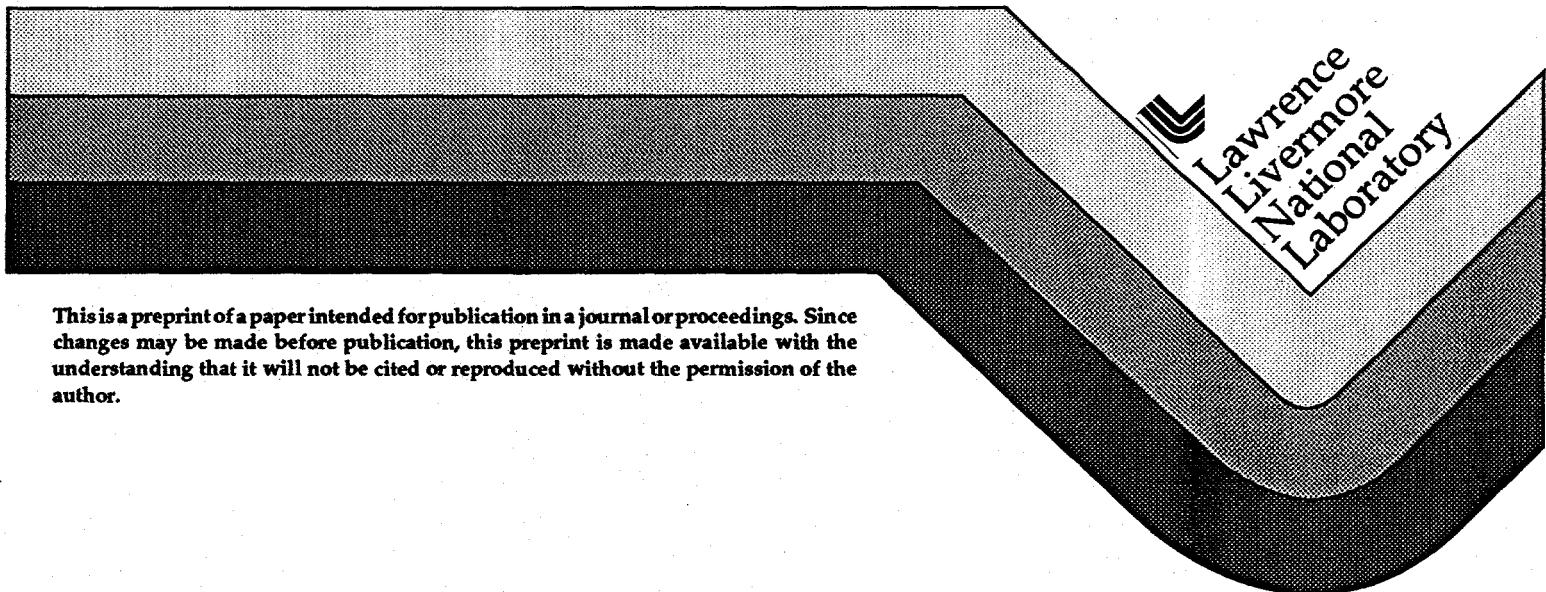
UCRL-JC-119253
PREPRINT

**Clean, Agile Alternative Binders, Additives and
Plasticizers for Propellant and Explosive Formulations**

**D. Mark Hoffman, Tom W. Hawkins, Geoffrey A. Lindsay,
Robert B. Wardle, and Gerald E. Manser**

**This paper was prepared for submittal to the
Life Cycles of Energetic Materials Meeting in Del Mar, CA
December 11-16, 1994**

December 1994



This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial products, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

Clean, agile alternative binders, additives and plasticizers for propellant and explosive formulations

**D. Mark Hoffman,
Energetic Materials Center
Lawrence Livermore National Laboratory
Livermore, CA 94550**

**Tom W. Hawkins,
Propulsion Directorate
Phillips Laboratory
Edwards AFB, CA 93524-5001**

**Geoffrey A. Lindsay
Naval Weapons Station
China Lake, CA 93555**

**Robert B. Wardle
Thiokol Corporation
Brigham City, UT 84302-0707**

**Gerald E. Manser
Aerojet Corporation
Sacramento, CA. 95852-1669**

Abstract

As part of the Strategic Environmental Research and Development Program (SERDP) a clean, agile manufacturing of explosives, propellants and pyrotechniques (CAMPEP) effort set about to identify new approaches to materials and processes for producing propellants, explosives and pyrotechniques (PEP). The RDX based explosive PBXN-109 and gun propellant M-43 were identified as candidates for which waste minimization and recycling modifications might be implemented in a short time frame. The binders, additives and plasticizers subgroup identified cast non-curable thermoplastic elastomer (TPE) formulations as possible replacement candidates for these formulations. Paste extrudable explosives were also suggested as viable alternatives to PBXN-109. Commercial inert and energetic TPEs are reviewed. Biodegradable and hydrolyzable binders are discussed. The applicability of various types of explosive formulations are reviewed and some issues associated with implementation of recyclable formulations are identified. It is clear that some processing and weaponization modifications will need to be made if any of these approaches are to be implemented. The major advantages of formulations suggested here over PBXN-109 and M-43 is their reuse/recyclability. Formulations using TPE or Paste could be recovered from a generic bomb or propellant and reused if they met specification or easily reprocessed and sold to the mining industry.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED 35

MASTER

I. Introduction

The objective of this work was to survey and assess technology for binders, plasticizers, and additives (BP&A) that could reduce waste and pollution from M-900 tank ammunition and GBU-24 Bombs. The explosive of interest is PBXN-109 and the propellant of interest is M-43. Other pertinent considerations include lower cost, increased safety, reduced vulnerability in the field including insensitive munitions issues, and performance. An assessment of current production materials and suggestions for improvements in binder, additives, and plasticizers based on the overall PEP survey for aiding and selecting technologies with a high probability of implementation and payoff is included.

II. Approach.

A kick-off meeting of the Binders Additives and Plasticizers team was held on March 25, in conjunction with the Solid Propellant Environmental Issues Technical Interchange Meeting in Ogden, Utah. The Processing team provided us with a preliminary waste stream flowchart for the M-900 round and the GBU-24 bomb. The salient features of these flow chart, showing where waste and pollution from the formulations occurs, are reproduced in Figures 1 and 2. The composition of PBXN-109 explosive is given in Table 1. M-43 gun propellant compositions are available to US government agencies only so a generic composition similar to an experimental gun propellant XM-39¹ is given in Table 2. Assessment of substitute materials and formulations were made and are given.

In our original assessment no analysis had been run on the percentage of pollution which occurred at any particular step during production and recycling or retirement. The team consensus was that modest pollutant would result from

processing while substantial amounts would be generated by demilitarization operations, especially considering the hazardous nature of the propellant and explosive. This has been confirmed recently by preliminary analysis using the PROMOS model.² The areas in processing which might be improved were electrical consumption for heating, methods for preventing or minimizing the possibility of a mixing error which causes a large cast-cure mix like PBXN-109 to be lost and residue which hangs up in the intensive mixer (perhaps as much as 15% of a 400 gallon mix). This effect, although significant, would be small compared to the ability to recycle or reuse the cast-cured explosive bomb fill at the end of its use life. The most significant effect on pollution prevention and waste minimization is the ability through modification of binder, plasticizers or additives to recycle or reuse decommissioned ordnance.

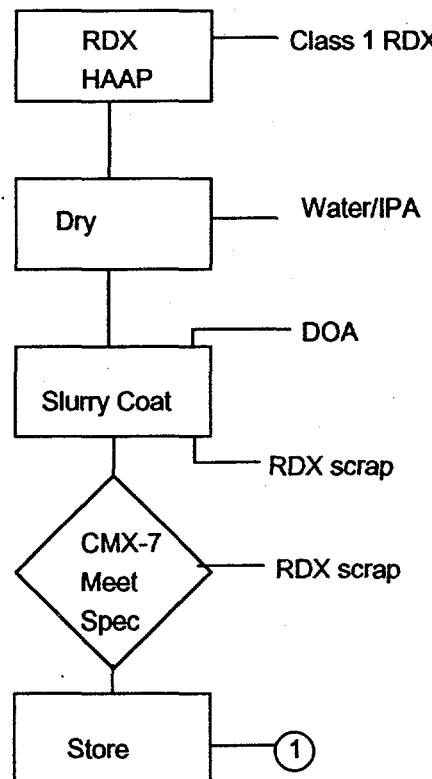
III. Results and Discussion

A. PBXN-109 and M-43

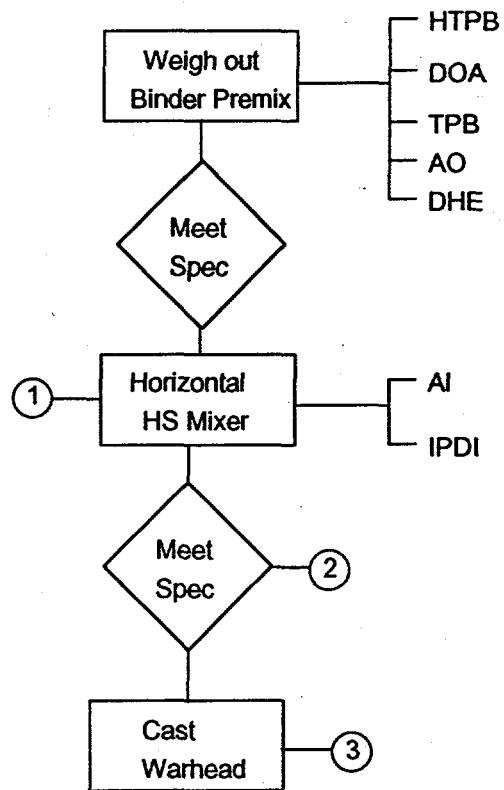
1. Binders additives and plasticizers currently used in PBXN-109³ and M-43⁴: The binder system currently used in PBXN-109 is a polyurethane based on Atochem Military grade hydroxy terminated polybutadiene (R45HT) and isophorone diisocyanate (IPDI) manufactured by Huls America. This urethane system cures extremely slowly and must be catalyzed. To that end, three different catalysts appear to have been used, Ferric acetylacetone (FeAA), dibutyl tin dilaurate, and the current "latent" cure system, triphenyl bismuth (TPB). To reduce the HTPB viscosity and improve processability an equal weight of di-2-ethyl hexyl adipate (DOA) is used. This plasticizer is available in quantity from several manufacturers including Eastman Chemical, Union Camp, and Huls. Because of the double bonds in the HTPB an antioxidant must be used. Cyanox AO-2246 manufactured by American Cyanamid,

Figure 1. Process Waste Generated from PBXN-109 Production

Process #1, Slurry Coat CMX-7



Process #2, Formulate PBXN-109



(2) =Waste PBX

(3) =heat cure, inspect, store bomb

Table 1. PBXN-109 composition.

Component	Wt %	Specification	Remarks
RDX	64.00	Mil-R-398	Thpe II Class 1
Al	20.00	WS 23150	Spherical type IV
HTPB	7.346	WS 23148	linear
DOA	7.346	DOD-D-23443	di(2-ethylhexyl)adipate
IPDI	0.9465	WS-16305	isophorone diisocyanate
BHT	0.01	WS-23151	2,2'-methylene-bis (4-methyl 6-t-butyl phenol)
Dantocol DHE	0.26	WS-23151	di(2-hydroxyethyl) dimethylhydantion
Catalyst (FeAcAc; TPB; DBTDL)	~.0015		Ferric Acetylacetone; triphenyl bismuth; or dibutyl tin dilaurate

Figure 2. Process Waste Generated from M-43 Production:

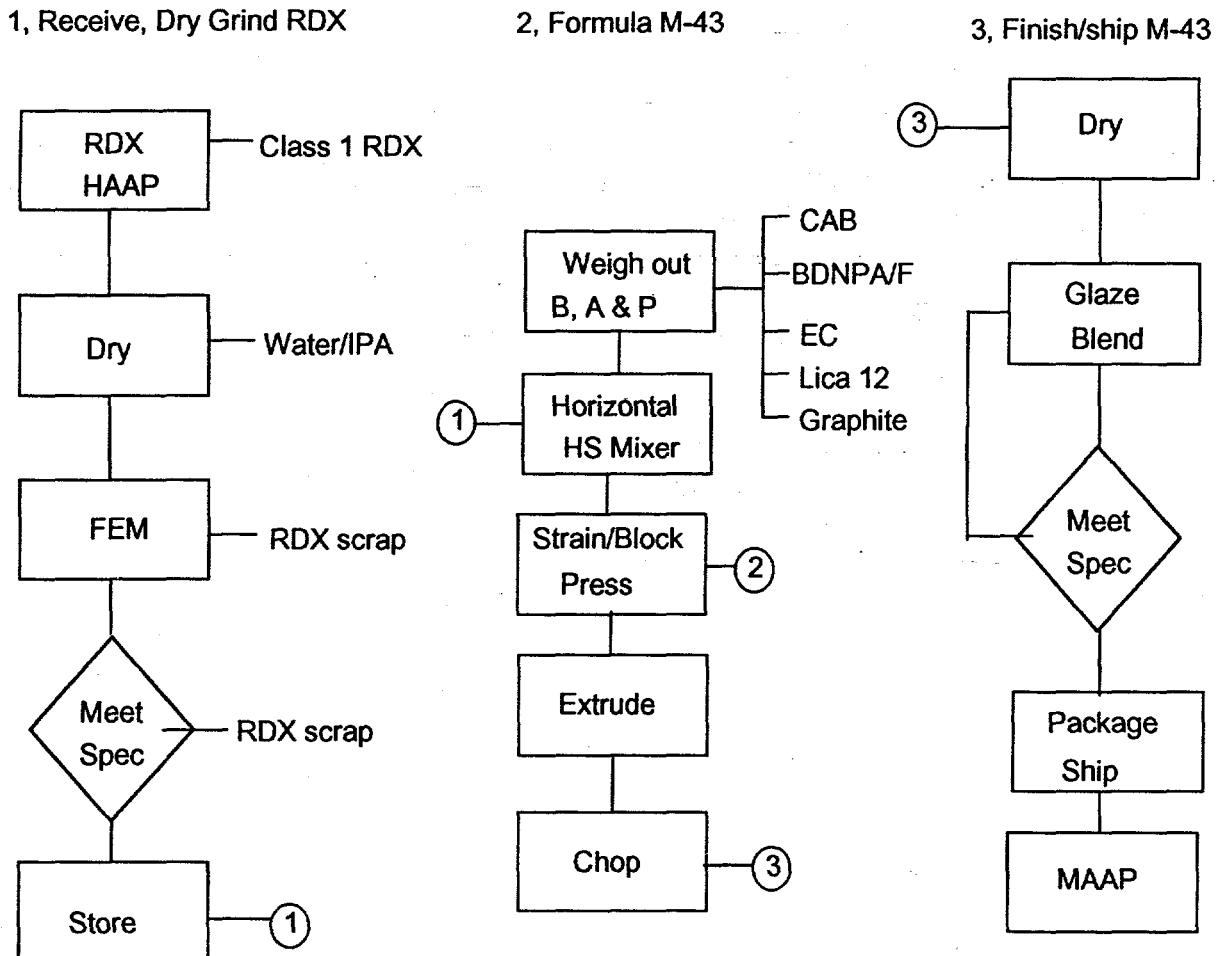


Table 2. Generic Composition of M-43 Gun Propellant (M-42 composition is not available to non-government agencies; Composition is based on XM-39 in ref. 1.

Component	XM-39* (Wt%)	Remarks
RDX	74	FEM**
Cellulose acetate butyrate	10	Binder
BDNPA/F	10	
Ethyl Centralite	0.5	Stabilizers
Nitrocellulose	4.5	Coupling agents
Lica 12	.5	Coupling agent
Graphite	0.5	

* M-43 composition is confidential, XM-39 is generically similar.

** RDX is reduced in size to 6-8 μm by fluid energy milling

the current antioxidant is a 2,2'-methylene bis(4-methyl-6-t-butylphenol. A small amount of bis (2-hydroxyethyl) dimethyl hydantion (Dantocol DHE) bonding agent or coupling agent is also used to improve mechanical properties of the formulation.

Cellulose acetate butyrate (CAB) is the binder in M-43 gun propellant. It is commercially available in large quantities, but only from Eastman Chemicals. In recent years there has been a decline in the CAB market, especially where cheaper petroleum based polymers can be substituted. In the M-43 formulation CAB is plasticized with a mixture of 50/50 by weight Bis (2,2-dinitropropyl) acetal or formal (BDNPA/F) currently available from Aerojet Corp. As demand for this material has decreased, costs have increased and the Army has developed an alternative sources of supply⁵ and plasticizers.⁶ An alternate source of this material appears to be Thiokol Corp. Acetals and formals have a tendency to hydrolyze over time. Small quantities of graphite lubricant, Lica 12 titanate coupling agent, Nitrocellulose bonding agent, and ethyl centralite stabilizer are also used.

2. Alternate explosives. Alternative ingredients/formulations for the PBXN-109 explosive were evaluated for the Advanced Bomb Family effort in 1991.⁷ At that time recyclability and environmental issues were not considered as significant as performance⁸ and vulnerability.⁹ Only cast cure and melt cast formulations were proposed. Melt cast formulations were based on TNT with a variety of other components and cast cure formulations were based on HTPB or other urethane binders with a wide variety of other ingredients including AP, insensitive crystalline explosives, sodium nitrate, energetic plasticizers, etc. Reports on alternative binders, additives, and plasticizers were also written at that time and are discussed below.

3. Alternate cast-curable binders. For improving the environmental life-cycle

management, a diisocyanate/polyol combination that can be readily hydrolyzed to non toxic components thus making the solids easier and safer to recover, was proposed as a replacement for Isophorone Diisocyanate (IPDI). Lysine diisocyanate methyl ester (LDIM), available from Toray Corp., was used in hydrolyzable binders in a research program at China Lake in the late 1970's.^{10,11} This work led to the development of an explosive composition, PBXC-125, and a simple method of recovery. PBXC-125 was soaked in dilute (5%) ammonium hydroxide for a day. The binder hydrolyzes to lysine and polyols which are non toxic and the solid explosive is recovered intact. Only RDX was considered for recycling (no aluminum or plasticizer was used). Many but not all of the NAVORD OD 44811 requirements for qualification of explosive main charges were met.

4. Alternate isocyanates. Other diisocyanates¹² have been proposed for use in place of IPDI in AP based propellants. Testing was motivated by the desire to find a domestic source of diisocyanate. Tetramethylxylene diisocyanate (TMXDI), hexamethylene diisocyanate (HDI), 2,4-toluene diisocyanate (TDI), and Dimethyl diisocyanate (DDI) were compared. The conclusion of the paper was that TMXDI, which is not a foreign produced, is superior to IPDI in that it is less toxic, gives comparable mechanical properties and cure times, has a longer pot life, has a lower end of mix viscosity, and only costs 0.3 cents more per pound. The testing program was stopped when IPDI became available from a New Jersey plant (Huls America).¹³

5. Replacing the Plasticizer, Diethyl Adipate (DOA): Triacetin and aliphatic esters (like DOA) would likely have lower toxicity. Compatibility with the binder and processability issues cannot be addressed completely in this evaluation, but a large number of commercial plasticizers are available and well characterized.¹⁴

If inert plasticizers are required for viscosity or processability modification, they would have to be compatible with the new binder in a formulation. Energetic plasticizers are also available. Four generic types which have been scaled to large quantities are listed in Table 3. Nitrate esters and nitrato nitramines provide up to 5% improvement in performance over DOA but suffer from thermal stability problems. BDNPA/F is only slightly better than DOA, and has supply problems already mentioned. FEFO has comparable performance to the nitrate esters and superior thermal stability, but aggressively attacks certain materials.^{15,16} Although DFF has good performance and thermal stability, it is not available in quantity. Other energetic plasticizers^{17,18} do not appear to offer any unique advantages for clean agile manufacturing efforts. The energetic plasticizers are desirable from a performance standpoint, but

are insoluble in HTPB which implies complete reformulation of the HTPB based explosive. They are also probably much more toxic than any of the conventional plasticizers.

6. Demil of Cast Cure Formulations. The major disadvantage of cast-cured explosive formulations like PBXN-109 is that they cannot be easily reprocessed and recycled into other weapons systems or commercial applications because of the chemically crosslinked nature of the cured binder. This crosslinked network allows the formulation to be processed and cast into shape prior to curing and after cure to develop excellent mechanical properties. However, this ease of processing makes it difficult to demil the explosive at the end of its use life.

Table 3. Plasticizers reviewed

Common Name	Chemical Name
TMETN	Trimethylolethane trinitrate
NG	nitroglycerin
FEFO	bis(2,2,2-fluorodinitroethyl)formal
BTTN	1,2,4-Butanetriol trinitrate
ethyl-NENA	Ethyl-2-nitrotoethyl-nitramine
methyl-NENA	methyl-2-nitrotoethyl-nitramine
butyl-NENA	n-butyl-2-nitrotoethyl-nitramine
BDNPA/F	bis(2-fluoro-2,2,-dinitropropyl acetal) or formal
TEGDN	triethyleneglycoldinitrate
DFF	bis(2-fluoro-2,2-dinitroethyl difluoroformal)

B. Clean agile alternatives for PBXN-109 (or generic cast cured explosives)

1. Generic Explosive Formulations.

Assume a new, clean-agile explosive is required as a replacement for PBXN-109 and beyond. What "knobs" could be turned to implement and optimize waste minimization and dual-use/recovery of the explosive components or

complete formulation? To answer this question, the possible explosive formulations and their advantages and disadvantages were considered and certain types which held promise were down selected for further evaluation. The types of explosive considered, their advantages and disadvantages with respect to clean-agile manufacturing, and one application of each explosive type are given in Table 4.

Table 4. Formulation types, advantages and disadvantages for clean-agile manufacturing.

Formulation type	Advantages	Disadvantages	Application
PBX's 95/5:HMX/TPE	Performance mold to shape recycle	more expensive new processing mtd	LX-14 in Shape charges
Cast non-cure (up to 80% HE) TPE N-109	minimum impact on processing; some strength	TPE requires temp control of processing and loading fixtures	PBXN-109 in GP bombs
Pastes (up to 75% HE)	minimum impact on processing; good vulnerability	energetic plasticizers may migrate; solids settling	like Comp C-4
Emulsions	Ease of processing; reuse; dual use	lots of development required	like ANFO
Melt Cast 100% HE and Al	simple processing no extra ingredients	high shrinkage red water if TNT based	Tritanol in AF GP bombs

A particular generic type of formulation described above often suggests various types of binders and plasticizers. Various processes may require specific additives to achieve a desired product. In our efforts we considered binder systems for cast non-cure formulations first. Emphasis was given to energetic binders and plasticizers but inerts were also considered. Next binders for PBX formulations were considered. Then pastes, emulsions and melt cast components were evaluated briefly.

2. Clean-Agile Alternative Binders, Additives and Plasticizers for RDX based

Explosives. Cast non-cure formulations could contain up to 80% solids. In these formulations the crosslinked polyurethane is replaced with either thermoplastic elastomer, thermoreversible gels, or ionomers with labile crosslinks. This class of formulations would also include China Lake's lysine diisocyanate methyl ester, where the crosslinks are hydrolyzable. Up to 80% solids could be achieved with these types of formulations. Scrap and composition errors could be reformulated for the labile network systems by heating above the transition temperature and

reprocessing or blending to meet specs. At the end of the life cycle, the explosive formulation could be removed from the weapon without special water jet or other extraction equipment. Simply heat and pour out the HE. The formulation could then be analyzed and reused if it remained in specs or sold to the mining industry for blasting, etc. The disadvantage with thermoreversible, cast non-cure formulations is the heating requirement for all stages of processing and demil. Gates and runners on any process would need to be heated above the transition temperature and kept hot to prevent plugging until loading operations were complete.

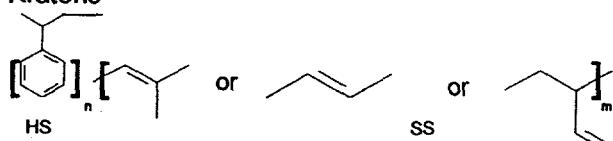
a. *Cast non-cure formulations* require a binder system which will gel or form a network below some phase transition temperature. Binders which might be appropriate for such a formulation are listed below. Energetic or inert plasticizers may be needed to optimize processability. These types of formulations would be relatively easy to implement into current production methods and so they receive the most attention. They also have substantial advantages over cast-cure systems for reuse/dual use and recycling.

Thermoplastic Elastomer (TPE) Binders:¹⁹

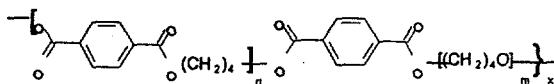
Thermoplastic elastomers are a natural when considering recycling since they are not chemically crosslinked, but rely on phase-separated "hard blocks" to develop the required mechanical properties at use temperatures (e.g., up to 70°). Figure 3 shows the various types of commercial TPEs. When heated above the softening temperature of the hard block, the compound can be cast or extruded as a viscous liquid. After mixing, the excess product can be heated and poured (or chipped) out of the mixer bowl and used again, unlike the current crosslinked systems where the excess simply becomes waste. The same is true for demil operations.

Figure 3. Commercial thermoplastic elastomers.

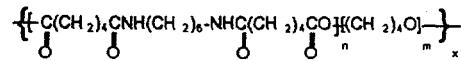
Kratons



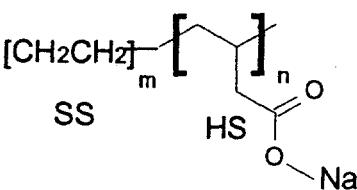
Hytrels



PEBAX



Ionomers (Nafion, Surlyn)

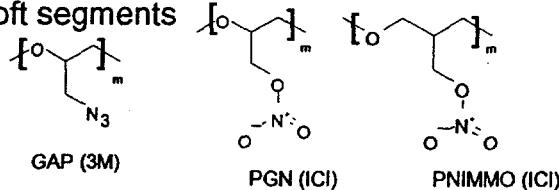


Thermoplastic elastomers have been under investigation as binders for energetic materials for at least 15 years.²⁰⁻²⁶ Early work with commercial glassy TPE's (such as Shell's Kraton) showed that

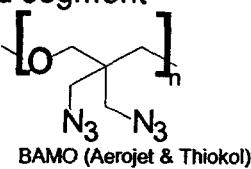
as solids were added at levels greater than 60%, the formulation could no longer be poured or cast due to extremely high viscosity. Twin-screw extrusion is a viable commercial processing technique that could be used for loading high viscosity TPE-bound explosives;²⁷ however, later it was found that crystalline TPEs gave much lower viscosity for a given solids loading. Work by Aerojet²⁸ and by the Navy²⁹ showed that partially crystalline polyolefinic block-TPE's have excellent mechanical properties and can be reheated and easily reprocessed. Later work using crystalline poly(ester-ether)-TPEs (such as DuPont's Hytrel) showed that higher levels of solids in the formulations could be processed.³⁰

Figure 4. Near-commercial energetic oligomeric thermoplastic elastomer components.

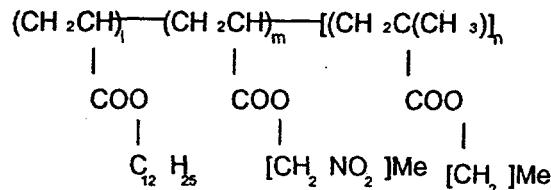
Soft segments



Hard segment



linear acrylic TPE



Although the oxetane polymers which are the precursors of most energetic TPEs have been known for some time,³¹ energetic TPEs³²⁻³⁵ have been formulated into explosives and propellants only recently. Energetic oxetane oligomers which are near commercialization are shown in Figure 4.

GAP,³⁶⁻⁴¹ NIMMO,⁴²⁻⁴⁵ and PGN^{46,47} have glass transitions below ambient and would make reasonable soft segments. BAMMO⁴⁸ is used as the hard segment because it is crystalline and melts at about 80°C. Recently work by Thiokol^{49,50} has shown that energetic polyurethane block-TPE's have satisfactory processability. Macromer technology recently developed by the Navy³⁴ showed that crystalline macromer TPE formulations are able to be processed at even higher solids levels.²⁴

Hydrogenated polybutadiene-co-isoprene (HyBIB and HyBBB) TPEs based on bulk chemicals butadiene and isoprene are being developed by Shell and GenCorp. These diene monomers are polymerized in relatively non-polar solvents under anionic conditions. In the case of the HyBIB, a difunctional center block of isoprene is prepared with flanking blocks of high 1,4 polybutadiene. The resulting ABA block copolymer is hydrogenated to produce an ethylene-propylene alternating center block which has a low T_g and good elastomeric properties. The melting point of the polyethylene A blocks is controllable by selecting the appropriate molecular weight of the segment. In the HyBBB TPEs The end blocks are identical to the HyBIB but the center block is initially a high 1,2-polybutadiene. Hydrogenation of this TPE results in a center block of polybutylene which is also a good elastomer with a low glass transition. Each of these polymers have exhibited excellent mechanical properties as gumstocks and the tailorability needed to optimize for the high loading of solids needed for PEP applications. These materials also have good thermal stability and will be able to handle the harsh conditions of PEP processing. All the inherent advantages of a TPE will be found in these materials.

b. Recyclable Binders For Energetic Formulations: Water-Dispersible TPE And - Hydrolyzable Binders: Formulations based on water-dispersible thermoplastic elastomers (WD-

TPEs) could be easily demilitarized by treatment with hot water, which facilitates separating the energetic ingredients for safe recycle. Recently China Lake³⁴ has developed polyethylene and polyBAMO macromers terminated with a methacrylate function that can be copolymerized with soft vinyl monomers to form thermoplastic elastomers that are potentially useful as binders for energetic materials. They have recently reduced to practice this macromer-TPE concept by copolymerizing a methacrylate-terminated polyethylene with lauryl methacrylate and other acrylic monomers.

A biodegradable polymer which has not received much attention was also suggested by Thiokol.⁵¹ Polyhydroxybutyrate (PHB) is a biopolymer prepared by several organisms in fairly high molecular weight. PHB, as the high molecular weight polymer has been used to make several "environmentally friendly" products since it can be woven and is completely biodegradable. While no solid propellants have been made with PHB, the hydroxyl functional endgroups should lend a reasonable handle for cure chemistry. The highly polar nature of the polymer should be compatible with nitrate ester plasticizers.

c. Summary: Energetic TPEs as binders for formulations which would most nearly emulate PBXN-109 in GP Bombs or M-43 gun propellant are under development by several groups. Thiokol and Aerojet have materials which are most near maturity. Other energetic TPEs would require several years of development. In the area of Biodegradable and reprocessable binders, China Lake's lysine diisocyanate hydrolyzable formulations are the most mature. These crosslinked systems would be difficult to implement as gun propellant formulations but could certainly be formulated into something equivalent energetically to PBXN-109. It remains to be seen whether or not TPEs will be effective as gun propellants. Their advantage is that they could be extruded continuously, but this is a very

different process than the current extrusion used at Indianhead to make M-43. There may also be little advantage to TPEs for recycling and reuse of gun propellant since there is no reason that the current formulation could not be reprocessed unless it is contaminated with D-38. The major advantage of TPEs for gun propellants is if they are energetic. Then they would increase performance over CAB.

3. *Plastic Bonded Explosive*: DOE plastic bonded explosives (PBX's) such as LX-14 offer the advantage of exceptionally high solids content and therefore performance. They can also be molded to shape, and recycled. IHE's such as LX-17 (TATB/Kel-F 800:93/7) can be reprocessed by a procedure developed by Mason & Hanger, Pantex Plant.⁵² This process should be applicable to M-43. However, for GP bombs these explosives would require retooling and large compression molding capabilities. Therefore, they received low priority in the initial screening.

4. *Paste Extrudable Explosives (PEX)*. Paste extrudable explosives (PEX) like C-4⁵³ or LLNL HMX⁵⁴ and TATB⁵⁵ pastes can be loaded to 75% solids. The viscosity can be adjusted by solids particle size distribution to prevent settling and allow processing in nearly any continuous or batch operation so there would be minimal impact on current processing capabilities. Improved vulnerability of paste formulations comes at a slight sacrifice in performance because of lower solids loading. No heat is required to process these explosives. The major disadvantages of paste explosives are migration of plasticizer and settling of solids. Migration of plasticizer will occur whenever plasticizer is used and pastes require plasticization. The issue could be resolved by appropriate bomb design such that the system was completely sealed at moderate pressures. The migration issue can be solved by using thixotropic agents with moderate yield characteristics such as carbon black or fumed silica or polymeric viscosity modifiers. At the end of the life cycle, these materials could be easily removed at ambient,

recertified and reused or extracted and sold to commercial mining or other HE users.

PEX may be the ultimate recyclable explosive. A very viscous, highly loaded explosive such as C-4 is made of a large quantity of RDX in an inert carrier liquid (motor oil) with a polymeric viscosity modifier (polyisobutylene) to prevent the RDX from settling out. C-4 is made by the same process as CXM-7 at Holston AAP. The molding powder is then extruded into bars at Longhorn AAP. LLNL has made PEX in high shear mixers identical to those used for PBXN-109 so no expensive modifications to the production line are required. No heating is required to cause flow and hang-up in the mixer can be cleaned out and saved for reuse in the next mix. Off compositions and mixing errors can be back-blended so that they do not need to be scrapped. Since the formulation doesn't cure, scrap from processing may be recycled easily. Pastes can be made from almost identical materials currently used in cast-cure formulations, but particle size distributions will have to be controlled to minimize viscosity. Some viscosity and thixotropy characteristics are required to prevent settling or migration of the RDX. Weaponization of a PEX such as aluminized C-4 would only require modifying the seals to prevent loss of plasticizer. This should already be in place since PBXN-109 contains DOA which would also migrate.

Recycling, reuse and dual use of PEX would be very cost effective. If the PEX viscosity were the consistency of ketchup, the bomb could be inverted and vibrated slightly and the explosive would pour out at ambient. If other bombs were being manufactured, the PEX could be analyzed easily by HPLC and if no decomposition products were observed, recertified and reused. If variations in the composition were required for underwater application or bunker busting, the PEX could be back-blended and recycled into a different weapons system. If there were no need in the DOD for the explosive at this time, it could be stored, sold to

the mining industry, or the RDX and aluminum could be recovered. Since the particle sizes would be different by an order of magnitude, for optimum viscosity, the binder and plasticizer could be dissolved away and the aluminum could be separated from the RDX by sieving. Both RDX and aluminum could be recovered and reused or sold.

5. *Emulsions*: Emulsions offer very easy reuse/dual use opportunities. ANFO and similar emulsions are made in billion pound quantities for the commercial mining industry. These interesting composite formulations require fuel, oxidizer and explosive or sensitizers and often have large failure diameters making them insensitive. Current formulations like ANFO are relatively reactive with various metals and would have to be inserted in a bladder. There are also major performance and initiation issues which would require substantial development time. For these reasons and because of our unfamiliarity with this area, this type of explosive received low priority.

6. *Melt cast* Melt cast explosives such as tritolal in the Air Force GP bombs have a long history of simple processing and reasonable performance and vulnerability. There are a minimal number of ingredients and the process involves melting the TNT in kettles similar to those used in the candy industry. The major issue here is the red water issue with TNT and the lack of a current US source of this explosive. It may be feasible to replace TNT with TNAZ or a TNAZ eutectic but no candidates have, as yet, received sufficient evaluation to be considered as viable in the next 2-3 years. This does not mean that TNAZ eutectics should be ignored, but performance and safety information are needed prior to major investments in formulation and development. For melt cast explosives end of life cycle demil is possible with existing steam washout equipment. Resale of TNT base explosives is excellent because of familiarity of commercial users with this explosive.

IV. Conclusions

The use of thermoplastic elastomers with semicrystalline hard segments could facilitate recycling of the several hundred pounds of explosive in each GBU-24 bomb. The impact on production would be substantial. The CXM-7 process at Holston could be modified to make TPE-7, the advantage of this are no wet or DOA coated RDX to deal with at the intensive mixing or extruder facility. The processing facility would have fewer steps and no curing. The disadvantage here is that all gates and runners or feeds to the weapon must be heated to $> 80^{\circ}\text{C}$, ie, hundreds of pounds of very hot explosive must be dealt with by the loading crew. There would need to be substantial modification of existing facilities to insure that the TPE-PBX remained hot, otherwise the runners and gates would plug. TPE-PBX demil would also require automation or handling of very hot explosive. Unlike TNT, this material would be viscous. If it were to stick to workers, serious burns would result. One very interesting possibility would be to control the crystal growth rate in the hard segments so that the TPE-PBX could supercool substantially before setting up. This might allow some rework or "pot-life". TPE's have substantial advantages for waste minimization and clean agile manufacturing, but there will be considerable cost in their implementation.

Paste extrudable explosives (PEX) present an alternative to TPE-PBX formulations. They do not require heat in their processing but, of course, they cannot be cured. Paste performance and vulnerability are excellent. PEX could be prepared by Holston in the same manner as C4, processed by continuous or batch processing equipment without temperature or devolatilization requirements, demilled at ambient and requalified or sold for alternate use. The bomb design would require seals around the fuse well to prevent loss

of energetic carrier liquids, but otherwise minimal impact on production is expected. PEX would not be suitable for gun propellant.

Highly filled PBX's and low viscosity emulsions would have major impacts on bomb production and be difficult to implement. Liquid gun propellants might be prepared as emulsions making transportation and recycling easier.

Melt cast formulations which do not present the pink water problem are very attractive. Considerable processing equipment is already available for war surge requirements. Unfortunately, there are several issues such as vapor pressure and lower melting temperature which need to be resolved before TNAZ becomes a 1 to 1 replacement for TNT. This approach is very attractive, however and probably should be pursued.

V. References

1. A. J. Beardell, A. Grabowsky, P. Hui and P. Lu, "Insensitive Propellants for Artillery", in Joint Government/Industry Symposium on Insensitive Munitions Technology, ADPA Proceedings, March 1990.
2. J.K. Otic, P.T. Reardon, R.Y. Parker and S. Nielson, "Life Cycle Inventory Predictions for the GBU-24 and M-900 Weapon Systems", CAMPEP Program Review, Washington, DC, Sept 1994
3. T.N. Hall and J.R. Holden, Navy Explosives Handbook, NSWC MP 88-116, Naval Surface Warfare Center, Dahlgren, VA (Oct 1988).
4. Private communication, Teresa Wise, Indian Head Divn. NSWC, June 1994.
5. R. Damavarapu, M. Mezger, J.M. Lovatob and K. Baumb, "New approaches to Synthesize of BDNPA/F", in US Army ARDEC DEA-A-76-G-1218 1994 Annual Meeting on Energetic Materials for Munitions, Edwards AFB, Edwards, CA (June 1994)
6. M. Mezger, T. Manning and B. Strauss, "Evaluation of bis(2,2-dinitropropyl formal and bis(2,2-dinitrobutyl) formal as a replacement for Nitroplasticizer in Insensitive High Explosive Compositions." in US Army ARDEC DEA-A-76-G-1218 1994 Annual Meeting on Energetic Materials for Munitions, Edwards AFB, Edwards, CA (June 1994)
7. G. A. Green, "Explosive Fill Baseline Status, Options and Selection Strategy", Adv. Bomb Family Quart. Rev., May 1990, China Lake, CA"
8. J. Leahy, "Preliminary Report of the Performance Evaluation of Candidate Explosives for the Advanced Bomb Family", US Navy, White Oak, MD, Dec. 1991.
9. J.C. Roquemore, "Advanced Bomb Family DT-IIA Explosive Fill Cookoff Evaluation Tests," NWCTP 7070, US Navy, White Oak, MD, February 1990.
10. B.Y.S. Lee, U. S. Patent #4,293,352 and NWC TP 6313, (Oct 1988) and R. Reed, personal communication, 27 May 1994 NAWCWPNS, Naval Weapons Center, China Lake, CA
11. B.Y.S. Lee, "Degradable and Hydrolyzable Binder Explosives, in US Army ARDEC DEA-A-76-G-1218 1992 Annual Meeting on Energetic Materials for Munitions, NAWCWPNS, China Lake, CA, (Sept. 1992) pp. 48-80
12. M. E. Ducote, "Evaluation of a New Curative TMXDI in HTPB Propellants." (TR-RD-PR-89-3) Naval Weapons Center, China Lake, CA, February 1990
13. Personal communication in April, 1994 with Mark Kram and Richard Hardy, NSWC, Indian

Head Division, Yorktown, VA; and John Leahy, NSWC, White Oak, MD

14. J.K. Sears and J.R. Darby, *The Technology of Plasticizers*, John Wiley & Sons, New York 1982

15. A.E. Oberth, *Principles of Solid Propellant Development*, CPIA # 469, Johns Hopkins University (1987)

16 R.A. Rhein, *Handbook of Energetic Polymers and Plasticizers*, NWC TP 6720 (July 1986) Naval Weapons Center, China Lake, CA.

17. K. Scribner, R. Elson, R. Fyfe, and J.P. Cramer, "Physical, Stability and Sensitivity Properties of Liquid Explosives", in Sixth Symposium on Detonation, Naval Surface Weapons Center White Oak, MD August 1976, p. 466

18. E.M. Williams, K.J. Graham, and R.D. Lynch, *New Explosives Concepts Technology*, TR-PL-13452, Atlantic Research Corp, (July 1993)

19. B.P. Grady and S.L. Cooper in "Science and Technol of Rubber, 2nd Ed., (J.E. Mark, B. Erman and F.R. Eirich, eds) Academic Press 1994, pp 601-674.

20. G.B. Butler, "Investigation of Thermoplastic Elastomers as Propellant Binders, Final Report," November 1979, Grant DAAG29-76-G-223.

21. J.A. Chien, " Annual Report on Thermoplastic Elastomers as LOVA Binders," December 1983, Technical Report No. 1, Contract # N00C14-83-K-0083.

22. L.H. Sperling, "Characterization of Novel Binders Based On Energetic Thermoplastic Elastomers," End of Fiscal Year Report October 1, 1983-September 30, 1984, Contract No. N00014-82-K-0050.

23. G.A. Lindsay, "Thermoplastic Elastomers in Energetic Formulations," July 1987, NWC TP 6805.

24. E.A. Murphy, T. Ntozakhe, C.J. Murphy, J.J. Fay, and L.H. Sperling, Characterization of Poly(3,3 bisethoxymethyl Oxetane) and Poly (3,3-Bisazidomethyl Oxetane) and their block Copolymers, *J. Appl. Polym. Sci.*, 37, 267 (1989)

25. C. Gotzmer and N. Johnson, Unpublished results, NSWC- WO (1987)

26. J. Akhavan and T.C. Burke, *Polymer Binders for High Performance Explosives, Propellants, Exp. and Pyrotech.*, 17, 271 (1992)

27. B. Nahlovsky in "Thermoplastic Elastomers as Solid Rocket Propellant Binders," CPIA Publication 519, pp. 77-86, 25 May 1989.

28. R.L.Willer, J.A. Hartwell, D.J. Park and P.J. Kaste, "Advances in TPE LOVA Gun Propellants".

29. M. Chan and J. Hoover, "Explosive Ingredients Evaluation (U), "NWC Technical Paper 6400-34, March 1990, China Lake, CA.

30. M.A.H. Talukder, et al. "Explosive Ingredients Evaluation (U),"NAWCWPNS Technical Paper 6400-48, Oct. 1993, China Lake, CA; NAWCWPNS Technical Memo 7750-01 and -02, April 1994, China Lake, CA.

31. T.D. Wilson, "New Solid Rocket Propellant Polymer Binder Materials", CPTR 87-42 Chemical Propulsion Information Agency, Johns Hopkins Univ., Laurel , MD (August 1987)

32. R.B. Wardle , "Method of Producing Thermoplastic Elastomers having Alternate Crystalline Structure for use as Binders in High-Energy Compositions:, US Patent 4,806,613 (Feb. 1989)

33. G.E. Manser and R.W. Fletcher, Synthesis of Energetic Thermoplastic Elastomers, Final Report Feb 1990, Aerojet Solid Propulsion, Sacramento CA
34. T.M. Atienza Moore, New Binders for Life Cycle Management of Explosives, 1st Conference on Life Cycles of Energetic Materials, Picacho Plaza Hotel, Santa Fe, MN, (Oct 1993)
35. E. Ahad, "Azido Thermoplastic Elastomers, US Patent 5,223,056, Jun 29 1993
36. P.F. Alelio and AP Manzara, "GAP Benefits", Proc. ADPA Int. Symp. on Energetic Mats. Technol. Oct 1992, pp. 144-150.
37. T.F. Comfort and J.D. Altland, 3M GAP Formulation Study, Final Report (Sept 1, 1993), Hercules Inc.
38. E. Ahad, "Branched Energetic Polyether Elastomers, US Patent 5,191,034 (March 1993)
39. E. Ahad, "Branched Energetic Polyether Elastomers, US Patent 5,130,381 (March 1993)
40. E. Ahad, "Direct Conversion of Epichlorohydrin to Glycidyl Azide Polymer", US Patent 4,891,438 (Jan. 1990)
41. T. Keicher and F-W Wasmann, Polymers with High-Energy Substituents: Polyesters Containing Azidomethyl Groups, Prop. Exp. & Pyrotech., 17, 182 (1992)
42. G. Begg, M.J. Stewart, W.B.H Leeming and P.F. Swinton, "Manufacture of Energetic Binders Using N_2O_5 " in Energetics Technical Papers, 1, ICI Explosives, Stevenston, Ayrshire, Scotland (1991)
43. D. Debenham, W.B.H. Leeming and E.J. Marshall, "New Energetic Formulations containing Nitratopolyethers" in Energetics Technical Papers, 1, ICI Explosives, Stevenston, Ayrshire, Scotland (1991)
44. H. Desai, A.V. Cunliffe, M.J. Stewart and A.J. Amass, "Synthesis of narrow Molecular Weight Distribution α,ω -Hydroxy Telechelic Polyoxetane by the Activated Monomer Mechanism", Polym. 34, 642 (1993).
45. H. Desai, A. V. Cunliffe, P.J. Honey and M.J. Stewart, "Synthesis and Characterization of α,ω -Nitrato Telechelic Oligomers of 3,3-(nitratomethyl methyl oxetane (NIMMO) and glycidyl nitrate (GLYN)", Proc. ADPA Int. Symp. on Energetic Mats. Technol. March 1994, pp. 272-301.
46. R. L Willer, "Poly(glycidyl nitrate): Synthesis and Energetic Formulations" Y789172B (160), Thiokol Corp, Elkton, MD. (1991)
47. A. Davis, D. Anderson, B. Clememts, M.E. Colclough, A. V. Cunliffe, and F.A. Kirby, AWE/DRA Energetic Binder Contract, Quarterly Progress Reports July and Oct 1992.
48. R.B. Wardle, W.W. Edwards, J.C. Hinshaw, R.L. Willer, and D.J. Parks, "Polyoxetane Thermoplastic Elastomers as Gun Propellant Binders,
49. R.B. Wardle, I.A. Wallace, R.R. Bennett, R.M. Hatch and R. S. Hamilton, "Development of an Oxetane Binder, Poly(BAMO/AMMO) as an Insensitive Propellant Binder", Proc. ADPA Int. Symp on Energetic Mats. Technol. March 1994, pp. 386-391.
50. T.S. Sumrall and W.H. Graham, "Melt Castable PBXW-124/125 Development", ADPA Insensitive Munitions Technology Symposium, Williamsburg, VA June 1992 pp. 167-175
51. R.B. Wardle, private communication, (1994)

52. G. Osborn, "Semi-Continuous Processing of explosives, Joint Explosives Processing Committee Meeting, DOE/AL/65030-942B, Oct. 1994.
53. W.L McVey, D.T. Chesnut and F.H. Berry, private communication and unpublished results (1994).
54. E. Von Holtz, D.M. Hoffman, and R.E. Whipple, "Paste-Extrudable Explosives (PEX)", in Energetic Materials Program Review; Special Issue: Formulations, UCRL-LR-109534-92-1, (Feb. 1992)
55. D.M. Hoffman, C.M. Walkup, L.E. Spellman, W. Tao and C. Tarver, "Transferable Insensitive Explosives (TIE), in preparation.