Central European Journal of Energetic Materials, **2010**, *7*(4), 325-334
ISSN 1733-7178

Impact Initiation of Compositions Ammonium Perchlorate with Inorganic Components

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Abstract: Experimental data on sensitivity to impact of compositions ultra- and nanodispersed AP with inorganic components are presented. Critical parameters of impact initiation of these compositions lay down on the straight line in co-ordinates (e_{cr}, P_{cr}^2) characterising balance of energy at the impact.

Keywords: sensitivity to impact, ammonium perchlorate

Introduction

Mechanical sensitivity of compositions of type an oxidizer-fuel is constantly in the centre of attention of technologists and researchers of explosive processes as these compositions are a basis practically all formulae modern rocket propellants and commercial explosives. Special interest to them has arisen in the early sixties the last century in connection with accidents on manufacture of mixed solid propellants which main component was and remains till now ammonium perchlorate (AP). Most often accidents occurred at a stage of dry mixture of an oxidizer with metal (aluminium) or explosive (octogen, HMX) fuel components. Sensitivity of the specified compositions to mechanical stimuli has really appeared exclusively high.

Attempts of an explanation of the reasons of high sensitivity of power-consuming compositions of the considered type were reduced to classical scheme F. Bowden et al. [1], according to which the initiator of explosive reaction is frictional interaction of solid particles of fuel among themselves and with contact surfaces of the striker (anvil) thanks to which the high-temperature

centres of a heating are starting explosive processes in adjoining sites of fuel mass are formed. As the temperature of melting and a condition of a surface of particles are powerful regulators of their frictional heating then sensitivity of discussed compositions to impact should depend essentially on the listed physico-mechanical characteristics of components, including dispersion and hardness of solid particles.

However F. Bowden's experimental data uncertainly testified in favour of the conclusion made him. In Table 1 formed by results of [1], frequency values of the explosions received at impact on HE charges with an admixture of the various nature presented at them are resulted. Though these data speak about presence of some parallelism between frequencies of explosions and temperatures of melting of an admixture entered into them, but close correlational connection between the specified parameters is not observed. Here it is necessary to make a reservation, having noticed, that details of conditions of carrying out of experiments are absent in the book **[1]**.

Discussing results of Table 1, F. Bowden has noticed that admixtures in the size to 20 microns better than a smaller particle are sensitizing HE. On the other hand, it has given an example with a diamond dust (the size to 0.5 microns) which raises sensitivity of HE.

Table 1. HE sensitivity to impact in the presence of an admixtures **[1]**

Admixture	T_m, °C	Relative frequency of explosions, %			
		PETN	Mercuric fulminate	Tetrazen	Gun Powder
Without admixture	-	2	0	0	-
Ammonium nitrate	170	3	-	-	60
Silver nitrate	212	2	0	0	100
Potassium nitrate	334	0	-	3	100
Silver bromide	434	6	0	31	80
Plumbum chloride	501	27	0	30	-
Bismutite	685	42	100	100	-
Glass	800	100	-	-	-
Rock-salt	804	6	-	-	-
Copper glance	1100	50	100	38	-
Tiff	1339	43	100	38	-

Analyzing other data given in Table 1, we will note influence of an admixtures on sensitivity black gunpowder (GP) − one of the most before known mixed systems. Actually listed in the table nitrates of potassium and silver, sensitizing GP, it is difficult to name inert admixtures as they are the same oxidizers, as well

as a part state of GP potassium nitrate and consequently are equal in rights partners of reactions of chemical interaction at formation of the centres of explosion (hot spots) in solid explosive at impact.

Following from F. Bowden works idea about influence of local reactions of chemical interaction on sensitivity of compositions type an oxidizer-fuel has been successfully developed in I.A. Karpukhin's et al. subsequent works [2, 3], mainly with reference to the analysis of the mechanism of explosion initiation in modelling compositions and propellants on the base of AP. The most important results on this way are received by them by means of representations about two-stage (low - and high-temperature) process of thermal decomposition AP in which working out the essential contribution have brought L. Birkemshou [4], B.S. Svetlov et al. [5], G.B. Manelis et al. [6] and other known domestic and foreign physico-chemists.

According to I.A. Karpukhin the depth of AP decomposition on the first (low-temperature) stage proceeding on structural and superficial defects of crystals increases with the size of particles d (within the accepted business fractions). Therefore mixtures on large (more than 100 microns) AP are more sensitive to impact, than on small (~10 microns) ones. From here follows that practically free of defects ultradisperse (UDP, $d \leq 1$ a micron) and nanodisperse (NDP, $d \leq 0{,}1$ microns) ammonium perchlorates should decay in one (high-temperature) stage and their behaviour in mixed compositions, including the compositions containing the admixtures of the various nature, should not differ from behaviour staffer single-stage decaying (in the macrokinetic plan) HE.

Experiments

In the present work the impact sensitivity of binary explosive compositions on the basis of UDP ($d \approx 1$ micron) and NDP ($d \approx 50$ nanometer), containing the second component inorganic substances of various nature − metals, oxide of metals, metalloids and so forth for the purpose of their sensitized or phlegmatized abilities for investigated ammonium perchlorates is investigated. Other purpose of the work pursued an establishment of correlation dependence between sensitivity and properties of components of investigated compositions.

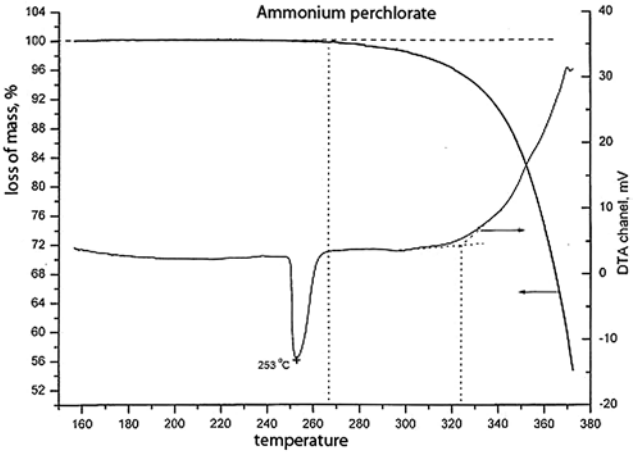

Figure 1. Derivatogram of UDP.

Derivatogram of used in the work UDP is shown in Figure 1. It follows from it, that UDP decays in one stage, since 267 °C. Weak endothermal peak on a DTA-curve at 253 °C is connected with polymorphic transition AP from rhombic in to cubic form (ΔH° transition 96 J/g). Presence of polymorphic transition at heating AP also proves to be true the data received by means of DSC-analysis.

Sensitivity to impact of investigated compositions was determined on drop-weight mashine K-44-2 by a method critical energies (CE) with use muffless a variant of instrument № 2 (according to N.A. Kholevo) with rollers in diameter D = 10 mm. Thus steel muff of the instrument was replaced by two layers of the glue together tracing-paper. We will underline, that the basic advantage of the instrument № 2 − a possibility of free movement of substance in a radial direction during the impact in our experiments remained completely.

Energy of impact E = MgH and a thickness of HE charge h is varied in method CE. Here M − mass of weight (usually − the constant of experiment), H − height of weight dropping. At the given thickness h find such height H_{50} at which frequency of explosions forms 50% in a series from 25 tests. The specified search is facilitated by use of Brucetone procedure [7] if height H_0 on which all refusals are fixed is known in advance.

Dependence E_{50} (h) received in experiments has characteristic minimum E_{cr} in a critical point h_{cr} [8]. Critical pressure of explosion initiation $P_{cr} = \sigma_s (1+0.1925D/h_{cr})$ corresponds to this h_{cr} on curve of HE charges strength. Usually value E_{cr} scale on the area of the striker (roller) $S = \pi D^2/4$ and receive size of specific critical energy of initiation $e_{cr} = E_{cr}/S$. Above specified σ_s − strength

of a charge in destruction by impact. At tool research the charges of various thickness are destructed by drop-weight impact and pressure of charge destruction is measured by means of gauges of pressure. The size σ_s is defined as factor at specified hyperbolic dependence P(h). However σ_s with sufficient accuracy for practice (≈10 %) can be calculated for binary compositions under the formula [9]:

$$\sigma_s = \sigma_0\{[1+\alpha\rho_0/(1-\alpha)\rho_1]/[1+\alpha\rho_0\sigma_0/(1-\alpha)\rho_1\sigma_1]\},$$

where σ_0, ρ_0 – strength and density of the basic component, σ_1, ρ_1, α – strength, density and the content of the second component in a mixture.

The list of components used in experiences and the most probable values of durabilities of the charges made of them, is resulted below (Table 2).

Table 2. Components used in experiments and values of their strengths on destruction

Component	Code	σ_s, MPa
aluminium oxide	OXA	860
silicon oxide (aerosil)	AS-200	620
aluminium powder	PAL-2	280
nanoaluminium ALEX	NAL	280
carbon	C	230
nano disperse AP	NDP	220
Talc		210
Ultradisperse AP	UDP	175
White graphite	BN	178
Boron	B	127
Dinitrotoluene	DNT	57
Sulphur	S	47.5

The specified values of material strengths are received in own experiments, adopted from different sources, calculated by data about their melting temperatures and adiabatical compressibility, found by selection from several sizes by the analysis of data for their definition. In Table 2 the received values of critical parameters of initiation of the investigated compositions on the basis of UDP and NDP are resulted. HE charges were made by a method of pressing under the pressure of 300 MPa with duration not less than 15 seconds. Drop-weight is 10 kg.

Results and Discussion

Analyzing data in Table 3, we will note the following:

1. On level e_{cr} the sensitivity NDP is less than sensitivity UDP. At first sight, this conclusion contradicts I.A. Karpukhin's statement about independence of sensitivity AP from the size of particles. However the obvious contradiction here is not present. Its essence is consist in peculiarity of NDP charges pressing. Unlike other compositions investigated which pressure of pressing at 15-second duration remains constants, pressure at pressing NDP constantly decreases and it consequently should be raised, sometimes at some times while it definitively is not stabilised at demanded level. As a result the density of pressed charges NDP comes nearer to crystal one, whereas density of charges UDP on 5-10% below its size, despite the increased duration of pressing. Accordingly the strengths of charges NDP almost on 20% more than strengths of UDP charges, its are more difficult for impact destruction and consequently critical energy and pressure of initiation at charges NDP higher, than for charges UDP in spite of the fact that critical thickness h_{cr} at them are identical. Equality of values $h_{кр}$ is powerful argument in favour of representations about insignificant distinction of levels of sensitivity of charges UDP and NDP though, proceeding from formal reasons, it is necessary to recognise smaller sensitivity NDP.

2. Sensitivities of compositions UDP with PAL-2, AS-200, talc, BN and corundum (OXA) are approximately identical with a base component, despite essential distinction in hardness and melting temperatures of the listed materials. All the matter is that at the given percentages of the second components the strengths and critical thicknesses of composed charges and essentially UDP not too differ among themselves, and the frictional effect of touching particles in this case has appeared is extremely insignificant.

Weak distinction in values e_{cr} the listed compositions is connected with various heat conductivity of admixtures.

3. High phlegmating effect is received at introduction in both AP ultradisperse carbon. Concerning AP carbon has shown chemical inertness, being rather strengthed substance with high melting temperature that allowed for mixed charge to accumulate the big mechanical energy before destruction. However owing to distinctive feature of the molecular structure, carbon in this case has played a role of greasing and a thermal ballast, reducing in a two-phasic stream of the destroyed charge frictional contact of particles and taking away superfluous energy of impact from the potential centres of explosion.

4. Fusible and low-strength DNT and sulphur which could play a role classical phlegmatizers for AP, being chemically active components, enter with

UDP in chemical interaction at impact, raising temperature of the centres of decomposition on AP particles. In which connection the single-stage of UDP thermo-destruction practically has not raised, contrary to expectations, critical parameters of impact initiation of compositions if AP decayed in two stages.

Table 3. Critical parameters of impact initiation in compositions on the base of UDP and NDP

№	Composition	σ_s, MPa	h_{cr}, mm	e_{cr}, J/cm^2	P_{cr}, GPa
1	NDP	220	0.47	21.2	1.12
2	NDP/NAL 72/28 (stoich)	240	0.85	14.6	0.78
3	NDP/PAL-2 72/28 (stoich)	240	0.56	12.7	0.98
4	NDP/AS 72/28	257	0.71	15.9	0.95
5	NDP/C 88/12 (stoich)	221	0.30	47.0	1.64
6	NDP/Talc 88/12	229	0.50	15.1	1.11
7	NDP/S 88/12	157	0.57	9.00	0.69
8	NDP/B 88/12	238	0.83	13.8	0.79
9	NDP/S/C 76/12/12	168	0.40	19.8	0.98
10	UDP	175	0.48	13.7	0.88
11	UDP/ NAL 72/28 (stoich)	240	0.90	9.0	0.75
12	UDP/PAL-2 72/28 (stoich)	191	0.50	15.0	0.93
13	UDP/PAL-2 80/20 (equim.)	186	0.49	13.7	0.92
14	UDP/AS 72/28	208	0.90	13.1	0.65
15	UDP/C 88/12 (stoich)	179	0.24	41.4	1.62
16	UDP/S 88/12	133	0.59	7.2	0.57
17	UDP/OXA 72/28	201	0.48	13.9	1.01
18	UDP/DNT 77/23 (stoich)	114	0.47	5.7	0.52
19	UDP/B 88/12	188	0.96	9.80	0.57
20	UDP/Talc 88/12	183	0.50	14.6	0.89
21	UDP/BN 88/12	187	0.48	16.9	0.93
22	UDP/S/C 76/12/12	140	0.21	12.5	0.92

The note: (stoich) − composition with zero oxygen balance; (equim) – equimolar composition

5. Expected there were test data on sensitivity to impact of ternary mix AP with S and C. According to [1] sulphur, being a fusible and reactive component, facilitate passing of decomposition processes for mix compositions, especially carbon contained. There is data about catalyzing influence of sulphur on process of interaction AP with C. However in binary composition with AP carbon proves as active flegmatizer.

6. Boron introduction has led to sensibilisation AP, despite high hardness and melting point of B. Rough estimates show in a hot spot of a charge up to 50% initial B reacts with AP and products of its decomposition.

7. On the reason of decrease in parameters of impact initiation NDP and UDP at introduction the NAL and the AS it is necessary to stop especially. The matter is that curves E_{50} (h) for these compositions differ presence of a characteristic cusp in a point $h \approx 0.5$ mm in which the minimum of the majority of other curves settles down. Apparently, at the specified thickness of a charge there is a change of the mechanism of explosion initiation from strenghed destructions with sharp dropping of impact pressure to initiation of explosion owing to an external ("dry") friction on contact surfaces of charge and rollers of the test device without charge destruction as whole at constant or poorly changing pressure of impact. If in the first case strong emission of the destroyed substance from under rollers is observed then in the second case the tested charge, poorly being deformed along a impact axis, is destructed only in two-three local sites on periphery of a charge and in the same place are visible local burning out of HE and symmetric burns on contact surfaces of rollers.

From the spent analysis with evidence follows, that mechanical characteristics (strength on destruction, structural plasticity) chemically inactive second component play the basic role in the course of initiation of the investigated AP-containing compositions. The physical mechanism responsible for explosion initiation, still is strengthening charge destruction during which time the potential (elastic) energy reserved in loading system (LS) of drop-weight mashine, is spent for movement and dissipative heating of destruction fragments. In critical conditions of explosion initiation, as shown in [8], relationship $e_{cr} = aP_{cr}^2$, following from the law of energy conservation should be carried out under the impact. The factor $a = S/k$ (k – mechanical rigidity of LS) equal 37.4 J/(cm GPa)^2 at the experiments with HE of organic nature.

The formula is received in the assumption that on destruction, movement and heating of HE charge is spent half of energy reserved in LS at initial stage of impact. For Figure 2 according to Table 3 are plotted in co-ordinates (P_{cr}^2, e_{cr}) experimental values of critical parameters of explosion initiation for AP-containing compositions and the dotted line is straight line with angular coefficient 17.1 J/(cm GPa)^2.

It has appeared approximately twice less received earlier for organic HE. It means, that practically all potential energy LS reserved in it at an elastic stage of impact is spent for a complex of effects at destruction of HE charges of inorganic nature. At that on a dotted straight line points with explosion initiation on the mechanism of a dry friction, and also a point characterising initiation of mix UDP-DNT have laid down. It is natural, as a leading stage of chemical process of explosion initiation for investigated systems is thermo-destruction of inorganic AP. Only in this case it proceeds not in two stages divided by some time interval,

and in one stage, but still on two channels – with formation of ammonia and chloric acid on the first channel and a set of oxidising and neutral products on the second channel.

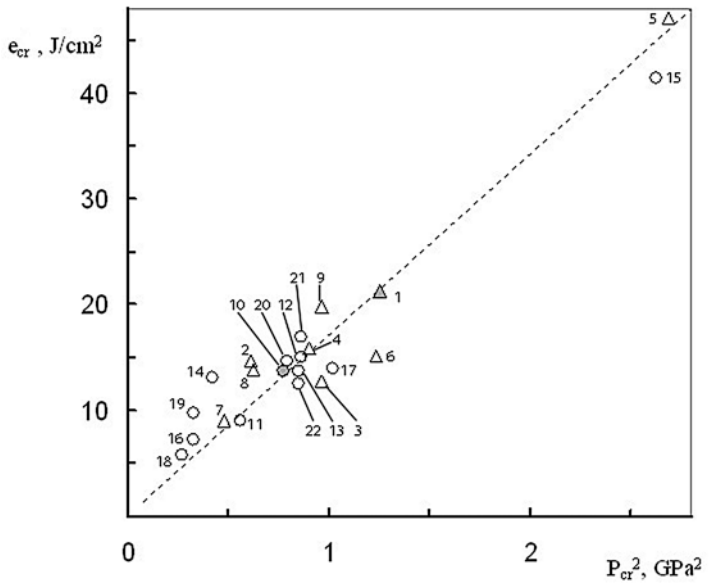

Figure 2. Dependence e_{cr} from P_{cr}^2 (Δ-compositions on the basis of NDP, ○-compositions on UDP). The figures corresponding to order of an arrangement of compositions in Table 3.

Conclusion

The received laws allow to define on one of parameters of explosion initiation (P_{cr} or e_{cr}) other parameter. Available calculated-experimental ways of definition of the specified parameters open possibilities of aprioristic creation of safe conditions for carrying out of technological processes with power-consuming materials.

Acknowledgements

The Foundation of Basic Research of RF supported the investigation through grant 10-03-00420-a.

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