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**This paper reviews the current status and future trends of aluminized explosives. The major focus is on cast compositions, which encompass both the melt-cast trinitrotoluene (TNT) based and the slurry cast polymer-based compositions. Widely reported RDX and HMX based aluminized compositions with TNT used as a binder are discussed in detail. Various researchers have suggested a 15–20**% **Al content as an optimum from the viewpoint of velocity of detonation. A higher Al content, however, is incorporated in most of the compositions for a sustained blast effect, due to the potential of secondary reactions of Al with detonation products. The effect of the aluminum particle size on performance parameters (velocity of detonation, etc.) is included. There are some recent works on nanometric Al based compositions, and the results obtained by various researchers suggest mixed trends for RDX–TNT compositions. Studies on nitrotriazol and TNT based compositions bring out their low vulnerability. Some of the interesting findings on ammonium dinitramide and bis(2,2,2 trinitro-ethyl)nitramine (BTNEN) based compositions are also included. The review brings out superiority of polymer based aluminized explosives, as compared to conventional TNT based compositions, particularly, with respect to low vulnerability. In general, aluminized plastic bonded explosives find numerous underwater applications. Ammonium perchlorate (AP) is also incorporated, particularly, for enhancing underwater shock wave and bubble energy. Hydroxyl terminated polybutadiene appears to be the binder of choice. However, nitrocellulose, polyethylene glycol, and polycaprolactone polymer based compositions with energetic plasticizers, like bis-dinitropropyl acetal/formal (BDNPA/F, 1/1 mix), trimethylol ethane trinitrate, and triethylene glycol dinitrate are also investigated. Polyethylene glycol and polycaprolactone polymer based compositions are found to be low vulnerable, particularly, in terms of shock sensitivity. Highly insensitive polymer bonded nitrotriazol based compositions are being pursued all over the globe. The highly insensitive CL-20/AP combination meets the demands of high density and high velocity of detonation. Glycidyl azide polymer and poly nitratomethyl methyl oxetane appear to be binders of interest for plastic bonded explosives in view of their superior energetics. The vulnerability aspects of these compositions, however, need to be studied in detail. Brief information on plastic bonded and gelled thermobaric explosives is also included.**

**Key words: PBX, HTPB, CL-20, FOX-7, RDX, HMX, NTO, trinitrotoluene, cyclotetramethylene tetranitramine, cyclotrimethylene trinitramine, aluminum, particle size, velocity of detonation, insensitive munitions, munitions with attenuated risk.**

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# **Notations**



# **INTRODUCTION**

Advent of RDX and HMX led to giant strides in the area of high blast explosives. RDX and HMX used in conventional TNT based cast compositions contribute toward improvement in velocity of detonation of the explosive composition due to superior heat of formation, oxygen balance, and density. It leads to improved fragment velocity and jet energy of warheads. The improvement in impulse leading to greater cratering and fragmentation effects requires addition of metal powder (Al, B, and Zr), generally aluminum [1–3]. Anderson [4] has reviewed the use of Al powder in plastic bonded explosives and established its potential as a total energy enhancer.

The first use of Al to increase the blast performance of explosives was patented by Roth in 1900 [1]. Exhaustive studies have been carried out to evaluate the effect of the Al content on the characteristics of explosive compositions [5]. Al powder is available in a number of grades and particle sizes ranging from a "bomb" grade flake (MIL-A-512) to spherical particles  $(<10 \ \mu m)$ (MIL-A-23950). Nanometric aluminum has also evinced interest during recent times.

Owing to the involvement of Al in secondary reactions in the Taylor rarefaction region behind the detonation wave, the classical thermochemical codes based on the Jones–Wilkins–Lee (JWL) and Becker– Kistiakowsky–Wilson (BKW) equations of state of explosion products do not provide accurate descriptions of the detonation phenomenon. Consequently, prediction of performance of these nonideal explosives is a difficult task. Over the last three decades, there has been a continued effort to understand the chemical, thermodynamic, and hydrodynamic interaction between decomposition products of composite explosives. However, it is widely accepted that the reaction of Al is relatively slow in the Chapman–Jouguet plane due to coating of Al particle by  $\text{Al}_2\text{O}_3$  having a high melting point  $(2030°C)$ , which impedes its reactivity. Thereby, a large amount of energy is liberated during subsequent reactions of Al with primary detonation products of high explosives, leading to sustained high pressure for longer duration [6]. The overall outcome of Al incorporation in high explosives is the enhancement of late-time effects, such as higher temperature, incendiary effect, air blast, and enhanced damage due to bubble energy during underwater blast [7].

Exhaustive studies have brought out that the velocity of detonation of cast charges continuously decreases on addition of Al beyond 20% [8–10]. It has been established that the heat of explosion  $Q_v$  increases with increasing Al content  $C_{\text{Al}}$  [11], whereas the volume of

#### TABLE 1

Effect of Aluminum Content on Heat of Explosion and Volume of Gaseous Products for TNT/Al Compositions

$C_{\text{Al}}$ , %	$Q_v$ , kJ/kg	$V_0$ , liter/g	$Q_vV_0,$ 10 <sup>4</sup> kJ·liter/kg <sup>2</sup>
0	4226	0.750	318
9	5188	0.693	360
18	6485	0.586	381
25	7280	0.474	343
32	7657	0.375	289
40	8452	0.261	222

gaseous products  $V_0$  decreases (Table 1). Consequently, the maximum power  $Q_vV_0$  is reached at the 18% Al content, and the optimum content of Al is considered to be 20%. Nevertheless, explosive compositions with a higher Al content are of interest for blast producing compositions. Brisance of aluminized compositions increases with the Al content up to 70% Al [9]. They are also of interest for underwater applications.

The basic chemical processes involving Al in the explosion phenomenon resulting in the blast effect are summarized below:

 $2Al_{(s)} + 3H_2O_{(g)} \rightarrow Al_2O_{(s)} + 3H_{2(g)} + 866 \text{ kJ/mole},$  $2\text{Al}_{(s)} + 3\text{CO}_{2(g)} \rightarrow \text{Al}_{2}\text{O}_{3(s)} + 3\text{CO}_{(g)} + 741 \text{ kJ/mole},$  $2\text{Al}_{(s)} + 3\text{CO}_{(g)} \rightarrow \text{Al}_2\text{O}_{3(s)} + 3\text{C}_{(s)} + 1251 \text{ kJ/mole}$ (the subscripts "s" and "g" refer to the solid and gas

phases, respectively).

The pressure–time profile of the aluminized composition exhibits a relatively lower pressure, but the pressure is sustained for a longer duration (by a factor of 2 or 3), as compared to that in the case of corresponding non-aluminized explosives, due to an exothermic reaction of Al with detonation products behind the reaction zone in the detonation wave front [12]. It is well known that Al reacts not only with oxygen fractions of detonation products but also with the nitrogen fraction to form aluminum nitride AlN:

$$
2Al_{(s)} + N_{2(g)} \rightarrow 2AlN_{(s)} + 346 \text{ kJ/mole.}
$$

The above-given reaction schemes suggest that Al oxidation may occur with reduction of  $H_2O$  to  $H_2$  and with reduction of  $CO<sub>2</sub>$  to either CO or solid carbon C. Application of the BKW code does not indicate formation of solid carbon. However, Volk et al. [13] have experimentally established significant involvement of Al toward reduction of  $CO<sub>2</sub>$  to solid carbon. Based on the analysis of detonation products [13], Baudin and



<b>TNT</b>	$80/20$ TNT/Al
227	
$-73.9$	$-72$
$-44.2$	$-44.2$
$-62.5\,$	
1210	1770
1.654	$1.71 - 1.78$ (theoretical) 1.793)
240	
6.9	$6.52$ for $\rho = 1.77$ g/cm <sup>3</sup>
90	84
17.8	11.0

TABLE 3 Effect of Aluminum Particle Size on the TNT/Al System



Bergues [14] concluded that only 18% of the molar fraction of  $H_2O$  and up to 50% of the molar fraction of  $CO_2$ were reduced by Al. The energy contribution  $Q_{A1}$  of this reaction pattern is 20.126 MJ/kg of Al. An empirical reactive flow model coupled with reaction kinetics for detonation and combustion was developed by Miller et al. [15] on the basis of experimental finding and thermochemical calculations. Baudin and Bergues [14] studied the reaction behavior of Al, HMX, and AP based high explosives. They developed a model for predicting high explosive performance in aerial small-scale tests and underwater explosions.

Although aluminized RDX and HMX based compositions with TNT as a binder find wide application in today's scenario, efforts are on to develop insensitive munitions (IM) widely known as munitions with attenuated risk (MURAT) to ensure that it does not detonate under any conditions other than its intended mission to incapacitate a target. Insensitive munitions utilize a polymeric binder in place of TNT in the compositions. It is desired that the munitions be immune to the impact of high-velocity fragments or a bullet and burn rather than detonate at extreme temperatures generated due to fire. The safety during packing, handling, transportation, and storage of insensitive munitions is high relative to that of conventional munitions.

# **1. CONVENTIONAL TNT BASED EXPLOSIVE COMPOSITIONS**

# **1.1. TNT/Al Compositions**

The well-reported aluminized explosive composition Tritonal contains 80% TNT and 20% flaked Al [16]. It was developed and standardized in the USA during WWII for realizing an improved blast effect. The blast properties of Tritonal (80/20) are widely reported in the literature [17–19] (see Table 2).

Tritonal is a general-purpose composition with moderately good performance for fragmentation and air-blast applications, particularly, in navy and air force bombs [4]. The desensitized tritonal is referred as destex.

Tao et al. [20] studied the effect of the particle size a on the heat release rate using Fabry–Perot laser interferometery. Brosseau [21] reported that addition of nanometric Al (Alex) to the TNT/Al system leads to a remarkable increase in velocity of detonation D as well as heat of detonation Q*<sup>d</sup>* (Table 3).

# **1.2. Aluminized RDX/TNT Based Compositions**

This class of explosive compositions is finding wide application in current scenario in view of much superior performance than tritonal. Although incorporation of Al in Composition B results in lowering of velocity of detonation, it leads to an increase in heat of detonation (Table 4) [22–23]. However, Gurney constants<sup>2</sup> ( $G_C$ ) for aluminized and non-aluminized explosive compositions lead to contradictory results. Thus, Torpex (18% Al) shows  $G_C = 2710$  m/sec close to cyclotol  $(70/30)$ RDX/TNT) and higher than those for RDX and composition B  $(G_C = 2680 \text{ m/sec})$ . On the other hand, H-6, HBX-1, HBX-3, and tritonal exhibit smaller G*<sup>C</sup>*

 $^{2}$ Energetic coefficient calculated per unit mass of the explosive charge, which characterizes the velocity of motion of body fragments.

### TABLE 4



Characteristics of Aluminized RDX/HMX/TNT Systems

**Note.** p is the maximal pressure in the detonation wave.

### TABLE 5





values, as compared to non-aluminized Composition B.

Dentex, Torpex, H-6, HBX-1, and HBX-3 are examples of well-known aluminized cyclotol (RDX/TNT) compositions. Dentex, Torpex, and H-6 are generalpurpose explosive compositions, like tritonal, whereas HBX-1 and HBX-3 find application in underwater mines and torpedoes. HBX-3 is a preferred choice for achieving the maximum bubble energy.

It is reported that incorporation of nanometric Al in Composition B instead of micro-sized Al leads to reduction in velocity of detonation, in contrast to the case with TNT where the velocity of detonation increases. Reduction in the Al particle size is found to increase heat of detonation of Composition B (Table 5) as in the case of tritonal [27–29].

#### **1.3. Aluminized HMX Based Compositions**

According to the general trend, addition of Al to the HMX/TNT based composition also leads to reduction in velocity of detonation (Table 6). The Al incorporated octol, designated as HTA-3 [30], finds application for its blast capability combined with brisance.

Gogulya et al. [31] determined the effect of variation in the Al content and particle size on the temperature and pressure profiles of the HMX/Al compositions (Table 7). They monitored the interaction of Al with HMX detonation products using a dual-channel pyrometer interfaced with a LiF window.

The results of the study [31] indicate that velocity of detonation of the HMX/Al combination is of higher magnitude in the case of compositions containing Al particles with  $a = 150 \mu m$ . The peak pressures for compositions containing Al particles with  $a = 150, 20$ , and  $0.5 \mu$ m, however, are commensurable. Gogulya et al. [31] also found that incorporation of 5% Al in HMX led to slightly higher or nearly the same temperature of detonation products in the first microsecond as for pure HMX (3772◦C) irrespective of the Al particle size. An increase in the Al content, however, led to a decrease in temperature of detonation products below the level typical for pure HMX, except in the case of a mixture with  $25\%$  Al of 150  $\mu$ m size. They interpreted that the energy needed for Al heating is compensated by the heat released during oxidation up to 5% Al. It was inferred that the relative sizes of Al and HMX particles played a major role. HMX particles of size less than that of Al  $(a = 150 \ \mu m)$  surround the latter and are available for the detonation reaction, whereas  $a = 0.5 \mu m$  Al particles being of smaller size than HMX, the latter are

Aluminized HMX/TNT Based Compositions

Explosive	$\rho$ , g/cm <sup>3</sup>	D, km/sec		$p, GPa \mid \Delta H_f, \text{kcal/mole}$	$G_C$ , m/sec
Octol: $70/30$ HMX/TNT	1.72	8.40			
HTA-3: $49/29/22$ HMX/TNT/Al	1.946	7.87		$1.05$ [30]	
H-6: $45.1/29.2/21.0/4.7$ RDX/TNT/Al/D2 Wax	1.76	7.49	24.5	$-1.09$ [24]	2620

#### TABLE 7

HMX/Al Characteristics Depending on the Al Particle Size and Content [31]

$a, \mu m$	$C_{\text{Al}}, \, \%$	$\rho,$ $\rm g/cm^3$	$\rho/\rho_{\rm max}$ , %	$D, \mathrm{km/sec}$	$p_{\text{max}}$ , GPa
Pure <b>HMX</b>		1.81		8.76	43.2
150	$\overline{5}$	1.84	95	8.74	38.8
	15	1.89	95	8.66	36.3
	25	1.95	95	8.55	32.1
50	5 15 25	1.84 1.88 1.93	95 94 94	8.73 8.63 8.44	$33.5 \pm 0.2$
20	5	1.83	95	8.72	40.0
	15	1.87	94	8.55	35.0
	25	1.92	93	8.37	35.0
0.5	$\overline{5}$	1.84	95	8.66	40.2
	15	1.87	94	8.35	34.5
	25	1.91	93	7.97	24.5

enveloped in a layer of Al particles in this case, leading to inhibition of HMX decomposition in the detonation wave front. This is reflected in the pressure drop being slower in the case of compositions with 150  $\mu$ m Al.

# **1.4. Aluminized PETN Based Compositions**

The explosive parameters determined for PETN/Al systems (Table 8) also reveal that velocity of detonation reaches the highest value for the composition with the lowest Al content.

Tao et al. [20] studied aluminized PETN using Fabry–Perot laser interferometery. They analyzed thermodynamics and hydrodynamics of detonation by applying the reactive flow model for the nature of the reaction zone and subsequent expansion of reaction products (Taylor wave). It was inferred that high detonation temperatures of PETN increased the mass transport rate and, hence, shorten the Al reaction time scale.



Explosive Parameters for PETN/Al Systems [20]



# **2. LOW VULNERABLE NTO/TNT BASED COMPOSITIONS**

It is well known that NTO belongs to the category of insensitive explosives being much less vulnerable to hazard stimuli than RDX/HMX. Extensive work on melt-cast compositions containing NTO/TNT/Al has been undertaken at U.S. Air Force (USAF) [19] to realize low vulnerability despite of using TNT as a binder. These compositions are designated as TNTO (Table 9).

To overcome the exudation problem observed due to low melting D2 Wax in TNTO IV, which is also known as the AFX-644 (air force explosive) composition, D2 Wax was substituted with a combination of Indramic-800 and Ganex WP-660 (98.5/1.5) in the composition AFX-645. The velocity of detonation of AFX-644 and AFX-645 were almost similar to that of the Tritonal standard. Their friction and impact sensitivities are beyond the upper limit of the instrument, suggesting that NTO based compositions are most likely candidates of extremely insensitive detonating substances (EIDS) and may meet the criteria of insensitive munitions of the HD 1.6 classification for both storage and transportation.

# **3. ADN AND BTNEN AS COMPONENTS OF ALUMINIZED EXPLOSIVE COMPOSITIONS**

# **3.1. ADN Based Composition**

Miller et al. [15] studied pressed aluminized ADN compositions. Their velocity of detonation, however, is on lower side, and even addition of nanometric Al did

Sensitivity and Performance of Melt-Cast Aluminized TNT/NTO

Composition NTO/TNT/Al/binder	$\rho$ , g/cm <sup>3</sup>	$D, \mathrm{km/sec}$	$d_{\rm cr}$ , mm	$H_{50\%}$ , cm	H	$H_e$ , J
TNTO 0 $38/40/16/6$ (D2 Wax)				>200.5	41.2	0.040
TNTO I $42/34/19/5$ (D2 Wax)	1.76	6.67	$25 - 51$	>200.5		
TNTO II 42/32/19/7 (D2 Wax)	1.74	6.84	$32 - 35$	>200.5	53.0	0.040
TNTO III 42/30/19/9 (D2 Wax)				>200.5		
TNTO IV 40/30/20/10 (D2 Wax)	1.70	6.96	$41 - 43$	>200.5	60.8	0.040
AFX-645 48/32/12/8 (I-800 Ganex) [18]	1.63	6.83	$51 - 64$	>200.5	60.8	0.040

**Notes.**  $H_{50\%}$  is the sensitivity to impact (load of 5 kg), H is the sensitivity to friction determined by the BAM method (BAM is an abbreviation for the Federal Institute for Materials Research and Testing, Germany), H*<sup>e</sup>* is the sensitivity to the electrostatic discharge, and  $d_{cr}$  is the critical diameter.

not influence velocity of detonation of ADN in its physical mixtures. Viton was found to have a positive effect on increasing velocity of detonation (Table 10, where  $\rho_{\text{max}}$  is the maximum theoretical density;  $\bar{\rho}$  and  $\bar{D}$  are the average values of density and velocity of detonation).

### **3.2. BTNEN Based Compositions**



Molecular formula:  $C_4H_4O_{14}N_8$ Molecular weight: 388.21 Density:  $1.96$  g/cm<sup>3</sup> Heat of formation: nearly zero Oxygen balance:  $+16.5\%$ Velocity of detonation: 8.5–8.66 km/sec Particle size: needle-shaped crystals  $15-40 \mu m$  in diameter and up to 500  $\mu$ m long

Gogulya et al. [31] investigated the effect of Al and its particle size in a BTNEN based composition. They prepared 85/15 BTNEN/Al combinations by mixing the components in a metal vessel in an inert liquid (hexane) in the presence of porcelain balls. A uniform distribution of Al particles in bulk was established by microscopic studies. BTNEN needles were transformed to elongated particles during the process, with the transverse size approximately equal to the diameter of original needles. The explosive charges 20 and 40 mm in diameter were pressed by applying cold unidirectional pressing to achieve density of about 93% of the theoretical value. These researchers observed that addition of Al results in a decrease in velocity of detonation and peak pressure  $p_{\text{max}}$  (Table 11). They observed that BTNEN renders the composition more sensitive than even typical secondary explosives including PETN. It may be an outcome of a positive oxygen balance of BTNEN in contrast to a negative oxygen balance of RDX and HMX. BTNEN mixtures with 0.1  $\mu$ m Al particles are even more sensitive (Table 12). This is attributed to chemical interaction of BTNEN decomposition products with Al in hot spots [32].

#### **4. PLASTIC BONDED EXPLOSIVES**

TNT based compositions are not able to retain the structural integrity on heating by frictional forces in high-speed supersonic missile systems eventually leading to "hot spot" formation. It renders the system prone to fast cook-off temperature and may result in premature functioning/explosion in the trajectory. Storage at high temperatures, particularly, in tropical countries also limits the storage life of TNT based ammunitions. Plastic bonded explosives (PBX) based on a polymeric binder offer a superior solution. Moreover, aluminized PBX compositions have low end-off viscosity, as compared to TNT based aluminized compositions, rendering filling and casting into warheads an easy task. The Al particle size in the range of  $a = 120{\text -}250 \ \mu \text{m}$  is akin to achieve low viscosity.

Composition	$\bar{\rho}$ , g/cm <sup>3</sup>	$\bar{D}$ , km/sec	$\rho/\rho_{\rm max},\%$
<b>ADN</b>	1.69 1.604	4.24 4.19	92.2 87.2
72/25 ADN/Al $(3 \ \mu m \text{ Al})$	1.794	4.10	90.5
$73/23/3$ ADN/Al/Viton $(50 \ \mu m \text{ Al})$	1.714	5.03	86.3
97/3 ADN/Viton	1.752 1.735	4.25 4.06	95.0 94.0

Explosive Properties of Pressable ADN/Al Based Compositions with a Change in Al Particle Size [15]

Properties of the 85/15 BTNEN/Al Composition [31]

$a, \mu$ m (charge diameter)	$\rho$ , g/cm <sup>3</sup>	$\rho/\rho_{\rm max},\%$	D, km/sec	$p_{\text{max}}$ , GPa $(\rho, g/cm^3)$	$Q_v$ , kJ/kg $(\rho, g/cm^3)$
$\overline{0}$	1.870	95.4	8.50	36.4(1.88)	5230(1.89)
$\overline{0}$	1.909	97.4	8.66		
150(20)	1.965	96.1	8.38		8280 (1.94)
15(20)	1.955	95.6	8.30	35.6(1.97)	8280 (1.94)
7(20)	1.955	95.6	8.28		8600 (1.94)
0.1(20)	1.910	93.4	8.07	34.1(1.92)	
0.1(20)	1.914	93.6	8.04		
0.1(40)	1.900	93.0	7.92		8350 (1.90)
0.1(40)	1.830	89.5	7.66		

# TABLE 12

TABLE 10

Critical Pressure of Explosions: Comparison of Mechanical Sensitivity

Explosive	$p_{cr}$ , GPa
Mercury fulminate/lead azide	$0.20 \pm 0.01/0.38 \pm 0.03$
<b>PETN</b>	$0.93 \pm 0.03$
<b>BTNEN</b>	$0.79 \pm 0.03$
TNT/RDX/HMX	$1.35 \pm 0.03/1.15 \pm 0.03/1.00 \pm 0.03$
BTNEN/Al $(0.1 \ \mu m)/(7.0 \ \mu m)$	$0.55 \pm 0.02/0.74 \pm 0.02$
$HMX/A1 (0.1 \mu m)/(7.0 \mu m)$	$0.67 \pm 0.03/0.95 \pm 0.03$

# **4.1. RDX/HMX Based PBX Compositions**

Development of aluminized PBX compositions for underwater applications commenced in the late 1950s. Both pressed and castable PBX compositions were introduced during the 1960s [33]. Castable non-aluminized PBX compositions based on Laminacstyrene binders were developed at the initial stage. PBXN-101 (82/18 HMX/Laminac-styrene), PBXN-102

(59/23/18 HMX/Al/Laminac-styrene), and PBXN-104 (70/30 HMX/Laminac-styrene) belong to this class. They became obsolete, however, due to drawbacks of being physically hard and highly sensitive, as was revealed by large-scale sensitivity tests. PEG and HTPB evinced interest as binders in PBX compositions instead of Laminac-styrene [4]. However, HTPB became a preferred choice as a binder. Aluminized PBX compositions based on RDX with HTPB as a binder are widely

TABLE 13





#### TABLE 14

Composition and Explosive Properties of Aluminized PBX Compositions [39]

RDX/Al/HTPB composition	$\rho_{\text{max}},$ g/cm <sup>3</sup>	ρ, $g/cm^3$	D. km/sec	$p_{d,calc}$ GP <sub>a</sub>
85/0/15	1.586	1.578	7.66	23.8
80/5/15	1.609	1.594	7.53	22.9
75/10/15	1.630	1.610	7.50	22.3
70/15/15	1.670	1.630	7.58	22.4
65/20/15	1.680	1.646	7.26	22.0
60/25/15	1.709	1.680	7.11	21.8

reported in the literature (Table 13). These compositions are reported to be inducted as the main charge fills in the anti-ship Penguin missile, Hellfire missile [34], and penetrator bombs, as well as for underwater applications.

The effect of the Al content on the performance of RDX-HTPB based aluminized PBX compositions was also studied at the High Energy Materials Research Laboratory (HEMRL, Pune, India) [39]. The Al content of 15% was found to be the optimum value in terms of velocity of detonation of the aluminized composition (Table 14). The aluminized PBX compositions developed at HEMRL exhibited low impact sensitivity  $(H_{50\%} = 115{\text -}129)$  and high chemical stability: they evolved less than  $1 \text{ cm}^3$  of the gas in a vacuum stability test at 120◦C for 48 h. The compression strength of the compositions ranged from 1 to 1.2 MPa.

Volk and Schedlbauer [40] observed a decrease in density  $(1.63 \text{ to } 1.62 \text{ g/cm}^3)$  and velocity of detonation (7580 to 7350 m/sec) of HXA-123 (70/15/15  $RDX/Al/HTPB$ ) on introduction of 5  $\mu$ m Al (Alcan 400) to an extent of 15%. A life assessment study of Rowanex 1400 (66/22/12 RDX/Al/HTPB) has been undertaken at 60◦C for 15 months. The sam-

# TABLE 15





ples withdrawn at different intervals were subjected to chemical analysis, differential thermal analysis (DTA), differential scanning calorimetry (DSC), and spectroscopic studies, as well as dynamical mechanical analysis (DMA). The simulation studies predicted a shelf life of 20 years [41, 42].

HMX based aluminized compositions are also well studied. As expected, they offer superior density and velocity of detonation, as compared to aluminized RDX based compositions (Table 15).

Radwan [46] studied the effect of incorporation of Al up to 30% at the cost of octogen (HMX) in polyurethane binder based PBX compositions, to the reference 84/16 HMX/PU composition. His findings (Table 16) revealed a decrease in brisance  $(B)$  and specific volume  $(V_0)$  of gases produced, as well as in velocity of detonation to an extent of  $\approx 5\%$ , whereas the heat of explosion  $(Q_v)$  and the temperature of explosion  $(T_v)$  exhibited a marked increase. The force of explosion  $(F)$  reached the maximum value at a 15% Al content. The power of the explosive in terms of the characteristic product  $Q_vV_0$ , i.e., the heat of explosion and brisance, reached the maximum value at a 25% Al content. The sensitivity to impact  $(H_{50\%})$ decreased markedly (20%) with an increase in the Al content. However, the compositions were sensitive to detonator No. 8. A typical aluminized HMX based composition  $(65/20/15$  HMX/Al/HTPB) is assigned a life of 67 years at  $25^{\circ}$ C [47].

Polycaprolactone (PCP) is also finding application as a binder for cast PBX compositions. The major advantage of PCP over HTPB is its miscibility with the nitrate ester class of plasticizers [48, 49]. The PCP/TMETN combination offers an advantage of low vulnerability without penalty on energetics. Aluminized HMX/PCP based compositions are also reported [17] (see Table 17).

Measured and Calculated Characteristics of Aluminized HMX Based PBX Compositions [46]

$C_{\text{Al}}$ , %	D, km/sec	B, kPa	$V_0, \text{ cm}^3/\text{g}$	$Q_v$ , kJ/kg	$T_v$ , K	$H_{50\%}$ , cm	$F$ , kJ/g	$V_0 Q_v$ , $10^4 \text{kJ} \cdot \text{liter/kg}^2$
$\overline{0}$	7.01	1073	1030	3974	2974	50	1.145	409
$\overline{5}$		1070	972	4694	3320	53	1.197	456
10		1059	902	5500	3715	56	1.244	496
15	6.82	1050	831	6286	4070	60	1.237	522
20		972	760	7072	4410	66	1.184	537
25		948	689	7858	4730	71	1.027	541
30	5.64	868	631	8031	4870	74	0.964	506

TABLE 17

Performance of PCP Based Aluminized Compositions [17]

Explosive	HMX/Al/TMETN/PCP composition	$\rho$ , g/cm <sup>3</sup>	D, km/sec	$Q_n^*, \, \%$
$RX-35-DW$	49.5/18/24.84/7.66	1.765	7.33	105
$RX-35-EN$	43.89/23.13/25.24/7.74	1.787	7.20	117
$RX-35-EK$	39.49/27.98/24.83/7.70	1.814	7.06	148

**Note.**  $Q_v^*$  is the blast energy, as compared to tritonal  $(80/20 \text{ TNT/Al})$ .

# TABLE 18

Composition and Characteristics of AP Incorporated Aluminized PBX Compositions

Explosive	$RDX/AP/AI/HTPB$ composition	$\rho$ , g/cm <sup>3</sup>	D, km/sec	$d_{\rm cr}$ , mm
PBXW-115/PBXN-111 [51]		1.790	$5.97 - 6.20$	37.6
DXD-03 [52]	20/43/25/12	1.78	$5.49 - 5.70$	
B 2211/PBXW-115(Aust) [51, 53]		$1.79 - 1.81$	5.50	$65 - 86$
$FPX-7 [51]$	20/40/25/15	1.80	5.50	50
KS-57 [37, 38, 54]	24/40/24/12	1.84	5.62	64
HXA-174 [35]	27/25/30/18	1.70	5.87	
$CD-06$ [43]	35/23/32/10	1.81	6.98	
HXA-178 <sup>[35]</sup>	42/25/15/18	1.63	6.63	
PBXN-103 [55] (PBXW-100)	AP/Al/NC/TMETN-TEGDN (40/27/4/25/2.3)	1.89	$6.20 - 6.31$	27.3
PBXN-105 [55]	RDX/AP/Al/PEG/(BDNPA/F) (7/49.8/25.8/3.13/14.47)	1.90	5.90	60.9
PBXW-123 [50]	AP/Al/TMETN/PCP (44.8/30.2/18.8/6.2)	1.92	5.50	>126

# **4.2. AP Incorporated Aluminized PBX Compositions**

AP based PBX compositions (Table 18) with HTPB as a binder are reported in the literature, particularly, for underwater applications to enhance underwater shock wave and bubble energy. PBXW-115 or PBXN-111 offer a superior alternative to conventional aluminized explosive compositions. PBX compositions equivalent to PBXW-115 also appear under different designations (see Table 18). Variations in reported characteristics of these compositions, particularly, with re-

Influence of Al and AP on the Total Energy and Detonation Energy [4]



#### TABLE 20

Performance/Application Equivalency of PBX with Conventional TNT Based Compositions [4]

Explosive type	Warhead	Equivalent compositions			
and application	applications	$non-PBX$	<b>PBX</b>		
General purpose	Bomb filling	$H-6$ Tritonal	PBXN-109 (64/20/16 RDX/Al/binder) PBXC-117 (71/17/12 RDX/Al/binder)		
High brisance	Shaped charges, fragmentation	Octol	$\text{PBXN-110}$ (88/12 HMX/binder)		
<b>Brisance</b>	Shaped charges, fragmentation	Composition B Cyclotols	PBXN-106 (75/25 RDX/binder) PBXN-107 (86/14 RDX/binder) PBXW-108 (85/15 RDX/binder) $AFX-108$ $(82/18$ RDX/binder)		
Metal acceleration	Shaped charges	Tetryl $CH-6$	PBXN-5 (95/05 HMX/binder) PBXN-6 (95/05 RDX/binder) PBXN-7 (60/35/05 RDX/Al/binder)		
Underwater shock, and bubble	Torpedoes, mines: anti-devices	$H-6$ $HBX-1$	PBXN-103 $(40/27/33 AP/Al/binder)$ PBXN-105 (7.0/49.8/25.8/17.4 RDX/AP/Al/binder) PBXW-115 (20/43/25/12 RDX/AP/Al/binder)		

spect to the critical diameter, is probably due to different sources of RDX used in the composition. Nitrocellulose (NC) and PEG binder based compositions are also mentioned in the literature. PEG based compositions offer a higher critical diameter. A typical PCP based composition with a critical diameter >126 mm is reported as PBXW-123. The composition exhibits initiation with a shock wave of 8 GPa, as compared to 5.9 GPa for PBXN-103 [50].

Incorporation of AP as replacement of RDX results in significant improvement in the total energy  $Q_{\Sigma}$ , whereas the detonation energy  $Q_d$  decreases [4] (Table 19).

AP incorporated HMX based PBX compositions have also evinced interest. Baudin and Bergues [56] studied the reaction behavior of Al in the HMX based composition B3103 (51/19/30 HMX/Al/binder) and HMX/AP based high explosive composition

B3100 (42/9/19/30 HMX/AP/Al/binder). Composition B3312 (51/19/30 HMX/LiF/binder) was selected as a reference explosive, where Al was replaced by LiF having mechanical impedance characteristics similar to Al and being known to remain inert in a reactive medium. Almost similar velocities of detonation for explosives B3103 (7760 m/sec) and B3212 (7790 m/sec) clearly established that Al acts like LiF and is not oxidized in the Chapman–Jouguet plane. Replacement of HMX with AP resulted in improved ballistic performance, which may be due to additional supply of oxygen made available by AP for the greater extent of the oxidation process.

Aluminized PBX compositions having performance almost equivalent to that of aluminized TNT based explosives are potential candidates for a wide range of systems (Table 20) with the added advantage of low vulnerability.

Explosive	<b>NTO</b>	<b>RDX</b>	<b>HMX</b>	AP	Al	<b>Binder</b>
PBXW-121 [58]	63	10			15	12 (HTPB)
PBXW-122 [59, 60]	47	5		20	15	13 (HTPB)
PBXW-124 [60]	27	20		20	20	13 (HTPB)
PBXW-125 [60]	22	20		20	26	12 (HTPB)
PBXW-126 [60, 61]	22	20		20	26	12 (PU)
B 2245 [62]	8	12		43	25	12 (HTPB)
B 2233 [63]	31		6	28	10	15 (HTPB)
PBXW-125 mod. 2 [17]	10	25		20	33	12 (HTPB)

French "B series" and American PBXW Compositions

TABLE 22

Composition of GAP Based Aluminized PBX Compositions (with and without AP) [7]

Explosive	<b>RDX</b>	Al	GAP	AP
GHX 86	82		18	
<b>GHX 78</b>	67	15	18	
GHX 83	62	20	18	
<b>GHX 84</b>	57	25	18	
GHX 85	52	30	18	
<b>GHX 87</b>	42	40	18	
GHX 89	27	50	18	
GHX 99	47	$30^{(a)}$	23	
<b>GHX 100</b>	47	$30^{(b)}$	23	
<b>GHX 101</b>	47	$30^{(c)}$	23	
GHX 76	42	15	18	25
GHX 80	37	20	18	25
<b>GHX 81</b>	32	25	18	25
<b>GHX 82</b>	27	30	18	25

**Notes.** (a) Specific surface  $0.134 \text{ m}^2/\text{g}$  and average particle size 150  $\mu$ m; (b) specific surface 0.229 m<sup>2</sup>/g and average particle size 50  $\mu$ m; (c) specific surface 1.144 m<sup>2</sup>/g and average particle size 5  $\mu$ m.

#### **4.3. NTO Based Aluminized PBX Compositions**

An exhaustive review on NTO based explosive compositions containing AP and Al is published by Smith and Cliff [57]. AP incorporated NTO based aluminized PBX compositions were developed at SNPE and designated as "B series" compositions, which are referred as PBXW in the USA (Table 21).

PBXW-126 having a density of 1.80  $g/cm<sup>3</sup>$  and velocity of detonation of 6.47 km/sec with a detonation pressure of 16.0 GPa [64] is reported to be superior among PBXW compositions. The peak pressure generated by PBXW-126 is found to be 1.29 times to that of TNT and 1.22 times to that of PBXN-109 [64]. Its delivered impulse is 1.06 and 1.25 times of that of TNT and PBXN-109, respectively. The unconfined critical diameter of PBXW-126 is smaller than 76 mm, establishing its high order of insensitivity. PBXW-124 and PBXW-122 have critical diameters of 76–109 and 178 mm, respectively, meeting the insensitivity criteria. A variant of PBXW-125 referred as mod. 2 is claimed to be more effective for application in warheads used against hard targets [17].

# **4.4. GAP and PolyNIMMO Based Aluminized PBX Compositions**

Keicher et al. [7] studied aluminized PBX compositions (Table 22) with GAP plasticized with 1/1 BDNPA/F as a binder cured with Desmodur N-100. The better oxygen balance of GAP assists in completion of reactions of Al. Keicher et al. [7] observed nearly the same impulse and peak pressure for the formulations containing Al in the range of 15–33%. A further increase in the Al content resulted in a decrease in the peak pressure. The bubble energy reached the maximum value at a 40% Al content.

Incorporation of AP in the compositions (see, e.g., GHX 76 and GHX 82 in Table 22) results in an increase in the bubble energy, although the peak pressure remains unaffected. Although the bubble energy increases with the Al content, the Al particle size  $(5-150 \ \mu m)$  did not have any significant effect on it. The pressure and impulse were also not influenced by the Al contents up

TABLE 23





to 30%. Langer et al. [65] have found that partial replacement of coarse AP by fine AP in RDX/GAP based aluminized compositions leads to improvement in velocity of detonation and to a decrease in impact, as well as sensitivity to friction (Table 23).

Recently, CL-20 has also found application as an explosive component of aluminized AP compositions for underwater explosions. Incorporation of CL-20 results in a remarkable increase in density and velocity of detonation, as compared to GAP based RDX/AP/Al compositions, due to inherent higher density and velocity of detonation, as well as improved oxygen balance of CL-20 proper (Table 24).

Aluminized NTO and HMX combination based plastic bonded explosive compositions with 10% Poly NitroMethyl Methyl Oxetane (PolyNIMMO) as a binder and 10% K-10 as an energetic plasticizer developed in UK are designated as CPX. CPX 458 offers superior velocity of detonation among the reported CPX compositions (Table 25).

# **4.5. Thermobaric PBX Compositions**

Thermobaric (TB) compositions are aimed at generation of high overpressure in enclosed spaces, such as caves and bunkers, and are most suitable to modern warfare threats. In 2003, the Naval Surface Warfare Center Indian Head Division (NSWC IHD) and the Talley Defense Systems (TDS) worked together to develop solid TB compositions containing a moderate-tohigh Al content for lightweight shoulder-launched penetrating or anti-cave warhead for the M72 LAW system [66]. Various compositions developed by NSWC-IHD with PBXIH-135 as the baseline composition are summarized in Table 26.

Hall and Knowlton [67] reported thermobaric compositions based on wax, HTPB, or GAP as a binder. The challenge of their study was to determine comparative TB characteristics for chosen composition in confined tests. They observed the highest impulse and average peak pressure for GAP based compositions. Ti/HTPB based compositions were found superior to the corresponding Al based compositions in terms of the average peak pressure and impulse. The researchers also studied compositions containing GAP in combination with propriety energetic plasticizers and achieved the average impulse up to  $975 \text{ kPa} \cdot \text{msec}$ . Hall and Knowlton [67] reported gelled thermobaric compositions incorporating  $60-70\%$  Mg/Al/Ti/Zr as a fuel with 20–30% energetic liquid nitromethane (NM) and isopropyl nitrate (IPN). NM based compositions exhibited a higher impulse, as compared to IPN based compositions. AN/AP/HMX are also incorporated as oxidizer/energetic components. The researchers found compatibility for all the combinations. The best results were obtained with the 30/30/40 NM/Al/HMX combination in terms of the average peak pressure (0.5 MPa) and average impulse  $(802 \text{ kPa} \cdot \text{msec})$ .

# **CONCLUSIONS**

Although the precise reaction of Al with detonation products is not understood fully to this day, it is widely accepted that the consumption of Al takes place over a longer time scale, as compared to TNT, RDX, or HMX. The investigation into the detonation performance of aluminized high explosive compositions [33] has revealed that the influence of Al on performance of the composition depends mainly on the nature of the high explosive and on the Al particle size. The Al consumed on the sonic (Chapman–Jouguet) surface can support the detonation front. The positive effect is observed for high explosives both with positive or negative oxygen balance, provided that there is a higher content of hydrogen and a lower content of carbon in a molecule [18]. Fine Al particles are expected to be consumed more rapidly in the CHNO reaction zone, as compared to larger particles. A tangible effect of the particle size of nanometric Al, however, can be revealed only if the time of Al interaction with detonation products is rather small. Many times contradictory results have been obtained. It has been observed that

Explosive Properties of CL-20 Based Underwater Explosives [35]

						Explosive CL-20   Al   AP   GAP $\rho$ , g/cm <sup>3</sup>   D, km/sec
GHX-106	27	30			1.95	6.87
GHX-107	22	35	25	18	1.96	6.58

# TABLE 25

Characteristics of CPX Compositions

Explosive	NTO/HMX/Al	PolyNIMMO	$K-10$	$\rho$ , g/cm <sup>3</sup>	D. km/sec
<b>CPX 450</b>	40/20/20	10	10		
CPX 455	40/20/20	10	10		
CPX 458	30/30/20	10	10	1.85	7.68
CPX 459	20/40/20	10	10	1.86	7.76
<b>CPX 460</b>	27.5/27.5/25	10	10	1.88	6.42

# TABLE 26

Explosive Compositions Developed at NSWC IHD



a decrease in Al particle size down to submicron and nanometric size is accompanied by a higher fraction of the oxide film  $(Al_2O_3)$  film on the Al particles, which may be responsible for decreased performance of Al in certain cases. Introduction of AP in aluminized PBX compositions led to bubble energies superior than that of HBX-3. The additional total energy derived from the oxygen content of AP entails a greater extent of the oxidation reaction enhancing the underwater and air-blast performance.

Castable PBX compositions with 97% of the theoretical density and solid loading of 87–88% have been realized. Introduction of EIDS opens a new avenue in PBX research and a possibility of achieving the objective of developing compositions with the hazard class 1.6 (insensitive munitions). The Indian Head of the U.S. defence has introduced a series of EIDS. I-RDX ("improved" RDX) is being investigated as a component of aluminized explosives to achieve improvement with respect to insensitivity. PBXIH-135 (HMX/Al/PU) is one of the best examples categorized under thermobaric (thermo means "high temperature" and baric means "high pressure") warhead systems. These insensitive munitions can be used against tunnels, caves, bunkers, and hard surfaces. Supersonic missiles and bombfill of the General Purpose category (500 and 2000 pound) de-

mand insensitive munitions. In general, all the military services are undertaking the task of replacing the existing TNT based main charges with insensitive explosives, mainly cast plastic bonded explosives with higher solid loading and better mechanical properties, as well as higher lethal performance. Efforts are on to develop explosive compositions based on insensitive explosives, such as FOX-7, which may proliferate to the aluminized class of explosives. HEMRL is also working in this direction. A series of aluminized PBX compositions have been evaluated and selected ones have been subjected to underwater testing.

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