

Military Technical College
Kobry El-Kobbah,
Cairo, Egypt



6th International Conference
on
Chemical & Environmental
Engineering
29 -31 May, 2012.

ENMC-4

**PREPARATION AND CHARACTERIZATION OF
DEMILITARIZED HIGH EXPLOSIVES
IN W/O EMULSION EXPLOSIVES.**

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Abstract

The present paper summarizes the results of the preliminary research conducted at the Institute of Energetic Materials, the University of Pardubice into the use of demilitarized energetic materials (TNT, RDX) in modification of the W/O emulsion explosives in the framework of grant project of MPO ČR No. FR-TI2/639. It describes the preparation of the emulsion explosives used, some physico-chemical parameters of demilitarized explosives and detonation parameters of the demilitarized and emulsion explosives mixtures. The results of study of certain mixtures containing no micro-balloons show that they have similar characteristics as the amatols and several dynamites. Incorporating of demilitarized explosives into the mixtures with emulsion explosives can be a solution to their health and environmental problems.

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1. Introduction

The emulsion high explosives of the water-in-oil type belong to the most widespread industrial explosives. They are favored due to their good performance parameters and exceptionally good safety parameters. A major drawback of emulsion high explosives is their insensitivity to shock wave, i.e. difficult initiation of these explosives. Hence the emulsion explosives have to be sensitized by addition of suitable sensitizer, such as, e.g., small glass or polymeric hollow spheres (micro-balloons), which introduce gas into the mixture or brisant explosive. In principle, an emulsion high explosive is a mixture of two immiscible liquids, in which one liquid is composed of a mixture of oxidizers and the other is a mixture of fuels. The mixture of oxidizers in liquid state is dispersed in the fuel in the form of droplets having the size below ca 10 μm . The emulsion thus produced is not stable: the droplets of dispersed oxidizer mixture can undergo agglomeration and/or recrystallization. Both these phenomena result in reduction of inter-phase surface with concomitant lowering of performance parameters of emulsion high explosives. These undesirable phenomena are suppressed by addition of emulsifiers, such as sorbite mono-stearate or mono-oleate, polymeric emulsifiers based on polyisobutylene etc. [Apolenis 2006, Kalatsey 1995, Maranda 2002, Mendoca 1996 and 1997, Zeman 2004 and 2005, Xuguang 1994, Zeman & Tamchyna, 2004 and 2005].

Applications of demilitarized high explosives are relatively restricted. Their direct use in blasting operations is unsuitable due to low detonation parameters and health-ecological problems. Chemical reprocessing to products of higher value is not frequent and tends to be very expensive. Demilitarized high explosives can contain impurities of polymeric nature (waxes, lacquers, paints used during filling into ammunition as internal protective coating); they exist in a variety of shapes, e.g., powders, cylinders, flakes. All these facts can affect their detonation parameters. Earlier research showed that a satisfactory sensitizing of emulsion high explosive can be achieved by addition of 30 % w/w of brisant high explosive or multi-perforated propellants. The use of demilitarized high explosives of TNT and RDX types in their original quality (without previous modification) for sensitizing emulsion explosives without the necessary addition of microballoons has been reported in literature quite insufficiently so far [Kohlicek, 2000 and 2001; Zeman 2003, Apolenis 2006, Kalatsey 1995, Maranda 2002, Mendoca 1996 and 1997, Zeman 2004 and 2005, Xuguang 1994].

2. Experimental

The emulsion matrix was prepared in a simple apparatus composed of a stirrer, container and thermostat. The solution of oxidizers was kept at the temperature of 95-100 °C, whereupon it was slowly added into preheated (ca 90 °C) solution of fuels and emulsifier with intensive stirring (2000 rpm). The obtained emulsion was stirred further for ca 2 min in order to achieve better distribution of particles. The composition of prepared emulsion matrices is presented in Table 1.

Ammonium nitrate, sodium nitrate and grounds (slack wax) were obtained from the comp. Explosia a.s. Calcium nitrate (under the name Lovoferit) was obtained from the comp. Lovochemie a.s., and the adopted oil from the comp. Lavat a.s. The emulsifier adopted was Anfomul S6 (sorbite mono-isostearate). All the demilitarized high explosives used were obtained from the comp. Poličské strojírny a.s. and were not purified or modified in any way except for sieving. The used demilitarized explosive on the basis of pure TNT was ground Politol, that based on TNT plus RDX (50/50) was ground Composition B. The grain size of Politol was in the range from 50 μm to 4 mm. Composition B was finely ground and contained 94 % w/w of grain size fraction below 2 mm and 74 % w/w of grain size fraction below 1 mm. Politol was submitted to sieving to give several fractions (see Table 2). The final mixtures of emulsion and demilitarized explosives were prepared by manual mixing of the

two components. Selected parameters were compared with those of some commercially manufactured (in Explosia a.s. comp.) high explosives (see Table 3).

Table 1: Composition of adopted emulsions A and B

Emulsion Component	A	B
	% w/w	
AN	72	42.8
SN	9.6	0
CN	0	31.4
Water	11	19.8
Oil	2.2	4
Grounds	2.2	0
Emulsifier	3	2

Table 2: Survey of adopted Politol fractions

Fraction no.	1	2	3	4	5
Grain size (µm)	< 100	< 200	100-200	200-400	400-800
Fraction no.	6	7	8	9	10
Grain size (µm)	800-600	1000-000	1600-4000	> 4000	No sieving

Table 3: Survey of commercially available high explosives manufactured by Explosia a.s.

Commercial high explosive			Nitro ester content (% w/w)	Detonation velocity (m s ⁻¹)	Density (g cm ⁻³)	RS (% BG)
Trade mark	Type	Application				
Emsit M	Emulsion	Mining	0	5100	1.05	63
Infernit 45	Gelatinized	Special		6400	1.45	70
Ostravit C	Semi-gelatinized	Safe for mining	11	1900	1.20	40
Perunit E	Gelatinized	Mining	22	6000	1.38	78
Permon 10T	Amatol	Mining	0	4000	1.05	89
Permonex V 19	Amatol	Mining	0	4400	1.05	91
Semtex 1A	Plastic	Special	84 (PETN)	7400	1.47	80
Semtinit 50	Gelatinized	Safe for mining	25	2280	1.50	34

2.1. Measurements of Detonation Velociti

The detonation velocities were measured in cylindrical charges of 37 or 60 mm diameter in polyethylene (PE) wrapping. The adopted actuator was 20 g high explosive Semtex 1A with 0-S detonator, Al cylindrical case (initiation power ~ no. 8). The charges were placed in sand – the maximum depth was 20 cm. The measurement was performed by means of an Explomet-fo-2000 apparatus (from Kontigro comp.) with three optical sensors. The distance of the first sensor from the actuator was at least 15 cm, the distances between the sensors being at least 10 cm. The data measured with pure emulsions are given in Table 4, those measured with the mixture of emulsion matrix A and Politol (50/50) are given in Table 5, and those measured with mixtures of emulsion matrices A and B and Composition B (in various proportions) are given in Table 6.

Table 4: Measured detonation velocities of emulsions A and B sensitized with 3 % w/w of micro-balloons

Emulsion	Detonation velocity (m.s ⁻¹)	Charge density (g.cm ⁻³)
A	5160	1.13
B	3900	1.17

Table 5: Measured detonation velocities of mixtures of Emulsion A and Politol in 50/50 proportion with various grain sizes of Politol

Fraction no.	Politol grain size	Charge density (g.cm ⁻³)	Detonation velocity (m.s ⁻¹)	Fraction no.	Politol grain size	Charge density (g.cm ⁻³)	Detonation velocity (m.s ⁻¹)
1	< 100 μm	1.43	6053	7.1	1-2 mm	1.47	5679
2	< 200 μm	1.45	5948	7.2	1-2 mm	1.52	5705
3	100-200 μm	1.45	5797	8.1	1.6-4 mm	1.4	5452
4.1	200-400 μm	1.42	5887	8.2	1.6-4 mm	1.39	5330
4.2	200-400 μm	1.41	5935	8.3	1.6-4 mm	1.43	5492
5.1	400-800 μm	1.39	5727	9.1	> 4 mm	1.4	5549
5.2	400-800 μm	1.45	5712	9.2	> 4 mm	1.48	5809
6.1	800-1600 μm	1.43	5697	10.1	original Politol	1.41	5562
6.2	800-1600 μm	1.47	5687	10.2	original Politol	1.4	5657

Table 6: Measured detonation velocities of mixtures of emulsions A and B with demilitarized Composition B

Compositi on	Detonation velocity (m s ⁻¹)	ρ (g cm ⁻³)	ρD^2 (GPa)	Compositi on	Detonation velocity (m s ⁻¹)	ρ (g cm ⁻³)	ρD^2 (GPa)
70 % Emulsion A + 30 % Compositi on B	5559	1.45	44.8	60 % Emulsion B + 40 % Compositi on B	6005	1.48	53.4
65 % Emulsion A + 35 % Compositi on B	5932	1.46	51.4	50 % Emulsion B + 50 % Compositi on B	6465	1.49	62.3
60 % Emulsion A + 40 % Compositi on B	6189	1.47	56.3	40 % Emulsion B + 60 % Compositi on B	6772	1.51	69.2
55 % Emulsion A + 45 % Compositi on B	6449	1.48	61.6				
50 % Emulsion A + 50 % Compositi on B	6749	1.49	67.9				

2.2. Measurement of Relative strength (RS)

The tested high explosive (10 g) was placed in a PE bag and fastened to igniting detonator in the arrangement having the sample at the front and in the axis of the detonator. The sample so arranged with detonator and igniter cord was run through the projectile and then fully inserted into the mortar body. After initiation of sample, the pendulum deflection was read from the scale. The results were compared with the calibration using blasting gelatin (BG). The measured RS values of Emulsion matrix A and its mixtures with Politol and Composition B are summarized in Table 7.

Table 7: Measured RS values of Emulsion A and its mixtures with demilitarized Politol and Composition B in the proportion 50/50

Composition	RS (% BG)
Emulsion A	89.0
50 % Emulsion A + 50 % Politol	85.0
50 % Emulsion A + 50 % Composition B	91.9

2.3. Calculations of Detonation Parameters

The theoretical calculation of detonation parameters was based on European standard EN 13631-15 (Grys and Trzciński 2010a and 2010b). Also the heat of explosion Q_v , specific force f , volume of gases V_g , explosion temperature T_v , explosion pressure P_v , and molar ratio CO/CO₂ in the explosion products were calculated. The values calculated for selected commercial high explosives, pure Emulsion A, and mixtures of Emulsion A with demilitarized high explosives in the proportion of 50/50 are given in Table 8.

Table 8: Calculated values of some detonation parameters of pure Emulsion A, of mixtures of Emulsion A with brisant demilitarized high explosives and some commercially available high explosives

High explosive	Q_v (J g ⁻¹)	f (J g ⁻¹)	V_g (dm ³ kg ⁻¹)	T_v (K)	P_v (GPa)	CO/CO ₂	Note
Emsit M	2570.6	638.2	891.7	1954.2	34	3.23*10 ⁻⁴	without techn additives
Permon 10	4123.7	973.6	936.2	2839.5	28.8	0.0093	
Polonit V	4591	1019	885.5	3142	25.5	0.0206	without techn. additives
Permonex V19	4281.4	916.2	916.2	2935.4	36.3	0.0056	
Danubit 1	4570.4	965.6	888.9	2965.9	78	0.0011	without techn. additives
Danubit 2	4546.8	915.5	837.1	2985.9	74.1	0.0014	without techn. additives
Danubit Geofex 2	5238.9	1018.2	851.7	3264	104	0.0064	without BaSO ₄
Emulsion A	3356	781	960	2219	4.77	0.0414	
50 % Emulsion A + 50 % Politol	4345	764.1	773	2698.7	8.84	0.0365	
50 % Emulsion A + 50 % Composition B	4304	784	830	2580	8.84	0.0327	

3. Discussion

The prepared Emulsion A exhibits a higher detonation velocity than Emulsion B after sensitization with 3 % w/w of micro-balloons. The decrease in detonation velocity of emulsion B can be explained by the presence of larger amount of calcium nitrate and water in Emulsion B. The shelf life of pure Emulsion A was at least 5 months, that of pure Emulsion B was 7 months from the day of preparation. In the slurry-type high explosives, the ideal TNT grain size is in the interval of 2-4 mm [Cook 1974]. According to our measurements with high explosives of water-in-oil emulsion type the opposite is true (see Fig. 1). The addition of Politol in the amount of 50 % (with regard to the mass of final high explosive) to Emulsion A increases the density of the mixture from 1.13 g.cm⁻³ to ca 1.40 g.cm⁻³.

Fig. 1: Comparison of detonation velocities of mixtures of Emulsion matrix A (Table 5) with Politol of various grain size values (from 50 μm to 4000 μm , Table 2) in 50/50 ratio

Detonation of mixtures of Emulsion A and Politol is not ideal [Němec 2011]. Therefore, these mixtures were found to be less suitable for practical purposes, and attention was focused on mixtures of the emulsions and Composition B. The mixtures of Emulsion A with Composition B have higher densities than those of the mixtures with TNT: about $1.50 \text{ g}\cdot\text{cm}^{-3}$ at the 50/50 ratio of the emulsion and Composition B in the resulting high explosive. Composition B was finely ground, which caused considerable separation of hexogen and trinitrotoluene grains during sieving. That is why it was virtually impossible to find the dependence of detonation velocity upon the grain size of Composition B.

The relationship between detonation velocity and content of Composition B in the mixture is presented in Fig. 2. The well-known dependence of detonation velocity on charge density is presented in Fig. 3.

Fig. 2: Dependence of detonation velocity on content of unmodified demilitarized Composition B

Fig. 3: Dependence of detonation velocity on density of mixture of Emulsion A and Composition B

With regard to the linearity of the relationship between detonation velocity and content of Composition B in the mixture, and the relationship between detonation velocity and charge density, the detonation of these mixtures is closer to ideality than in the case of mixtures of Emulsion A and Politol. Figure 2 shows that a change in content of Composition B in its mixture with Emulsion A can be used to change the detonation parameters within relatively broad limits.

A comparison of performance of the emulsion high explosive fortified in this way with performance values of selected, commercially available high explosives manufactured by comp. Explosia a.s. is presented in Fig. 4.

Fig. 4: Comparison of detonation parameters of commercially available high explosives manufactured by Explosia a.s. comp. with those of pure Emulsion A and mixtures of Emulsion A with brisant demilitarized high explosives

Not only the mixture of Emulsion A with 50 % w/w of demilitarized high explosives based on TNT, but also the Emulsion A alone with sensitization additive of micro-balloons are in their performance abilities approximately at the level of performance values of Permonex V19, Permon 10T and Perunit E.

4. Conclusion

An addition of demilitarized TNT as sensitizer to emulsions of W/O type could give acceptable results unless the grain size of adopted TNT exceeds 400 μm , with its content in the final W/O explosive being 50 % w/w. Nevertheless, due to the wide variety of demilitarized ammunition objects it is impossible to attain a precisely defined quality level of demilitarized TNT. Thus the application of TNT in this sense would require simultaneous sensitization of final W/O mixture with micro-balloons.

Application of demilitarized Composition B in similar way in the amount above 30 % w/w of its content in W/O high explosive enables modification of detonation velocities of resulting emulsion mixtures within a broad range.

Relative performance ability (RS) of the W/O mixtures with added TNT is equivalent to the RPS of original W/O matrix that has been sensitized by addition of 3 % w/w of micro-balloons. Even in the case of addition of Composition B, its effect upon relative performance ability is by far not as distinct as the effect on the detonation velocity. Irrespective of these facts, however, the addition of Composition B to the W/O matrix – in particular – can provide explosives for rock shooting and blasting, their performance being close to the performance values of industrial powdery amatols (e.g., the Czech Permonex v19 or Permon 10T) or some dynamites (Danubit), as the case may be; these industrial products exhibit relatively low detonation velocities. However, an addition of TNT to the W/O emulsion has no significant effect on the performance of resulting high explosive.

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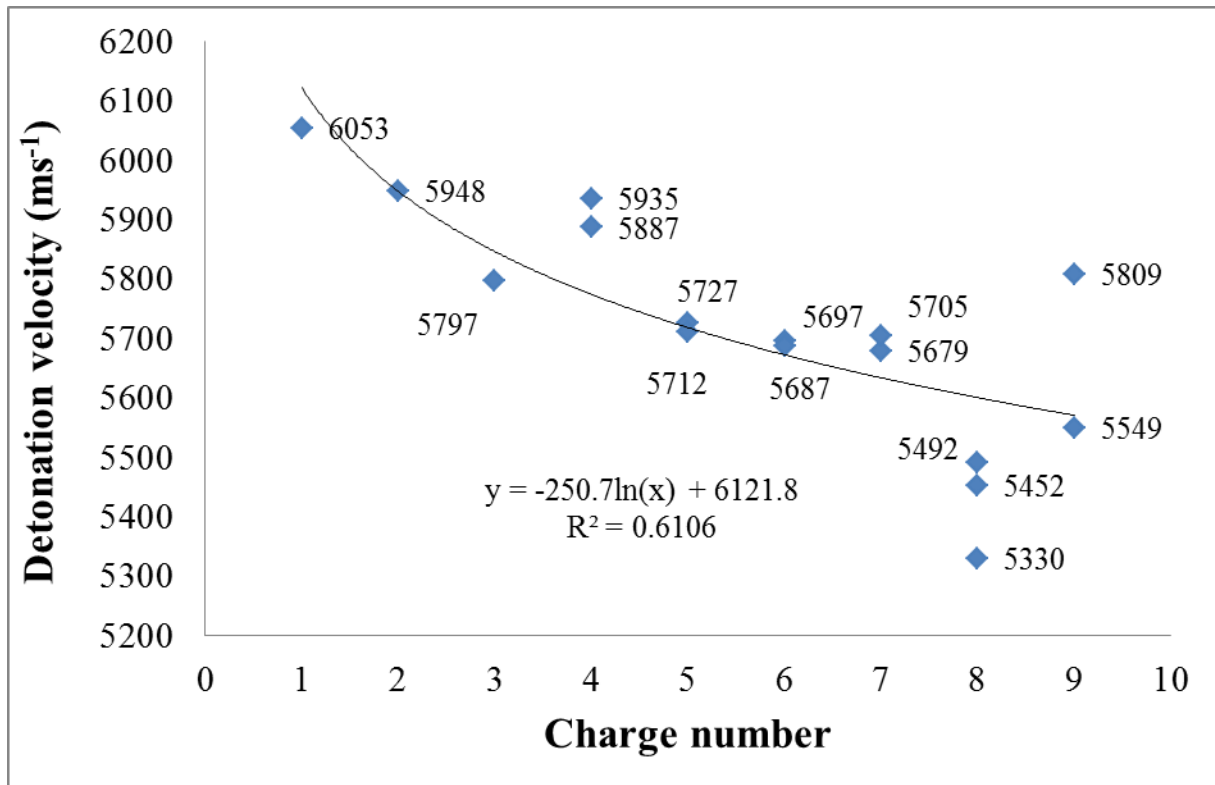


Fig. 1: Comparison of detonation velocities of mixtures of Emulsion matrix A (Table 5) with Politol of various grain size values (from 50 μm to 4000 μm, Table 2) in 50/50 ratio

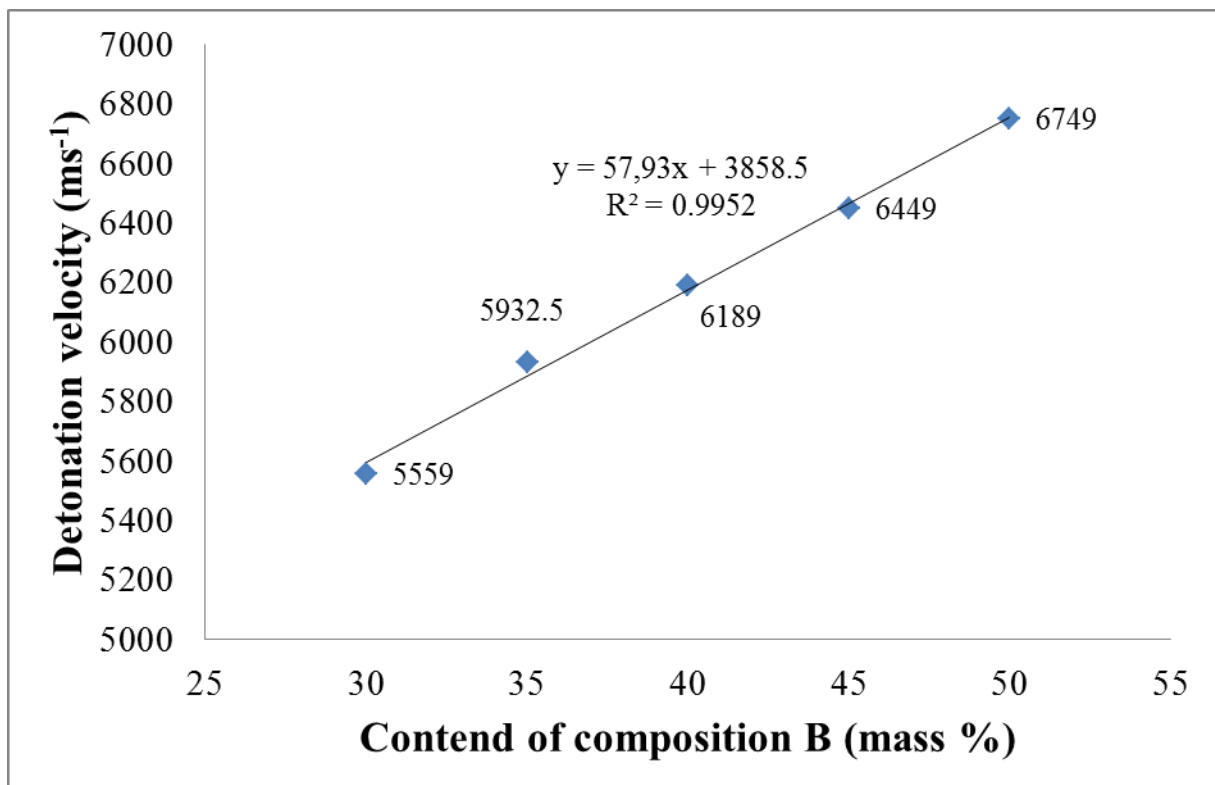


Fig. 2: Dependence of detonation velocity on content of unmodified demilitarized Composition B

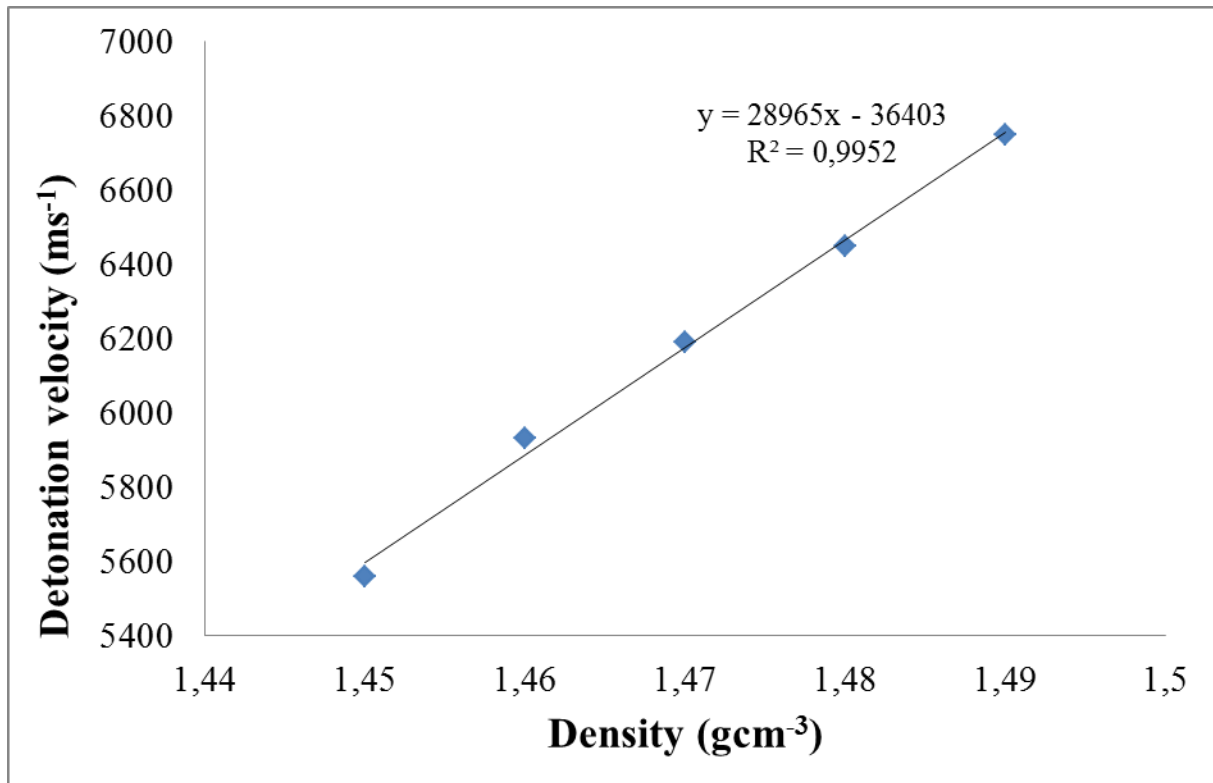


Fig. 3: Dependence of detonation velocity on density of mixture of Emulsion A and Composition B

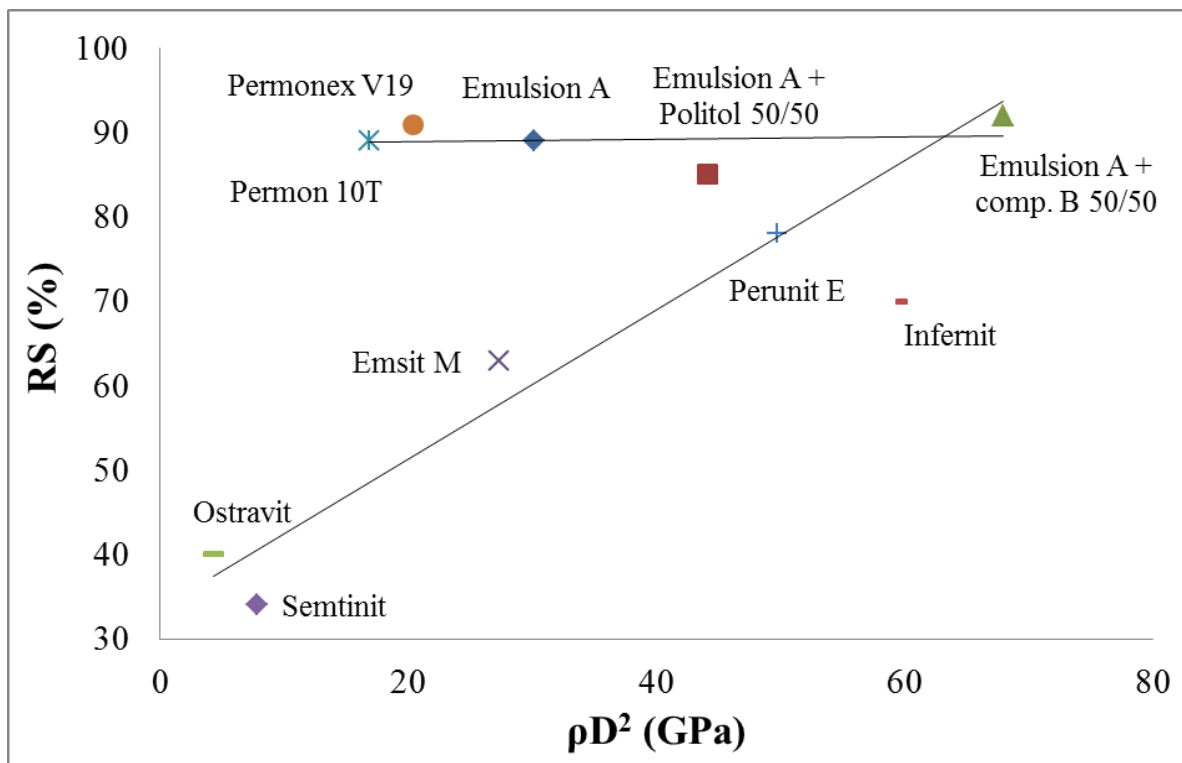


Fig. 4: Comparison of detonation parameters of commercially available high explosives manufactured by Explosia a.s. comp. with those of pure Emulsion A and mixtures of Emulsion A with brisant demilitarized high explosives