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Characteristics of cast PBX with aluminium

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The results of research of cast composite explosives based on octogene and polyurethane binder (PBX) containing aluminium are presented. Influence of Al and HMX content and particle dispersion on rheological, physical-chemical, mechanical and explosive characteristics of PBX is investigated. It was established that the presence of metal powder has a significant effect on composite explosives' characteristics, especially on detonation wave parameters. The PBX detonation velocity and pressure, as well as the particle velocity and shock sensitivity are reduced and chemical reaction zone width and duration are increased with increased content of aluminium.

Key words: **cast explosives, composite explosives, octogene, polyurethane binder, aluminium, detonation parameters.**

Abbreviations

TNT	– Trinitrotoluene
PBX	– Polimer Bonded eXplosives
UbS	– Ammunition
HTPB, R45	– Hydroxyl terminated polybutadiene
NP,BDNPA/F	– Bis (2,2 dinitropropyl) acetal / formal (1/1)
FEFO	– Bis(2-fluor-2,2 dinitroethyl) formal,
DFF	– Bis(2-fluor-2,2 dinitroethyl difluor) formal
PGN	– Poliglicidyl-nitrate Polimer
GAP	– Glicidyl Azide Polymer
BTTN	– Butanetriol Trinitrate
TMETN	– Trimethylolethane trinitrate
PolyNMMO	– Polymer of 2-Nitratomethyl-3-methyloxetane
K10	– Dinitroethylbezene / Trinitroethylbenzene (65/35)
TEGDN	– Triethylene glycol dinitrate
PEG	– Polyethylene glycol
NC	– Nitrocellulose
DOA	– Dioctyladipate
IDP	– Isodecyl pelargonate
PU	– Polyurethane
PCL	– Polycaprolactone
NTO (ONTA)	– 3-Nitro-1,2,4-Triazole-5-One
HMX	– Cyclotetramethylenetetranitramine, Octogen
RDX	– Cyclotrimethylenetrinitramine, Hexogen
TDI	– Toluenediisocyanate
FH-5	– Phlegmatized hexogen
GRDT	– Plane wave generator

Introduction

MORE explicit demands for explosive charges quality and limitations in the application of conventional, TNT-based compounds have stimulated the research of a new generation of cast high-energy explosives.

Unvulnerable, the so called "lova" explosives, containaining polymer binder along with the crystall brisance explosive, have been produced in attempt to decrease the ammunition vulnerability and reduce the danger from undersigned stimuli. Due to the rubber-elastic properties of the binder, these composite compounds have small sensitivity to mechanical effect, decreased sensitivity to detonation transmition and can withstand high impulse loads.

Cast PBX development has started in the early 60th of XX century for the needs of US navy and has continued ever since. It developes in three ways /1/:

- Compounds with inert polymer binder (polyurethane binder based on poliol or HTPB),
- Compounds with inert binder and energetic plasticyzer (nytroplasticyzer BDNPA/F, FEFO, DFF),
- Compounds with energetic binder, with or without energetic plasticizer (nytro- and azide-oxetanes, PGN, GAP, BTTN, TMETN or TEGDN, PolyNIMMO, K10).

PBX are divided into three categories, based on their energetic blast potencial:

- Brisance – without Aluminium; they are used as explosive charge for blast and shaped missiles,
- Aluminized compounds; they are loaded in avio bombs and underwater armament,
- Blast explosives which contain an oxidizer (ammonium-perchlorate), besides aluminium, and which are used for underwater purpose and specific actions.

Most frequently, all three categories have been developed based on the same or similar binder (main prepolymer). RDX and HMX have been used as explosive components of composite compounds, and as binders, the most comercial are polymers based on polyurethane HTPB-elastomers with modified characteristics. Polymer mechanic characteristics are used for estimating the time of usage, because recent research indicates that mechanical

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stability is the characteristic which limits the exploation of PBX systems.

The possibility to use new high explosives with high performances has of recent been intensively researched. The most frequent replacement for hexogen and octogen, with the aim of sensitivity reduction, has been ONTO (ONTA), high-energy explosive with load density of 1.91 g/cm³ and detonation velocity of 8590 m/s, which is used for aluminized compounds and compounds with oxidizer examination in combination with RDX/HMX [2].

The composition and characteristics of standardized PBX are presented in Table 1 [3].

Table 1. Cast PBX composition and characteristics

Cast explosive	PBX composition (mas.%)								Characteristics	
	Explosive/Inert component				Binder component					
	HMX	RDX	Al	AP	Polymer/Plasticizer	Polymer	Plasticizer	Additive	ρ (g/cm³)	**D** (m/s)
PBXN-103	-	-	27.0	40.0	NC/TMETN/TEGDN					
PBXN-105	-	7.0	25.8	49.8	PEG/NP	3.13	12.92	1.35	-	-
PBXN-106 PBXW-106	-	75.0	-	-	PEG/NP	4.50	18.55		1.634	7840
PBXN-107 PBXC-116	-	86.0	-	-	Acrilat/-	14.00	-		1.650	-
PBXN-109 PBXW-109	-	64.0	20.0	-	R45/DOA	7.35	7.35	1.30	1.660	7600
PBXN-110	88.0	-	-	-	R45/IDP	5.37	5.37		1.672	8330
PBXW-107	-	55.0	20.0	-	PEG/NP	4.50	18.55	1.95	1.757	-
PBXW-114	78.0	-	10.0	-	R45/IDP	5.37	5.37	1.27	1.711	-
PBXN-111	-	20	25.0	43.0	R45/IDP	5.70	5.70	0.60	1.782	5700
PBXW-123	-	-	30.2	44.8	PCL/TMETN	4.20	18.8	2.0	1.92	5560
PBXW-126	-	20.0 22.0*	26.0	20.0	PU	12.00	-	-	1.80	6470
Note: *- NTO (ONTA)										

Aluminium is abviously a component of most standardized PBX. Its presence affects specific detonation behavior of these explosives, which stands out from the clasical detonation theory of condensed systems, because chemical reactions have been realised throught stages:

- Crystall explosive components decomposition (primary reaction),
- Al ignition and
- Al oxidation and supplementary combustion in detonation products' flow (secundary reaction).

The final detonation stage of aluminized exposives is determined by the content, dispersity and mechanism of aluminium oxidation in the detonation wave. The detonation heat increases with the increase of metal powder content, and therefore the PBX blast effect is more significant.

PBX are homogenous suspensions, from rheological point of view, in which the dispersion phase is the polymer binder, and dispersion means are crystall explosive and Al/oxidizer. Rheological behaviour of these mixtures, whose viscosity must not be too high for better dispersing of solid components and not too low to prevent sedimentation, is influenced by compounds and mixing conditions. It is important to point out that time dependance of PBX viscosity is a nonlinear function because viscosity change is caused by the reactions of polymer binder curing.

The subject of this article are PBX with aluminium. Octogen is used as explosive component and polyurethane elastomere as polymer binder. The influence of Al powder on rheological, physical, mechanical and explosive characteristics of the explosives is examined.

Experimental results and discusion

PBX processing

PBX are produced by using technologycal process defined in [4]. Technological parameters and content of solid phase (80 mass %.) were constant in all experiments. Al content in composite compounds varied from (10 - 30) mass %. Next raw materials were used:

- Bimodal mixture of coarse (HMX-K or HMX-K/2) and fine (HMX-S) octogen fraction,
- Al powder; mean radius is 15 μm and 45 μm and
- Polyurethane binder, prepared by toluene diisocyanate (TDI) polycondensation and polyethar poliol [5].

Three octogen granulation for producing cast explosives, HMX-I, HMX-II and HMX-III, were obtained by mixing HMX-K (200-600) μm and HMX-S (50-150) μm in mass ratio 70:30, 85:15 and 55:45, respectively. The fourth granulation, HMX-IV, was prepared by mixing HMX-K/2 (100-800) μm and HMX-S in mass ratio 85:15. The distribution of octogen particle size is shown in Figures 1-4.

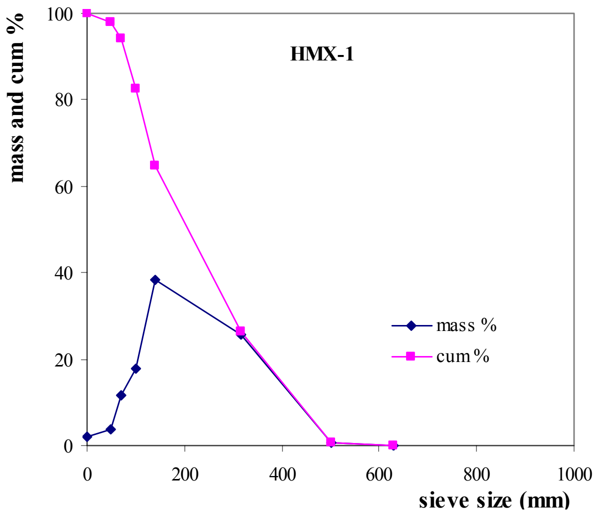

Figure 1. Particle size distribution curve for HMX-I

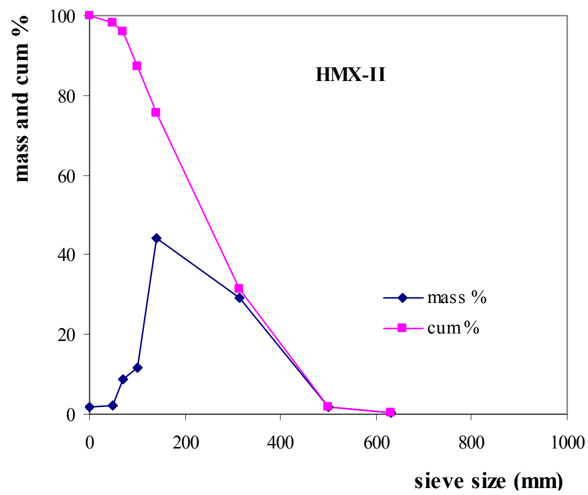

Figure 2. Particle size distribution curve for HMX-II

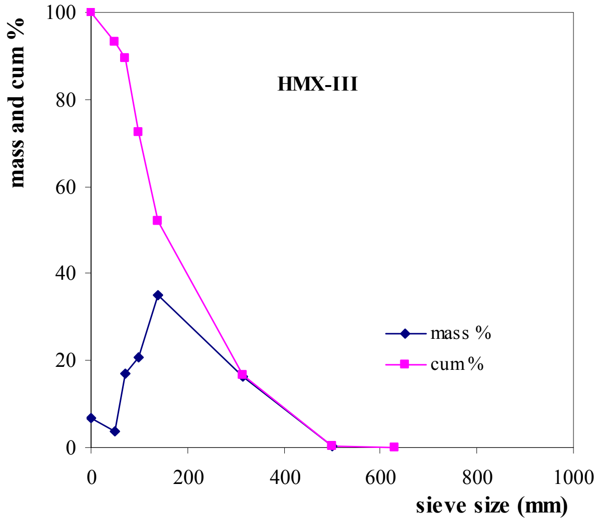

Figure 3. Particle size distribution curve for HMX-III

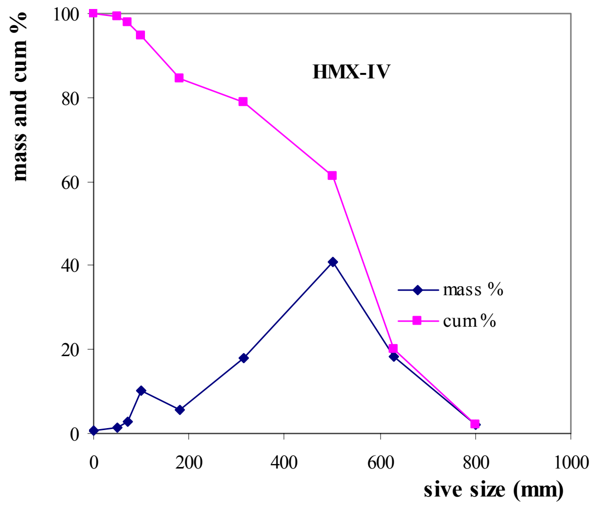

Figure 4. Particle size distribution curve for HMX-IV

With this quality of starting components cast explosives with 20 mass % of polyurethane binder, (50-70) mass % of HMX and (10-30) mass % of Al were prepared.

Rheological and physico-chemical characteristics of PBX

Time dependence of PBX viscosity was examined, depending on the following factors:

- Al particle magnitude,
- Granulometric content of PBX bimodal mixture and
- Al mass part in the composite compound.

Viscosity measuring was performed at the temperature of 30°C, on Brookfield viscosimeter of HBT type and spindle velocity of 5 min^{-1}.

PBX physico-chemical characteristics, depending on octogen and aluminium content and dispersion, were analysed by density determining on six segments of explosive charge and by calculating the relative porosity (ν).

Table 2 shows the compound, start values and main characteristics of the cast PBX. Time depedence of viscosity for the analysed compounds (PBX-1 to PBX-8) is shown in Fig.5. Fig.6 shows positive Al influence on processing characteristics. Distribution of density in compliance with the charge height and its depedence on mass proportion of Al are presented in Figures 7 and 8.

Table 2. Compound and PBX characteristics

PBX	PBX (mass.%) compound HMX and Al granulation		Viscosity (Pa.s)	ρ_e (g/cm^3)	ν(%)
	HMX	Al d_{sr} (μm)			
PBX-1	80 HMX-I	- -	104	1,583	3,20
PBX-2	50 HMX-II	30 45	104	1,715	3,04
PBX-3	70 HMX- III	10 45	248	1,620	3,40
PBX-4	70 HMX- III	10 15	256	1,627	2,97
PBX-5	70 HMX-II	10 15	144	1,677	1,79
PBX-6	50 HMX-II	30 15	64	1,768	3,06
PBX-7	60 HMX-I	20 15	88	1,722	2,04
PBX-8	70 HMX-II	10 45	168	1,622	3,26
PBX-9	70 HMX-IV	10 15	-	1,602	4,39
PBX-10	60 HMX-IV	20 15	-	1,660	3,60
PBX-11	50 HMX-IV	30 15	-	1,691	4,28

$\nu = (1-\rho_e/\rho_T) \times 100$ (%),
ρ_e - experimental value of density, g/cm^3,
ρ_T - theoretical value of density , g/cm^3.

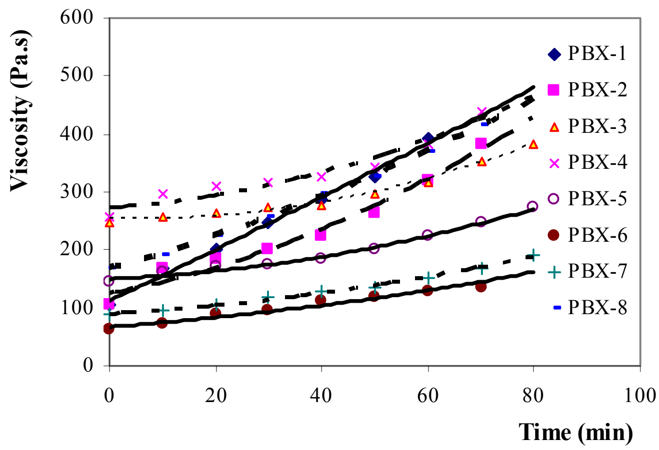

Figure 5. $\eta(t)$ dependence in function of PBX compound

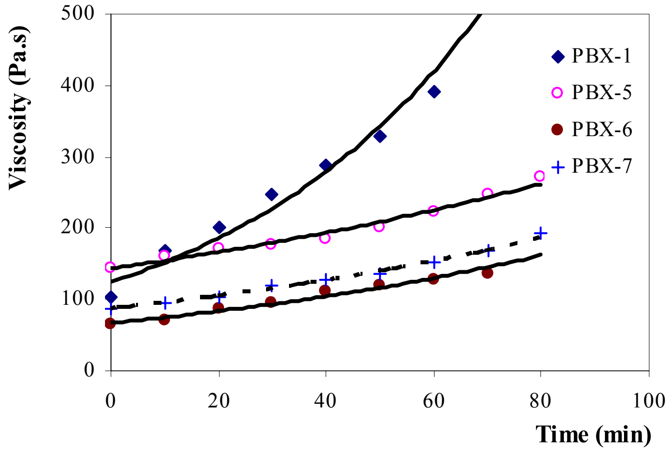

Figure 6. PBX viscosity in function of Al content.

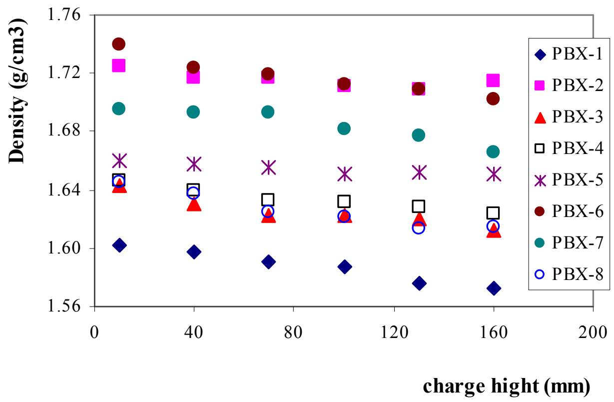

Figure 7. Distribution of charge segment density

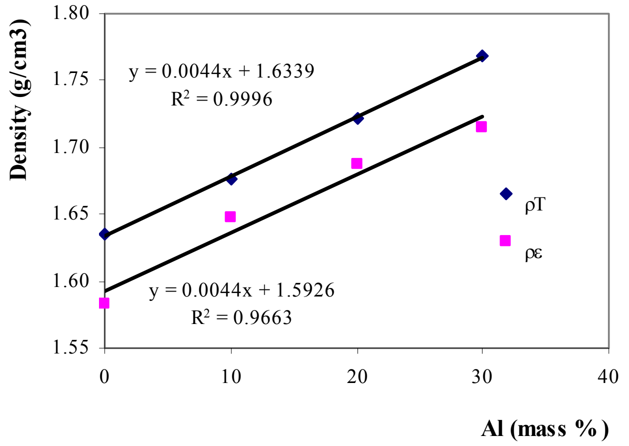

Figure 8. Influence of Al mass portion on PBX density

It can be seen that a significant influence on rheological characteristics of composite compound is exhibited by content and particle size distribution of octogen and Al, Figures 5 and 6. PBX viscosity has a tendency of decreasing by geting aluminum into composite compound, compared with compound without Al. Also, it can be noted that viscosity increasing with curing time is more tempered with aluminised compounds.

Presented results of density measuring and density distribution curves (Table 2, Figures 7 and 8) indicate a relatively uniform density distribution in compliance with the hight of explosive charge. Porosity value is in the range between 1,79 and 4,28 %, so it can be concluded that homogeneous composite explosives have been obtained.

The influence of HMX and Al granulometric compounds on PBX density value (and porosity) is most apparent when manifested on compounds with 10 mass % of Al. PBX density was (1,602-1,647) g/cm³ depending on solid ingredients granulation. The most advantageous are HMX-I (octogen granulation with 15 mass % of fine fraction) and aluminium with middle diameter of 15 μm for practical use.

As it is illustrated in Fig.8, PBX density linearly increases with mass portion of Al increasing in the composite compound.

Thermal stability of PBX-1, PBX-9, PBX-10 and PBX-11 has also been examined. This was done on DSC, with heating velocity of 10ºC. PBX decomposition temperature (Table 3) was determined based on the obtained thermograms. Representative thermograms are shown in Figures 9 and 10.

Table 3. PBX decomposition temperature

PBX (mass % Al)	T (°C)
PBX-1 (without Al)	261,32
PBX-9 (10)	264,86
PBX-10 (20)	256,82
PBX-11 (30)	258,37

Based on the results, it can be concluded that thermaly stabilised PBX, which are applicable for ammunition laboration from the safeness point of view, were obtained.

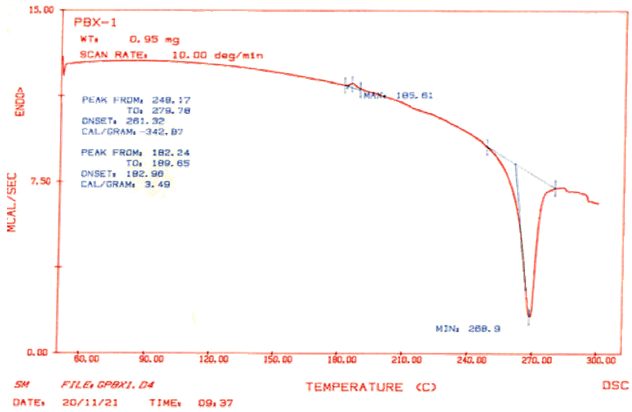

Figure 9. DSC thermogram of PBX-1.

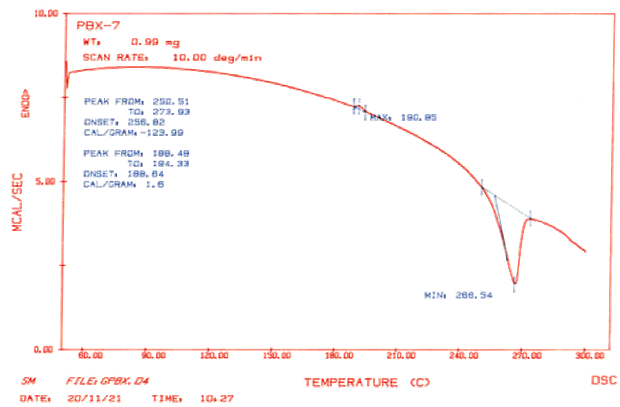

Figure 10. DSC thermogram of PBX-10

PBX mechanical characteristics

Mechanical characteristics of the three compounds, PBX-9, PBX-10 and PBX-11 (with 10, 20 and 30 mass % Al, respectively), on temperatures of 25ºC and 50ºC (Table 4), have been examined. Ultimate tensile strenght (σ_m), elongation at rupture (ε_r) and elastic modulus (E) were determined under uniaxial tensile test of standardized capsules, under strain rate of 50 mm/min.

Table 4. PBX mechanical characteristics

T (ºC)	PBX	σm (MPa)	εr (%)	E (MPa)
25	PBX-9	0,131	9,25	1,42
	PBX-10	0,219	9,79	2,24
	PBX-11	0,169	11,85	1,43
50	PBX-9	0,132	8,36	1,58
	PBX-10	0,125	8,32	1,50
	PBX-11	0,051	8,16	0,63

Measured values are almost the same in case of compounds with 10 mass % of Al, but compounds with (20 and 30) mass % Al have values which decrease with increasing temperature. They are not essentially changed with Al content increasing. The highest values of ultimate tensile strenght and elastic modulus are found in compound with 20 mass % of Al. Elongation at rupture of the analysed PBX varies between 9,25% - 11,85% and is slightly reduced with the increase of temperature.

PBX shock sensitivity

The shock sensitivity determination of PBX-10 and PBX-11 was carried out by GAP-test, on the system: the booster (FH-5) - the polyamide attenuator - the tested PBX explosive charge - copper cylinder.

Critical initiation conditions were determined by a copper cylinder deformation. The critical shock pressure value was calculated from the following expression [6]:

$$P_{cr} = 203,32 \cdot e^{-72,284 \cdot l}, \qquad (1)$$

where:
P_{cr} - the critical shock pressure (GPa),
l - the polyamide thickness (mm).

Results of the shock sensitivity determination are presented in Table 5.

Table 5. PBX shock sensitivity

PBX	No of experiments	l (mm)	Pkr (GPa)
PBX-10	13	33,6	1,792
PBX-11	10	32,8	1,899
Hexolite 60/40	-	-	1,955
Octolite 80/20	-	-	2,020

It can be concluded that there is a small reduction of PBX shock sensitivity with the increase of mass portion of Al from 20 % to 30 %. P_{cr} values are compared with the conventional melt-cast TNT-based explosives [7] and found that PBX shock sensitivity values are similar to sensitivity of hexolite 60/40 and octolite 80/20.

PBX detonation velocity

The PBX detonation velocity was measured in the steady-state detonation zone by using ionization gages and electrical counter, SNO 1475. Results, in the function of metal powder content, are shown in Table 6.

Table 6. PBX detonation velocity

PBX	Al content (mass.%)	ρ (g/cm3)	Dsr (m/s)
PBX-9	10	1,602	7800
PBX-5**	10	1,647	7840
PBX-10	20	1,660	7590
PBX-7**	20	1,686	7600
PBX-11	30	1,691	7240
Note: ** charges aged for two years			

It is evident from Table 6 that detonation velocity linearly decreases with Al content increasing. High level of agreement between detonation velocities of the aged PBX charges, PBX-5 and PBX-7, and respective compounds confirms physical stability and reproducibility of the quality of aluminised compounds.

Accomplished detonation velocities agreed with some references for PBX based on HTPB with almost the same starting components and Al dispersion [8].

PBX particle velocity

The PBX particle velocity was measured by using the electromagnetic method with the pulse magnetic field [9]. PBX charge was initiated by electromagnetic actuator EMA-1M and by plain detonation wave generator. Results were oscilograms $u=f(\tau)$.

The results of octogene-based PBX particle velocities (Table 7) were compared with detonation parameters for HMX/PU=82/18 compound [10]. Representative oscilograms $u=f(\tau)$ for a compound without aluminum and for two examined explosives (PBX-10 and PBX-11) are presented in Figures 11-13.

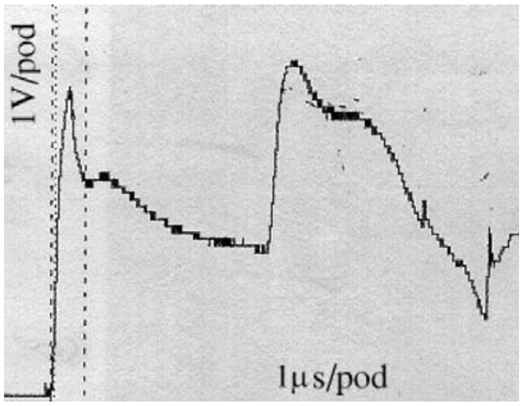

Figure 11. Registered gage record for a compound without Al

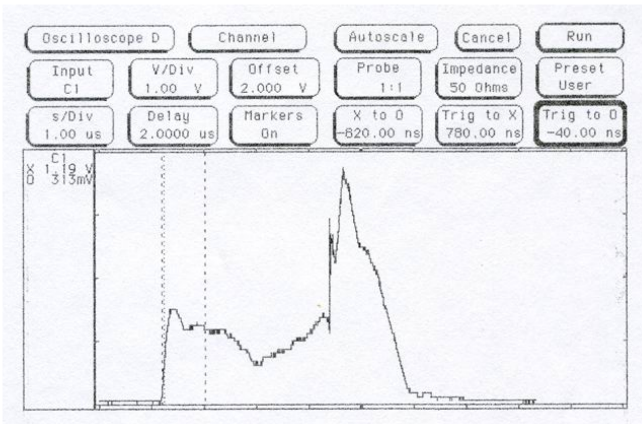

Figure 12. Registered gage record for PBX-10

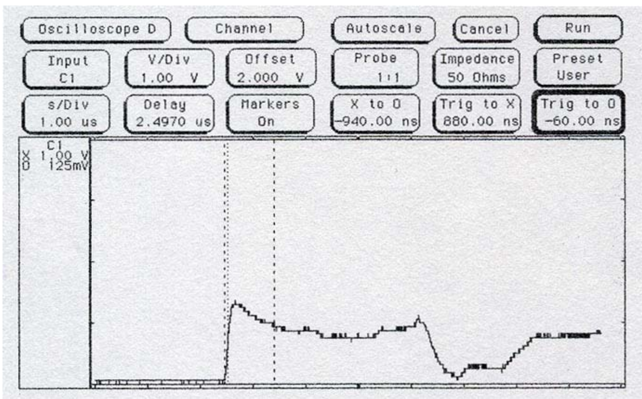

Figure 13. Registered gage record for PBX-11

Based on experimentaly determined values for D, τ and u_{CJ} and hydrodinamic theory relations other detonation parameters for Champan - Jougeut condition were calculated: chemical reaction zone width a, detonation product density ρ_{CJ}, polytropic exponent of explosive products n and detonation pressure P_{CJ} (Table 7).

Table 7. Results of PBX particle velocity measurement

PBX	ρ_e (g/cm^3)	D (m/s)	e_{CJ} (V)	τ (μs)	u_{CJ} (m/s)	a (mm)	n	ρ_{CJ} (g/cm^3)	P_{CJ} (GPa)
HMX/PU 82/18	1,630	8230	-	0,310	1776,9	1,98	3,63	2,079	23,83
PBX-9	1,602	7800	1,38	0,570	1500	3,48	4,20	1,983	18,75
PBX-10	1,664	7590	1,25	0,800	1250	4,97	5,07	1,992	15,79
PBX-11	1,691	7240	1,13	0,987	1103	5,89	5,58	1,995	13,51

It was concluded that the registered $u(t)$ records are specific by analysing results of particle velocity measurement of composites. A composite without Al has triangular $u(t)$ profile with clearly marked von-Neumman's peak, Fig.4. Compounds with Al addition have plateau on the record with "hump", i.e. secundary peak at the end of the chemical reaction zone, which indicates a more complex chemical decomposition mechanism in the detonation wave.

Particle velocity and detonation pressure decrease with the increase of Al content, but chemical reaction zone and chemical reaction time increase. Values of these parameters for PBX with 30 mass % of Al is about three times higher than for compounds without Al, which puts in doubt the hypothesis of some authors that metal powder behaves as inert material in the chemical reaction zone.

Particle velocity and detonation pressure decreasing have confirmed the fact that there is no possibility of their increasing with aluminium loading. However, simultaneous increasing of chemical reaction time and zone is experimental evidence that metal powder does not behave as inert material, but partially oxidises in the detonation wave front and reacts with decomposition products of the composite explosive.

Registered $u(\tau)$ profiles differ from classical triangular records presented by ZND model for high explosives, but have characteristic trapezoidal shape without clearly marked von Neumman's spike.

Conclusion

Aluminised PBX with 20 mass % of polymer binder and (10-30) mass % of Al were obtained. Quality of the compounds is reporducible and they are convenient for laboration in ammunition.

Rheological characteristics of composite compounds are significally influenced by content and particle size distribution of solid phase. The presence of Al exhibits positive influence on average PBX characteristics – the higher the Al content, the lower the composite explosive viscosity and moderate viscosity increasing with curing time.

PBX density linearly increases, but detonation velocity decreases, with decreasing of explosive component portion, i.e. with increasing of Al content up to 30 mass %. The influence of Al particle size is not evident.

PBX mechanical characteristics do not change significantly with Al content increasing in composite compounds. Mechanical behavior is more influenced by experimental temperature, which is especialy evident in compounds with 20 mass % and 30 mass % of Al. Ultimate tensile strenght, elastic modulus and elongation tend to decrease as the temperature increases.

Shock sensitivity is reduced with metal powder content. It is as high as sensitivities for conventional TNT-based explosives, hexolite 60/40 and octolite 80/20.

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Karakteristike livenih PBX sa dodatkom aluminijuma

Prikazani su rezultati istraživanja livenih kompozitnih eksploziva na bazi oktogena i poliuretanskog veziva (PBX) sa dodatkom aluminijuma. Ispitivan je uticaj sadržaja i disperzije čestica Al i oktogena na reološke, fizičke, mehaničke i eksplozivne karakteristike PBX. Pokazano je da prisustvo metalnog praha ima velikog uticaja na karakteristike kompozitnih eksploziva, posebno na parametre detonacionog talasa. Sa povećanjem sadržaja aluminijuma, brzina i pritisak detonacije, masena brzina i osetljivost na udar PBX se smanjuju, a širina i vreme zone hemijske reakcije se uvećavaju.

Ključne reči: **liveni eksplozivi, kompozitni eksplozivi, oktogen, poliuretansko vezivo, aluminijum, dteonacioni parametri.**

Характеристики литых ПВВВ с добавлением алюминия

В настоящей работе показаны результаты исследования литых композитных взрывчатых веществ на основе октогена и полиуретановых вяжущих веществ (ПВВВ) с добавлением алюминия. Здесь испытывано влияние содержания и дисперсии частиц Ал и октогена на реологические, физические, механические и взрывчатые характеристики ПВВВ. Тоже здесь показано, что присутствие металлического порошка оказывает большое влияние на характеристики композитных взрывчатых веществ, а особенно на параметры детонационной волны. С повышением содержания алюминия, скорость и давление детонации, массовая скорость и чувствительность на удар ПВВВ уменьшивается, а широта и время зоны химической реакции увеличиваются.

Ключевые слова: литые взрывчатые вещества, композитные взрывчатые вещества, октоген, полиуретановое вяжущее вещество, алюминий, детонационные параметры.

Les caractéristiques des PBX fondus contenant l'aluminium

Dans ce papier on présente les résultats des recherches sur les explosifs composites fondus à ma base d'octogène et le liant polyurethante contenant l'aluminium (PBX). On a éxaminé l'influence de la teneur et la dispersion des particules de Al sur les caractéristiques rhéologiques, physiques, mécaniques et explosives des PBX. On a démontré que la présence de la poudre métalique a une grande influence sur les caractéristiques des explosifs composites, en particulier sur les paramètres de l'onde de détonation. Si la teneur de l'aluminium, la vitesse et la pression de détonation augmentent, la vitesse de masse et la sensibilité à l'impact chez les PBX diminuent, alors que la largeur et le temps de la zone de réaction chimique augmentent.

***Mots clés*: explosifs fondus, explosifs composites, octogène, liant polyurethane, aluminium, paramètres de détonation.**