



Cast Porous Charges on a Base of Ammonium Nitrate–Urea Eutectic

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Abstract: There are great number tasks of explosive technique, requiring the charges with low pressure and detonation velocity. Powerful tool of regulation of these parameters is lowering of charge density. The main goal of this work is elaboration of technology of manufacture and investigation of explosive properties of charges on a base of eutectic ammonium nitrate-urea mixtures (AN/UR) that have melting point $T_m < 100$ °C. The physicochemical properties of these mixtures were investigated by means of DSC method and fusion diagram of them was plotted. The composition AN/UR 80/20, that has $T_m = 80-90$ °C was chosen for subsequent investigation. The molten composition was mixed with fine aluminum powder, portion of it was placed into paper tube. The level of a liquid was less than length of the tube. Crystallization of melted mixtures was carried out in vacuum chamber, the level of liquid increased at pumping because of expansion of air bubbles introduced with aluminum particles and reached the upper cork of tube. In such a way porous charges were formed. The dependence of charge density vs. population of tubes by melted mixtures was plotted. Calculated heat explosion of mixtures at content of aluminum Al = 10-15% is $Q_v = 4.5-5.3$ MJ/kg, calculated detonation velocity at density $\rho = 0.5-1$ g/cm³ changes from $D = 3.2$ to 5.2 km/s. Detonability of charges was investigated experimentally. Failure diameter (d_f) of detonation was measured, it was $d_f = 22$ mm ($\rho = 0.6-0.7$ g/cm³) for charges without confinement at initiation by means of booster or blasting cap.

Keywords: eutectic, ammonium nitrate, urea, fusion diagram, detonability, detonation velocity

Introduction

Change of charge density is one of the main means of regulation of explosive properties: velocity and pressure of detonation of charges. In practice requirement of charges with low density is often necessary one. Use of such charges decides many problems of military and peace application of charges of explosives, e.g. soft throwing, soft crushing of valuable rocks, metal working etc. Production of charges with bulk density is more simply put into practice, but use of them is not comfortably.

The explosive properties of foamed liquid – nitromethane and diethyleneglycoldinitrate are described in work [1].

The properties of cast porous charges on base of TNT are described in work [2]. These charges are prepared by melting TNT by means of water bath with following aeration of melt or addition of fine-dispersed aluminum. Then mixture is exposed to vacuum forming. The application of safe melting of mixtures on a base of ammonium nitrate (AN) by means of water bath for production of these charges is impossible one because of high melting point of AN ($T_m \sim 170^\circ\text{C}$).

It is known from literature, that AN is capable to form eutectic mixtures with urea (UR), with nitrates of some amines and with some other substances. In present work this fact was used for decrease of melting point of ammonium nitrate and for production of cast porous charges on a base of eutectic mixture.

Experimental Investigation of Physicochemical Properties

The study of physicochemical properties of mixtures of AN with UR was carried out by means of method differential scanning calorimetry (DSC).

The method DSC was used for measurement of endothermic effects modification transitions of AN in our previous work [3]. The many values of melting point of nitrocompounds, that introduce into data base of National Institute of Standards and Technologies of USA (NIST), had been obtained by means of this method and the data had been analyzed in work [4].

Dependencies of heat flow vs. temperature for AN and UR are presented in Figure 1.

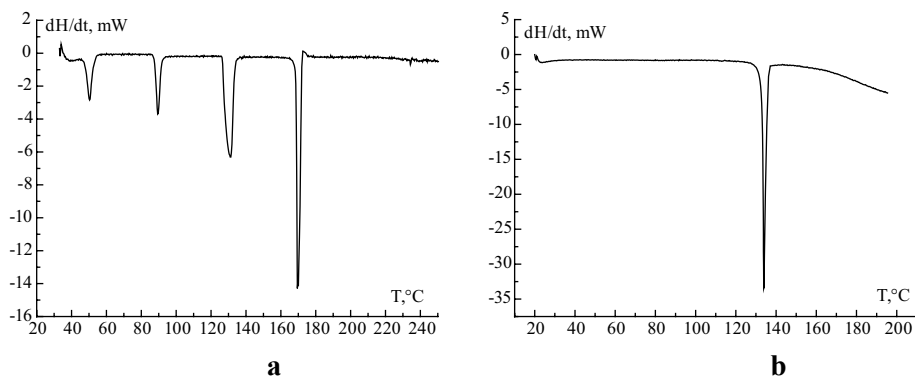


Figure 1. Dependencies of heat flow vs. temperature for AN (a) and UR (b) under investigation.

AN (Figure 1a) has three endothermic peaks of modification transitions besides melting peak. UR in Figure 1b has melting peak only.

Eutectic mixture is formed at proportion of mixture AN/UR 60/40. Peaks of phase transitions of ammonium nitrate are absent in this mixture in graph (Figure 2a). Only melting peak is registered at temperature $T = 47\text{ }^{\circ}\text{C}$. If ammonium nitrate is in excess in eutectic mixture (80% AN - 20% UR, Figure 2b), melting occurs in the range $80\text{--}90\text{ }^{\circ}\text{C}$. Peaks of phase transitions of ammonium nitrate are present in graph, but temperatures of these transitions are slightly displaced in comparison with pure ammonium nitrate (Figure 1b). Diagrams of fusibility of mixtures AN/UR are presented in Figure 3.

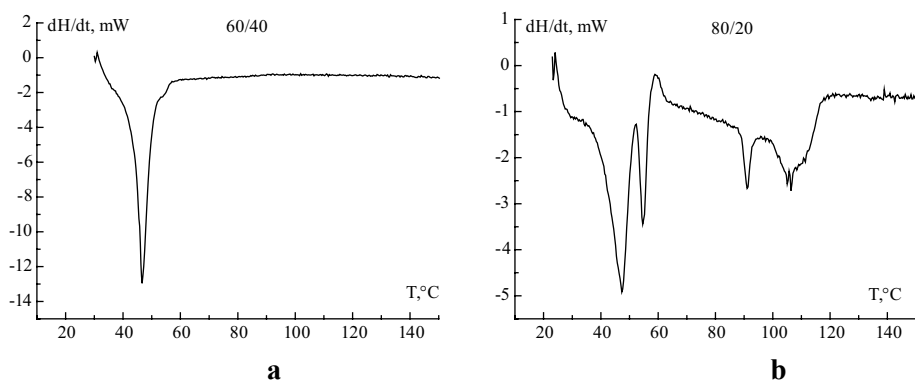


Figure 2. Dependencies of heat flow vs. temperature for mixtures AN-UR 60/40 (a) and 80/20 (b).

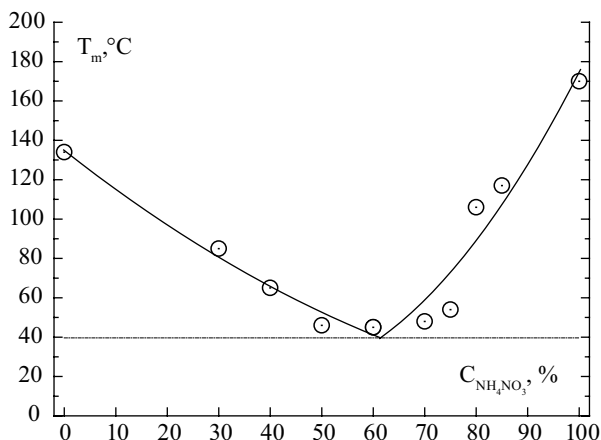


Figure 3. Diagrams of fusibility of mixtures AN-UR.

Hence, it is possible to get mixture with melting point on a base of mixture AN-UR lower than $T_m = 100$ °C at content of ammonium nitrate 60-80%. These mixtures can be melted in water bath.

Explosion Characteristics

Calculations

Accounting of parameters of detonation of mixtures on base of eutectic with aluminum was following stage of work. Calculation was carried out by means of SD code [5]. Dependence of heat explosion for mixture AN/UR 75/25 vs. aluminum content is presented in Figure 4. Heat explosion of mixtures with content of aluminum $C_{\text{Al}} = 10-15\%$ changes in the range 4.5-5.3 MJ/kg, detonation velocity for these mixtures at identical density slightly depends from proportion of ammonium nitrate and urea. Detonation velocity changes from $D = 3.2$ to $D = 5.2$ km/s at change of density from $\rho = 0.5$ to $\rho = 1.0$ g/cm³.

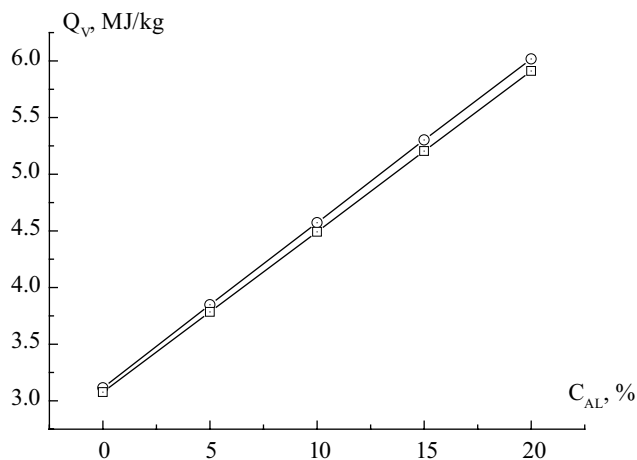


Figure 4. Heat explosion of mixtures AN/UR 75/25 with content of aluminum 10% (squares) and 15% (circles).

Preparation of cast charges

The main quantity of detonability and detonation velocity measuring of cast porous charges was carried out with mixtures AN/UR 70/30 and 75/25 with 10% aluminum powder. For improvement wettings of small particles of aluminum with melt addition of polyacrylamide was used $C_{paa} = 0.5\%$.

Charges for runs were obtained by means of vacuum formation. All components were weighted in corresponding proportions and mixed in closed glass flask during $t = 20$ min. Then dry mixture was placed into glass reactor with jacket for heating water circulation. Water was heated to $T = 90\text{--}98$ °C and was pumped by means of thermostat. At temperature about $T = 80$ °C mixture began to melt. It was carefully mixed to obtain porous homogeneous liquid mass.

Melted mixture was flooded into paper tubes of different diameter. Tubes were closed by means of gas-permeable corks. The level of a liquid was less than length of the tube (between corks). The level of liquid (h_1) and length of the tube (h_2) were measured. Crystallization of melted mixtures was carried out in vacuum chamber ($P \sim 0.2\text{--}0.1$ at), the level of liquid increased at pumping because of expansion of air bubbles introduced with aluminum particles and reached the upper cork of tube. Charges were held at vacuum about 2 hours.

Paper confinement was deleted, after full crystallization. Then mass, diameter, length of charges were measured, and densities of charges were calculated. Charge density depended from level of a liquid and length of the tube ratio (population of paper tubes by melt – h_1/h_2). Dependence of density vs. population of paper tubes – h_1/h_2 is presented in Figure 5.

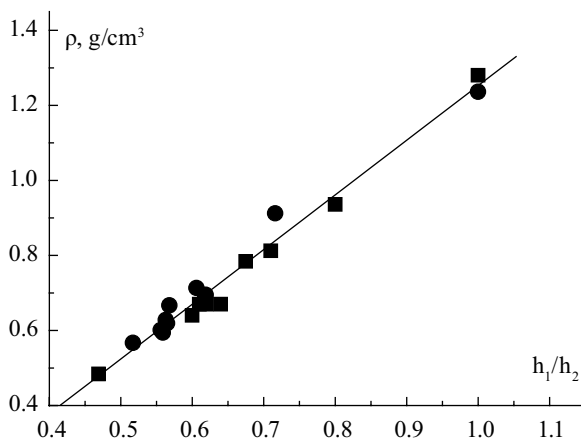


Figure 5. Dependence of density vs. population of paper tube by melt. Squares are composition (AN/UR 70/30)+10% Al, circles are composition (AN/UR 75/25)+10% Al.

To check uniformity of density along the length some charges were parted, and densities of every part were measured. Densities of every part were found to be the same ones practically.

Detonability and Detonation Velocity

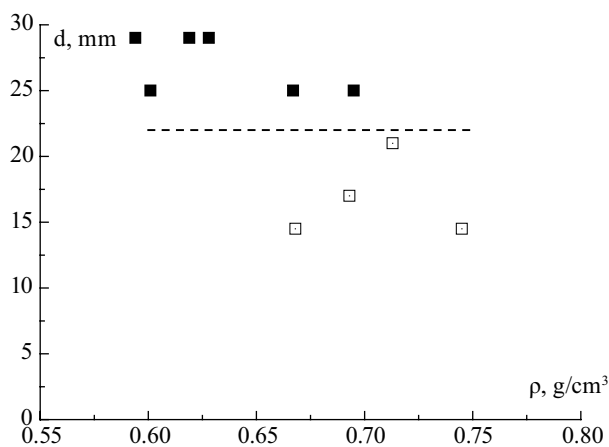
To measure failure diameter of detonation of charges they were fixed to thin steel witness-plates. Plate was placed on massive steel plate to prevent strong deformation of witness-plate. Initiation of detonation was realized by means of pellets that were pressed from retarded RDX (diameter was $d = 11$ mm, mass was $m = 1.5$ g and density was $\rho = 1.67$ - 1.68 g/cm³). Detonation of charge or damping of process was identified according to deformation of witness-plates surface.

Velocity of detonation of charges under investigation was measured by means of Russian fotoregister GFR-3 in steel tubes ($d = 10$ mm, wall thickness was $\delta = 13$ mm, length was $l = 125$ mm). Radial holes were drilled in steel wall. The photorecording procedure of detonation in steel tubes was the same one that was thoroughly described in works [6, 7].

Results of measuring of failure diameter of detonation of mixture AN/UR 75/25 with 10 % aluminum powder are demonstrated in Table 1 and in Figure 6.

Table 1. Results of runs with porous charges of mixture AN/UR 75/25 with 10% aluminum powder

Charge number	Charge length, mm	d, mm	ρ , g/cm ³	Result
33	126	14.5	0.668	Damping, track length 50 mm
34	120	14.5	0.745	Damping, track length 50 mm
29	199	17	0.693	Damping, track length 50 mm
25	183	21	0.713	Damping, track length 70 mm
23	153	25	0.667	Full detonation
27	180	25	0.601	Full detonation
32	193	25	0.695	Full detonation
24	151	29	0.628	Full detonation
28	170	29	0.594	Full detonation
31	177	29	0.619	Full detonation

**Figure 6.** The dependency of detonability vs. density (black points are detonation, white ones are attenuation of detonation).

One can see, that stable detonation of charges under investigation propagates at densities $\rho = 0.6\text{--}0.7$ g/cm³ at charge diameter $d = 25$ mm and greater d . Detonation damps at charge diameter $d < 25$ mm. Deformation of witness-plate is shown in Figure 7.

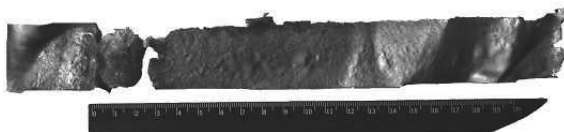


Figure 7. Witness-plate after detonation.

Results of measuring of detonation velocity of charges (composition AN/UR 75/25+10% Al) are shown in Figure 8 as points.

Discussion

Decreasing of D with growth of density that is seen in Figure 8 is well known fact for mix porous explosive [8]. It is explained by growth of failure detonation diameter with extension of density [8, 9].

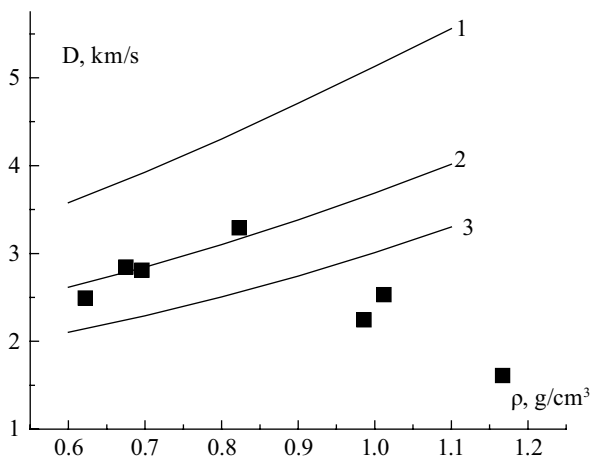


Figure 8. The comparison of results of measured detonation velocity of porous (composition AN/UR 75/25+10% Al) charges (points) with calculation. 1- results of calculation in assumption that all AN (part of AN forming eutectic and crystalline part) reacts in detonation wave, 2 - the same one in assumption that 26% of crystalline AN does not react, 3 - the same one in assumption that all crystalline AN (34%) does not react.

The line 1 in Figure 8 represents result of calculation D according to SD code [5] for composition AN/UR 75/25+10% Al. One can see that measured velocities of detonation at densities $\rho = 0.6\text{--}0.8 \text{ g/cm}^3$ are less than calculated one on 1 km/s approximately. Results of runs that were carried out by means of DSC method (Figure 2 b) are basis for explanation of this fact. Part of AN in mixture AN/UR 60/40, as one can see from this figure, is crystals that are mixed with aluminum much worse than liquid eutectic. It could be supposed that crystalline part of AN (~34%) did not react in detonation wave. Calculated dependence D vs. ρ in this case is described by line 3, that is situated lower than experimental points. Obviously some part of crystalline AN reacts with aluminum nevertheless. The line 2 is result of calculation with the assumption that only ~26% of crystalline AN does not react. Experimental points at $\rho = 0.6\text{--}0.8 \text{ g/cm}^3$ are situated not far from this line.

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References

- [1] Kondrikov B.N., Kozak G.D., Starshinov A.V., Critical Conditions of Low and High Velocity Regimes in Liquid Nitrocompounds, *Paper summaries - The 11th Int. Detonation Symposium*, USA, Snowmass, Colorado, **1998**, pp. 231-234.
- [2] Kozak G.D., Kondrikov B.N., Sumin A.I., Dependence of Detonation Velocity on Charge Density for Foamed Alumotole (Al/TNT) and TNT Mixtures, *Combustion, Explosion and Shock Waves*, **1998**, 34(4), 448-452.
- [3] Litovka O.B., Starshinov A.V., Kozak G.D., Design-Experiment Investigation of ANFO Mixtures on a Base of Different Brand Marks of Porous Grill Ammonium Nitrate, *Trans. of the 10th seminar "New trends in research of energetic materials"*, Univ. Pardubice, Czech. Republic, April, **2007**, pp. 742-752.
- [4] Arinina S.V., Kozak G.D., Heat of Melting of Nitrocompounds Measuring by Means of the Differential Scanning Calorimeter Method, *Trans. of the 9th seminar "New trends in research of energetic materials"*, Univ. Pardubice, Czech. Republic, April, **2006**, p. 473-479.
- [5] Sumin A.I., Gamezo V.N., Kondrikov B.N., Raikova V.M., Shock and Detonation General Kinetics and Thermodynamics in Reactive Systems Computer Package, *Trans. of the 11th Int. Detonation Symposium*, USA, Bookcomp, Ampersand, **2000**, pp. 30-35.
- [6] Kozak G.D., Akinin N.I., Raikova V.M., Arinina S.V., Explosion Hazard of Some Organic Peroxides, *Proc. 6th seminar "New trends in research of energetic*

materials”, Univ. Pardubice, **2003**, pp.173-181.

- [7] Kozak G.D., Raikova V.M., Aleshkina E. I., *Critical Conditions of Diffusion and Photorecording Procedure of Detonation Process*, (Rus.), Publish center of Mendeleev University of chemical technology, Moscow **2005**.
- [8] Annikov V.E., Kondrikov B.N., Akinin N.I., Kozak G.D., Properties and Safety of Explosive Slurry in: *Reliable and safety of technological processes*, (Rus), Publish center of Mendeleev University of chemical technology, Moscow **2006**, pp. 5-25.
- [9] Kondrikov B.N., Annikov V.E., Kozak G.D., Generalized Dependence of Failure Diameter of Detonation of Porous Substance vs. Density, (Rus.), *Combustion, Explosion and Shock waves*, **1997**, 33(2), 111-123.