

Studies of effect of aluminium powder on selected parameters of emulsion explosive sensitized with microballoons

Ewelina BEDNARCZYK*, Andrzej MARANDA, Józef PASZULA, Andrzej PAPLIŃSKI - Military University of Technology, Warsaw, Poland

Please cite as: CHEMIK 2016, 70, 1, 41–50

Introduction

Main component of emulsion explosives (EE) is matrix that is an "water in oil" emulsion. Dispersed phase is a supersaturated aqueous oxidiser solution, while continuous (oil) phase is a liquid (immiscible) fuel and an emulsifier [1]. Other EE components include various agents modifying its physicochemical properties. Usually ammonium nitrate (V) mixed with sodium nitrate (V) or calcium nitrate (V) that modify properties of aqueous solutions is used as oxidiser. They lower the critical point of the solution and increase oxygen balance. Oxidiser content is over 90%. Organic liquids forming or not forming solutions with water serve as fuel. Solid fuels (both organic and inorganic) can be also added to emulsion explosives; these are additional fuels to modify explosive properties. Often used inorganic fuel is aluminium powder, e.g. [2 – 6] which effect on selected detonation parameters of EEs is presented in this work.

Experimental part

Experimental material

Matrix by AUSTIN POWDER, Hydrox U, viscosity 120,000 cP density 1.42 g/cm³ and following composition, %: ammonium nitrate (V) – 64.4; sodium nitrate (V) – 14.6%; organic phase – 6.0%; water – 15.0%.

Microballoons Expance DE461DET40d25 by Akzo Nobel: grain size D(0.5) 35–55 µm; density 25±3 kg/m³ [7].

Flaked aluminium powder, aluminium content ~93% of grain size 100 µm.

Milled aluminium powder BLITZ Aluminium DEPUVAL 3083 by BENDA-LUTZ:

- produced from aluminium of purity at least 99.7% Al
- surface width 29,000 cm²/g
- mesh plus fraction 45 µm (—325 mesh) max. 0.8%
- average grain size 7 µm (analysed before dust removal)
- bulk density 0.4 kg/L.

Aluminium Depuval is a dust-free coated aluminium powder (Fig. 1). This effect is obtained by adding 0.2% of inert additive to the milling process. The powder may slowly react with water, which is accompanied by hydrogen generation [8].



Fig. 1. Images showing aluminium powders, on the left – DEPUVAL aluminium; on the right – flaked powder [8]

Corresponding author:
Professor Andrzej MARANDA – Ph.D., D.Sc., (Eng.), e-mail: amaranda@wat.edu.pl

Detonation parameter measurement results

Detonation rate determined using method of short circuit sensors. Explosives were placed in PVC envelopes of diameters $\Phi_{\text{inner}} = 26 \text{ mm}$ and $\Phi_{\text{outer}} = 33 \text{ mm}$ (charges for optimisation of microballoon content) and of diameters $\Phi_{\text{inner}} = 50 \text{ mm}$ and $\Phi_{\text{outer}} = \text{mm}$ (400 g charges for measurement of blast wave overpressure). The tested emulsion explosives were initiated with ERG-type electric fuses.

The first phase of experiments involved measurement of detonation rate for six different microballoon contents: 0.2%, 0.3%, 0.4%, 0.6%, 1.0% and 1.4%. Test results are presented in Table I.

Table I
Summary of changes in detonation rate and density for tested charges to optimize the content of the microballoons

Microballoon content % w/w	Density g/cm ³	Detonation rate m/s
0.2	1.28 ± 0.01	no detonation
0.3	1.24 ± 0.01	no detonation
0.4	1.20 ± 0.01	5380 ± 30
0.6	1.08 ± 0.01	5190 ± 20
1.0	0.93 ± 0.01	4650 ± 20
1.4	0.80 ± 0.01	4130 ± 20

Density of tested materials decreases linearly for increasing microballoon content in a tested range (Fig. 2), while detonation rate of the EEs decreases also linearly (Fig. 3). Maximum rate was obtained for sensitizer content of 0.4%. For lower content there is no detonation of the explosive.

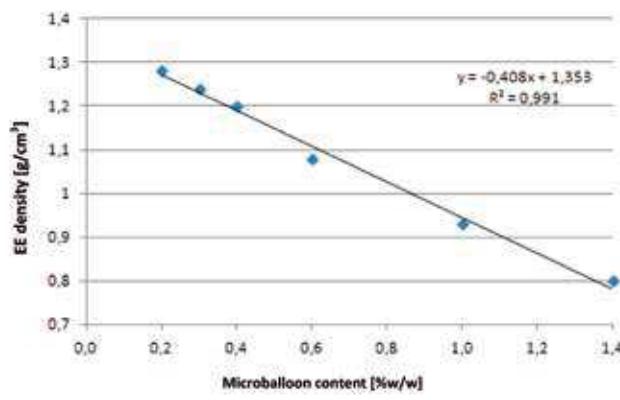


Fig. 2. Dependence of density of tested EE on microballoon content

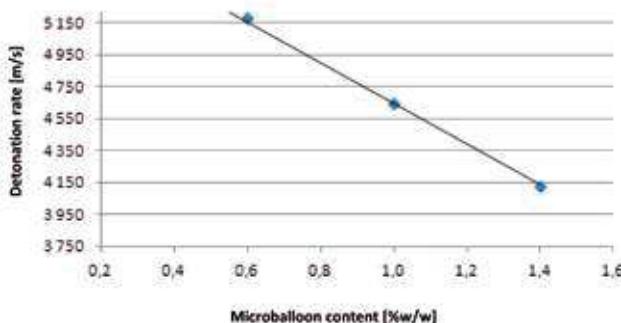


Fig. 3. Dependence of detonation rate on microballoon content

Then, detonation rate measurements were conducted for EEs containing: microballoons – 0.4%, aluminium powder – 5 ÷ 30%, rest – matrix. Experiment results are showed in Figures 4 and 5.

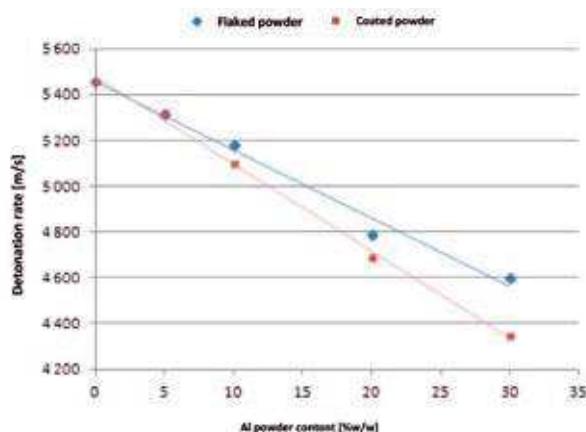


Fig. 4. Dependence of detonation rate on aluminium powder content

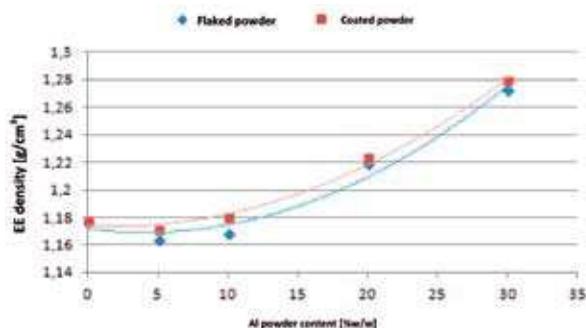


Fig. 5. Dependence of EE density on aluminium powder content

Measurements of blast wave overpressure were conducted using pressure sensors PCB Piezotronics, Inc., 137A series. Two sensors were placed at distance 2 m and 2.5 m from the charge, which was suspended at 1.5 m above the ground.

Figures 6–8 present curves of blast wave overpressure recorded for the selected EEs. While, the subsequent figures present obtained air blast wave overpressure (Fig. 9 and 11) and estimated pulses (Fig. 10 and 12).

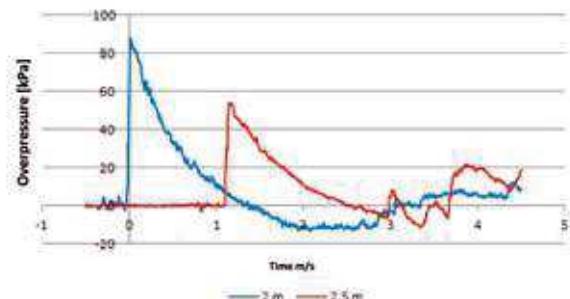


Fig. 6. Overpressure curve for 0% content of aluminium powder

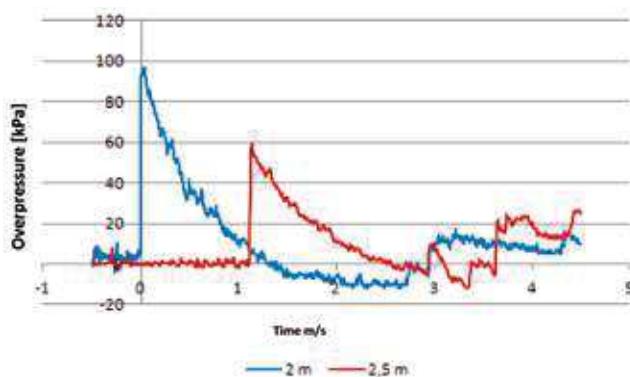


Fig. 7. Overpressure curve for 5% content of flaked aluminium powder

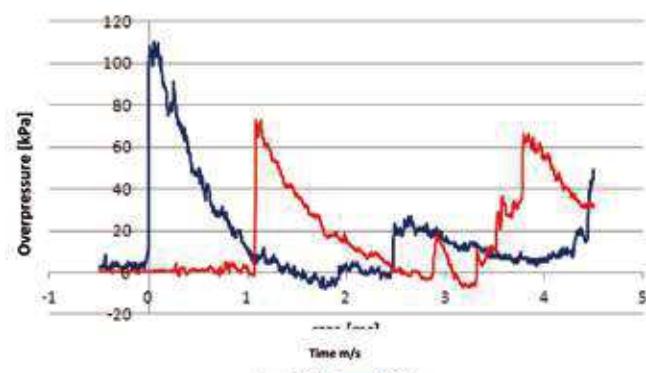


Fig. 8. Overpressure curve for 30% content of dust-free aluminium powder

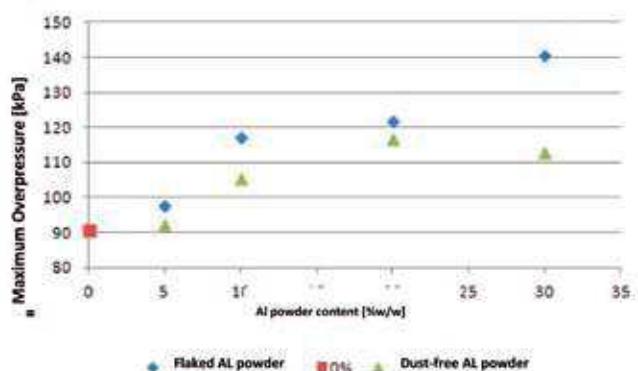


Fig. 9. Maximum overpressure of blast wave generated by detonation of EEs of various aluminium powder content, 2 m away from the charge

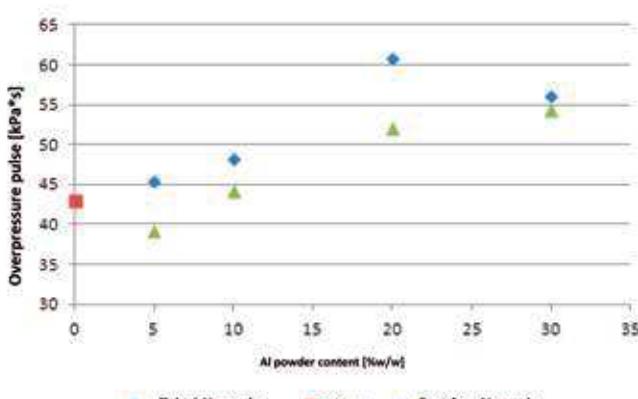


Fig. 10. Dependence of overpressure pulse on aluminium powder content, 2 m away from the charge

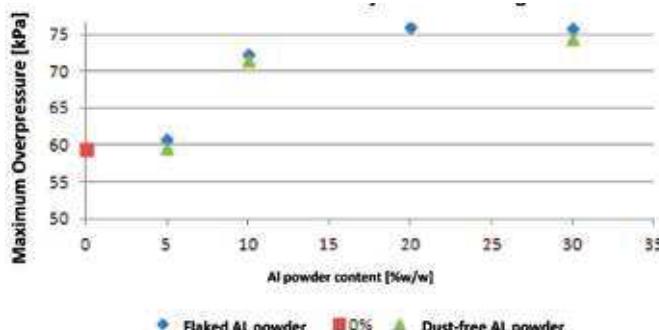


Fig. 11. Maximum overpressure of blast wave generated by detonation of EEs of various aluminium powder content, 2.5 m away from the charge

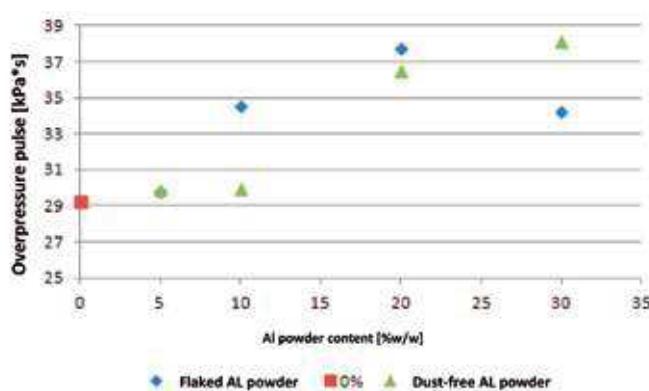


Fig. 12. Dependence of overpressure pulse on aluminium powder content, 2.5 m away from the charge

Estimation of thermodynamic parameters of tested EEs

Calculation methods

Numerical analysis comes to help in determination of degree of conversion of aluminium powder grains in strict detonation zone, between front of detonation wave, where explosive is compressed and Chapman-Jouguet (C-J) plane, where thermodynamic equilibrium is shaped within formed conversion products. The work presents also calculations of detonation parameters of tested high-energy mixtures using MWEQ software, which methodical bases are presented in [10]. Software determines chemical composition and thermodynamic parameters of equilibrium state of reactive mixture.

The calculations are based on extensive database of characteristic thermodynamic properties of chemical substances that may potentially occur in composition of conversion products. The database contains values of enthalpy of formation and sets of coefficients that allow to determine specific heat, enthalpy and entropy as a function of temperature. Calculation methods presented in [10] allows to iteratively determine molar concentrations, temperature, pressure, internal energy and other parameters of the mixture for systems containing large numbers (dozens, above 100) of substances present in gas form and in condensed, liquid and solid, phases.

Product state corresponding to stationary value of detonation speed is determined using Chapman-Jouguet hypothesis, which states that in C-J plane entropy of reactive mixture is minimised.

Due to high pressures and temperatures in detonation products, it is necessary to account for own volume of molecules on the form of equation of state.

The conducted calculations used for description of non-ideal properties of substances under high matter comprimation

conditions, BKW equation of state was used. The application of BKW equation for description of properties of combustion and explosion products is presented more broadly in [11]. Effect of nonideality in the BKW equation is characterised by four constant parameters α , β , κ and θ and volume coefficients that characterise given chemical substances, known also as covolumens(k). For calculations, BKW equation parametrisation determined experimentally in paper [12] was used.

Due to the presence of explosive sodium nitrate (V) in material composition, it was necessary to include sodium compounds in products. Fraction of the following substances was considered: $Na_{(g)}$, $Na_{2(g)}$, NaH , Na_2O , $NaOH$, $Na_2O_2H_2$, $NaNO_{2(g)}$, $NaNO_{3(g)}$, and in solid phase $Na_2O_{(s)}$, $NaOH_{(s)}$, $Na_2CO_{3(s)}$. As the paper [12] did not consider sodium content in tested explosives, covolumens for sodium compounds were approximated using the concept of geometric covolumens[13]. Detailed estimations are presented in [14].

Calculation procedure

Numerical interpretation of parameters of tested explosive mixture was conducted for two cases. In the first one it was assumed that it is possible that total aluminium (Alakt) contained in powder grains added to the explosive mixture can undergo conversion. In the second, the contrary was assumed. It was assumed that in the space between front of the detonation wave and Chapman-Jouguet point the total material in powder grain, both metallic aluminium, as well as Al_2O_3 layer that encloses it are left as an inert component (Alinert) that only absorbs the heat. The obtained results are presented in tables (Tab. 2 and 3).

Table 2
Estimated EE parameters containing flaked aluminium powder (purity 93% Al)

Characteristics of tested EEs			Aluminium powder composition adopted in calculations g/kg of EE			Calculation results					
Mass fraction of powder in EE, %	ρ_{OE} , kg/m ³	D_{exp} , m/s	Al_{akt}	Al_{inert}	Al_2O_3	D_c , m/s	P_{C_J} , MPa	T_{C_J} , K	Q_v , MJ/kg	$\Sigma(g)$, mol/kgMW	
0	1.177	5460 ± 160	-	-	-	5340	8159	2237	2.688	43.572	
			4.6500	-	0.3500	5437	8436	2620	3.472	41.84	
5	1.164	5320 ± 170	-	4.6500	0.3500	5175	7459	2177	2.564	41.37	
			9.3000	-	0.7000	5332	8254	2953	4.191	38.09	
10	1.165	5070 ± 60	-	9.3000	0.7000	4903	6619	2114	2.439	39.17	
			18.6000	-	1.4000	5265	8768	3644	5.796	30.88	
20	1.219	4790 ± 140	-	18.6000	1.4000	4606	599	1968	2.189	34.79	
			27.9000	-	2.1000	5226	8864	4267	7.361	24.21	
30	1.272	4610 ± 180	-	27.9000	2.1000	4260	5114	1803	1.934	30.45	

where: ρ_{OE} – density of explosive, D_{exp} – detonation rate determined experimentally, D_c , P_{C_J} , T_{C_J} – detonation rate, detonation pressure and temperature, respectively, determined for Chapman-Jouguet point, Q_v – explosion heat, $\Sigma(g)$ – volume of explosion products.

Table 3
Estimated EE parameters containing aluminium powder Depuval (purity 99.7% Al)

Characteristics of tested EEs			Aluminium powder composition adopted in calculations g/kg of EE			Calculation results					
Mass fraction of powder in EE, %	ρ_{OMW} , kg/m ³	D_{exp} , m/s	$\text{Al}_{\text{akt.}}$	Al_{inert}	Al_2O_3	D_c , m/s	$P_{c,j}$, MPa	$T_{c,j}$, K	Q_v , MJ/kg	$\Sigma(g)$, mol/kg MW	
0	1.177	5460±160	0.00	0.00	0.00	5340	8159	2237	2.688	43.572	
5	1.171	5320±110	4.9850	0.0000	0.0150	5433	8407	2649	3.529	41.15	
			0.0000	4.9850	0.0150	5156	7379	2177	2.564	41.37	
10	1.205	5200±120	9.9700	0.0000	0.0300	5504	9001	3008	4.328	37.86	
			0.0000	9.9700	0.0300	5049	7159	2109	2.440	39.17	
20	1.223	4690±80	19.9400	0.0000	0.0600	5320	9029	3760	6.068	30.47	
			0.0000	19.9400	0.0600	4631	5993	1965	2.189	34.79	
30	1.279	4390±150	29.9100	0.0000	0.0900	5364	9237	4413	7.741	23.82	
			0.0000	29.9100	0.0900	4300	5210	1798	1.934	30.45	

where: designations as in Table 2.

Summary

Aluminium powder is often used as an additive to blasting explosives, rocket propellants and pyrotechnical products in order to modify their properties.

Aluminium increases energy generated in combustion reaction of rocket propellants, which results in increase in blast ability and explosion energy of underwater explosives. Usually, aluminium powder of micrometre-order grain size is used. There are also available aluminium powders of large specific area and grain size of nanometre order.

In case of ideal explosives, application of Al as an additive results in decrease in detonation rate, which is due to chemical inertness of aluminium particles in chemical reaction zone which is behind front of detonation wave. High-energy oxidisation reaction of Al occurs only in detonation product zone. High amounts of energy generated at this stage improve air parameters of blast waves. Additionally, some aluminium is oxidised with oxygen from air. This after-burning effect is used in thermobaric ammunition.

Use of aluminium powder in non-ideal explosives gives rather different results. Let us consider ammonium saltspetre-based materials of ammonal group. Aluminium powder there serves as a sensitizer in order to sensitize ammonium nitrate and improve its detonation parameters. As aluminium powder content increases, detonation rate increases also, while critical diameter decreases. This is due to the fact that aluminium serves as a fuel for the other mixture component – ammonium nitrate (V).

Emulsion explosives that are mixture of oxidisers, fuels and other additives, in this case behave as ideal explosives. Addition of aluminium powder results in decrease of EE detonation rate, and as aluminium content increases, parameters of air blast waves improve; however to a smaller extent than for molecular explosives.

Estimated values confirm idea of analysis of detonation parameters adopted in assumptions for conducted numerical analysis. Values of detonation rate are obtained for the assumption that detonation rate is defined by thermodynamic equilibrium state, which is reached in gaseous detonation product, are close to experimentally obtained values.

High explosion heat, with assumption of complete conversion of aluminium, confirms suitability of aluminium powder as energizing ingredient for explosive mixtures. At the same time, consistence

of experimental data with data calculated with the assumption of inert role of powder grains in processes occurring between front of the detonation wave and Chapman-Jougueta point confirms the hypothesis of extension of aluminium powder reaction time in comparison to processes occurring in the gas phase, which determine experimentally measured values of detonation rate.

For high powder concentration, calculation results may be underrated, as complete thermal equilibrium is not reached in the detonation zone.

In the actual detonation process, powder grains take over heat from formed reaction products, however temperature within the grain is not fully equilibrated. Internal part of the grain has lower temperature than the very centre.

Energy deficit (loss) absorbed by non-reacting part of the grain is then lower than adopted for calculations, when temperature equalisation in the entire grain volume is assumed.

Conclusions

Based on the conducted research, we arrived at the following conclusions:

- addition of aluminium powder results in decrease in detonation rate of emulsion explosives, just as for ideal explosives, which is a result of chemical inertness of aluminium in the reaction zone,
- rise of overpressure pulse, as well as overpressure on blast wave front compared to aluminium-free charge is a result of strongly exothermic oxidisation reactions of this metal in a detonation product zone,
- in a detonation product zone, flaked powder is more active; charges containing higher amount of this powder have better detonation parameters: detonation rate as well as parameters of powder air blast wave.

Literature

- Maranda A., Gołębek B., Kasperski J.: *Materiały wybuchowe emulsyjne*. WNT, Warszawa 2008.
- Mendes R., Ribeiro J., Plaksin I., Campos J.: *Non ideal detonation of emulsion explosives mixed with metal particles*. AIP Conf. Proc. 2012, **1426**, 267.
- Wang L., Wang N., Zhang L.: *Study on key factors affecting energy output of emulsion explosives in underwater explosion*. Propellants, Explosives, Pyrotechnics 2012, **37**, 83 -92.
- Takahashi K., Murata K., Kato Y., Fujita M., Itoh S.: *Non-ideal detonation of emulsion explosives*. Journal of Materials Processing Technology 1999, 85.
- Paszula J., Maranda A., Gołębek B., Kasperski J.: *Zdolność do wykonania pracy górniczych materiałów wybuchowych w teście wybuchu podwodnego*. Górnictwo i Geoinżynieria 2004, **28**, 3/1.
- Murata K., Takahashi K., Kato Y.: *Measurements of underwater explosion performances by pressure gauge using fluoropolymer*, 12th International Symposium on Detonation, August 11–16, 2002, Wyndham San Diego at Emerald Plaza.
- https://www.akzonobel.com/expancel/system/Images/AkzoNobel_Expan-cel_DE_product_specification_tcm65-49451.pdf (15.06.2015).
- http://www.bendalutz.com/sites/default/files/documents/DEPUVAL_Product_Information_20130415_E.pdf (15.06.2015).
- Grishkin A. M., Dubnov L. V., Davidov V. Yu., Levshina Yu. A., Mikhailova T. N.: *Effect of powdered aluminum additives on detonation parameters of high explosives*. Combustion, Explosion and Shock Waves 1993, **29**, 2.
- Papiński A.: *An implementation of the steepest descent method to evaluation of equilibrium composition of reactive mixtures containing components in condensed phases*. Central European Journal of Energetic Materials 2007, **4**, 1–2.
- Papiński A.: *Modelowanie rozwoju spalania i wybuchu w niejednorodnych fizycznie ośrodkach reaktywnych*. Wojskowa Akademia Techniczna, Warszawa 2009.
- Fried L. E., Souers P. C.: *BKWC: An Empirical BKW Parameterization Based on Cylinder Test Data*. Propellants Explos. Pyrotech. 1996, **21**, 215–223.
- Hobbs M. L., Baer M. R.: *Nonideal Thermoequilibrium Calculations Using a Large Product Species Data Base*. Shock Waves 1992, **2**, 177–187.

14. Papliński A., Maranda A.: *Investigation of the influence of cooling salts upon explosive performance of emulsion explosives*. Central European Journal of Energetic Materials 2015, **12**, 3.

*Ewelina BEDNARCZYK – M.Sc., (Eng.), has graduated from the Faculty of Advanced Technologies and Chemistry of the Military University of Technology (2015). Specialisation: explosives and pyrotechnics.

Professor Andrzej MARANDA – Ph.D., D.Sc., (Eng.), has graduated from the Faculty of Chemistry of the Warsaw University of Technology (1971). Currently he works at the Military University of Technology and at the Institute of Industrial Organic Chemistry (IPO) in Warsaw. Scientific interests: chemistry and technology of explosives, environmental protection. He authored or co-authored five monographs, 21 patents and over 580 papers printed in scientific journals and presented at national and international scientific conferences.

e-mail: amaranda@wat.edu.pl, tel.: +48226837541

Józef PASZULA – Ph.D., (Eng.), has graduated from the Faculty of Chemistry and Technical Physics of the Military University of Technology. He has received his Ph.D. from the Faculty of Mechatronics (2000). Currently, he works at the Faculty of Advanced Technologies and Chemistry of the Military University of Technology. He co-authored over 100 scientific papers (articles and conference presentations).

Andrzej PAPLIŃSKI – Ph.D., D.Sc., (Eng.), Associate Professor of the Military University of Technology, majored in Technical Physics (1971). Currently he works at the Department of Safety Engineering of the Institute of Aviation Technology at the Faculty of Mechatronics and Aviation of the Military University of Technology. He authored or co-authored over 130 scientific papers (articles and conference presentations). Specialist in process modelling of high-energy material conversion, numerical modelling of loading homogeneous and multiphase media, analysis of material and dynamic hazards.

Aktualności z firm

News from the Companies

Dokończenie ze strony 45

STYPENDIA, STAŻE

INNOCHEM – nowy program NCBR dla branży chemicznej

Wzmocnienie zdolności przedsiębiorców do generowania innowacyjnych rozwiązań we współpracy z sektorem nauki oraz poprawa pozycji konkurencyjnej na rynkach światowych polskiego sektora chemicznego – oto cel nowego programu sektorowego INNOCHEM Narodowego Centrum Badań i Rozwoju. Pierwszy konkurs już ruszył. Uruchomiony w ramach PO Innowacyjny Rozwój program sektorowy INNOCHEM to kolejna, po programach INNOMED i INNOLOT, inicjatywa NCBR mająca na celu wspieranie prac badawczo-rozwojowych w konkretnej branży. Na dofinansowanie projektów w ramach pierwszego konkursu programu INNOCHEM Narodowe Centrum Badań i Rozwoju przeznaczyło 120 mln PLN. Beneficjentami programu będą przedsiębiorcy i konsorcja składające się z przedsiębiorców. Minimalna wartość kosztów kwalifikowanych wynosi 1 min PLN, a maksymalna to 20 mln PLN. Nabór wniosków w ogłoszonym dziś przez NCBR konkursie rozpoczęcie się 1 lutego i będzie trwał do 1 marca 2016 r. (kk)

(<http://www.ncbir.pl/>, 21.12.2015)

NCBR ponownie wesprze branżę metali nieżelaznych

Opracowanie i wdrożenie innowacyjnych rozwiązań, które podnoszą konkurencyjność polskiej branży metali nieżelaznych, to cel programu CuBR – wspólnej inicjatywy Narodowego Centrum Badań i Rozwoju oraz KGHM Polska Miedź SA Nabór wniosków w trzeciej edycji konkursu zacznie się w styczniu 2016 r.. Na badania naukowe, prace rozwojowe i działania wspierające transfer ich wyników w przemyśle metali nieżelaznych w tej edycji konkursu organizatorzy przeznaczyli wspólnie 108 mln PLN. Finansowanie otrzymają wyłonione na drodze konkursowej innowacyjne projekty obejmujące badania przemysłowe i prace rozwojowe związane z nowymi technologiami wydobycia, procesami metalurgicznymi, przetworzonymi, nowymi wyrobami i ich recyklingiem przy jednoczesnym obniżeniu kosztów środowiskowych. Wnioski można składać w ramach czterech obszarów tematycznych: górnictwo i geologia, przeróbka (*mineral processing*), metalurgia, przetwórstwo, nowe materiały, a także ochrona środowiska, zarządzanie ryzykiem i efektywność w biznesie. (kk)

(<http://naukawpolsce.pap.pl/>, 22.12.2015)

NCBR finansuje innowacje w medycynie

Firmy z branży medycznej otrzymają ponad 57,5 mln PLN na realizację innowacyjnych projektów. NCBR ogłosiło wyniki drugiego konkursu programu sektorowego INNOMED. NCBR realizuje program INNOMED we współpracy z firmami zrzeszonymi w Polskiej Platformie Technologicznej Innowacyjnej Medycyny. Drugi konkurs programu Centrum przeprowadziło w ramach działania 1.2 „Sektorowe programy B+R” PO Inteligentny Rozwój, służącego realizacji dużych przedsięwzięć B+R, istotnych dla rozwoju poszczególnych branż i sektorów gospodarki. Jego budżet wynosił 95 mln PLN. O dofinansowanie ubiegało się 18 przedsiębiorstw. Wsparcie z NCBR w łącznej wysokości ponad 57,5 mln PLN otrzyma 10 firm, których wkład własny wyniósł ponad 38 mln PLN. Centrum dofinansuje innowacyjne projekty, mające na celu opracowanie technologii i rozwiązań służących poprawie jakości życia i zdrowia Polaków. Wsparcie uzyskają m.in. prace nad zwiększeniem skuteczności diagnostycznej obrazowania dynamicznego, innowacyjnym lekiem przeciwnowotworowym wykorzystującym mechanizm reaktywacji białka p53 oraz badania przedkliniczne i kliniczne substancji aktywnych o działaniu przeciwnowotworowym. (kk)

(<http://www.ncbir.pl/>, 23.12.2015)

III edycja programu „Atom dla Nauki”

„Atom dla Nauki” to ogólnopolski projekt informacyjno-edukacyjny PGE EJ 1. Celem III edycji programu, podobnie jak w latach ubiegłych, jest popularyzacja wiedzy na temat energetyki jądrowej zarówno wśród studentów, jak i kadry naukowej uczelni wyższych. Ideą, która przyświeca projektowi, jest promocja młodych, polskich naukowców oraz wspieranie ośrodków naukowych w tworzeniu zaplecza eksperckiego dla rozwijającego się w Polsce sektora energetyki jądrowej. W ramach tegorocznej edycji programu wystartowały dwa konkursy. Pierwszy, skierowany do studentów, polega na rozwiązaniu zadania problemowego związanego z energetyką jądrową. Spółka chce zainteresować tą tematyką studentów nie tylko kierunków ścisłych i technicznych, ale także społecznych, przyrodniczych medycznych, prawa, czy turystyki. W drugim, adresowanym do doktorantów i kadry naukowej, zostaną nagrodzone najlepsze publikacje naukowe poświęcone szeroko rozumianej technologii jądrowej. Nagrodami dla laureatów konkursów będą m.in. wyjazd studencki do wybranej elektrowni jądrowej oraz nagrody pieniężne. (kk)

(<http://naukawpolsce.pap.pl/>, 12.01.2016)

Dokończenie na stronie 54