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BORON REACTIONS IN AN EXPLOSION

V. I. Penekin, et al

Army Foreign Science and Technology Center  
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220 SEVENTH STREET NE.  
CHARLOTTESVILLE, VIRGINIA 22901

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AUTHOR: Penekin, V. I., M. N. Makhov and A. Ya. Apin

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ABSTRACT: Reactions of boron and orthoborane in explosions of their mixtures with Hexogen and TEPN were studied. A certain optimum content of boron in explosive mixtures was found, beyond which excessive formation of energetically unfavorable carbides and nitrides takes place. Orthoborane affects explosion energy unfavorably, since energy is used to break the chemical bonds and the hydrogen and carbon content of the mixtures is increased.

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Metal bonding of explosives is widely used in practice. The addition of a metal to explosive leads to an increase in the heat of the explosion and efficiency. At present, aluminum-bonded explosives have been investigated in detail and have come into practical use [1-7].

This work is devoted to experimental study of the heat of explosion and the reactions of the explosive conversion of metal-bonded compounds based on boron. One of the major problems in setting up this investigation was clarification of the question of completeness of oxidation of boron during an explosion.

The tests were carried out with hexogen ( $C_3H_6N_6O_6$ ) and TEPN ( $C_5H_8O_{12}N_4$ ). Boron was introduced into the composition in the form of a metal powder of particle size  $d \sim 0.005$  mm and in the chemically-bound state, in the form of the organometallic compound orthoborane ( $C_2B_{10}H_{12}$ ). Three combinations were investigated: hexogen-boron (H + B), TEPN-boron (TEPN + B) and TEPN + orthoborane (TEPN + o-B). Hexogen and TEPN, with particle size  $d \sim 0.005$  mm, precipitated from acetone, were used in manufacture of the compositions.

Boron was introduced into the explosive by means of prolonged mixing in a special apparatus, in a benzene medium. The TEPN + o-borane composition was prepared by applying o-borane from dichloroethane solution. Uniformity of the composition was monitored by the heat of combustion and a calorimetric unit. Nonuniformity of the compositions was not over 0.5% boron. The charges had a diameter of 15 and height of 60 mm. The density of the H + B compositions was  $1.77 \text{ g/cm}^3$ . TEPN + B and TEPN + o-B compositions had a relative density of 0.98. The tests were carried out in brass casings with a wall thickness of 7.5 mm.

Determination of the heat of explosion was carried out in a calorimetric bomb with a self-sealing cover [8]. The heat value of the unit was determined by the heat of combustion of benzoic acid ( $31,600 \pm 100 \text{ cal/degree}$ ). Before a test, the bomb was washed with helium and evacuated (residual pressure 1-2 mm Hg). After a test, chemical analysis of the explosion products (EP) was carried out.

The EP content of gaseous oxides and carbon dioxide was determined by the absorption method, and of hydrogen, by burning it over copper oxide at a temperature of 285°C. The presence of boron oxide was determined by titration in the presence of mannitol. The quantitative content of boron nitride was found from the pressure after the explosion and the nitrogen balance. Qualitative determination of boron nitride was carried out by ammonia extraction, while boiling the boron nitride with alkali. Boron carbide was detected in the EP by X-ray structural analysis.

Data on the heats of explosion of various mixtures are presented in Table 1, from which it follows that the introduction of boron into the explosive charge leads to considerable increase in the explosion energy. In this case, the increase in explosion energy depends essentially on the explosive oxygen balance: the higher the oxygen balance, the greater the energy given off during explosion of metal-bonded compositions. Heat emission in the TEPN + B system is higher than the explosion energy of the H + B system (Fig. 1, 1, 3).

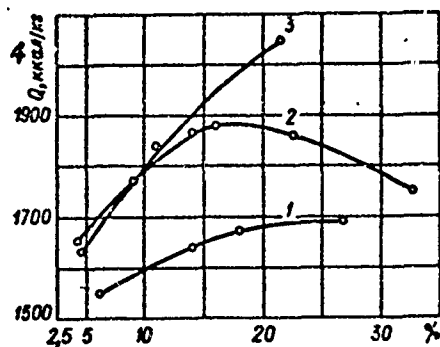


Fig. 1. Heat of explosion vs. per cent metal content:  
1. TEPN + o-borane; 2. hexogen + boron; 3. TEPN + boron; 4. Q, kcal/kg

It follows from Fig. 1, 2 that metal must be introduced within specific limits to increase the explosion energy. Thus, for the H + B system, the maximum heat emission is observed with introduction of 16.5% metal. Further increase in metal content in the mixture leads to a decrease in explosion energy. It is evident that the maximum heat emission is determined by the oxygen balance for various explosives.

It has been assumed that increase in heat of explosion in mixtures of explosives with metals takes place as a result of reduction of the water and carbon dioxide by the metal vapors. We have demonstrated that the maximum

heat emission in the H + B mixture corresponds to practically complete reduction of the water vapors and carbon dioxide (Fig. 2, 1, 6). However, in distinction from aluminum-bonded compositions [6], boron does not reduce carbon dioxide. The latter follows from the parallel nature of curves 3 and 5, Fig. 2. The increase in heat of explosion of the H + B mixture (Fig. 1, 2) to the maximum point is determined basically by the formation of boron oxide. The maximum point corresponds to the maximum boron oxide content in the EP.

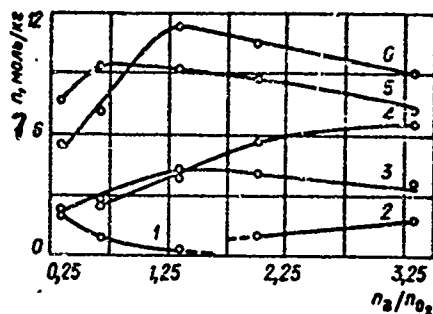


Fig. 2. EP composition of H + B mixture vs. metal content in initial mixture ( $n_B$  and  $n_{O_2}$  are the numbers of atoms and moles of boron and oxygen in the initial mixture): 1.  $CO_2$ ; 2.  $B_4C$ ; 3.  $B_2O_3$ ; 4.  $BN$ ; 5.  $CO$ ; 6.  $H_2$ ; 7.  $n$ , mole/kg.

Further increase in boron content of the mixture leads to decrease in explosion energy, which is explained by the reduction of boron oxide content in the EP. The latter is caused by decrease in the relative amount of oxygen in the initial mixture. As a consequence of this, there is an appreciable flow of energetically unfavorable nitride and carbide reactions of the metal (Fig. 2, 2, 4). It should be noted that the formation of boron nitride is observed with a low metal content in the mixture.

The results obtained in investigation of the compositions TEPN + B and TEPN + o-B permit a comparison of the effectiveness of use of free and chemically-bound boron. It is suggested that introduction of an organoboron compound with high metal content (~75%), o-borane, into the explosive composition should lead to more complete oxidation of the metal, since, by decomposition of o-borane molecules during the explosion, the boron should be in the form of individual atoms and valence-unsaturated particles. In this state, boron should be very reactive and easily enter a reaction with oxygen. However, experiment did not confirm this proposition. It follows from Fig. 1, 1, 3

that heat emission in the case of TEPN + B is higher than in the TEPN + o-B system: curve 1 passes considerably below curve 3.

This experimental fact is explained by the fact that, during explosion of the TEPN + o-B composition, the flow of carbide-metal reactions becomes of significant value. It was found that, in the EP of the TEPN + o-B composition, the boron carbide content was twice that in the TEPN + B composition (Figs. 3, 4). In this case, boron carbide was found in the EP of the TEPN + o-B composition at a low metal content in the mixture (Fig. 4, 1). The formation of boron carbide in the EP is caused by the fact that there already are boron carbide fragments in the initial o-borane molecule, in which carbon atoms, in the 6-coordination state, which is unusual for it, are bound to four atoms of boron [9]. The formation of boron carbide in the EP apparently is explained by the fact that the pressure and temperature developed in the explosion of the TEPN + o-B mixture is insufficient for complete decomposition of the o-borane molecules into its component elements.

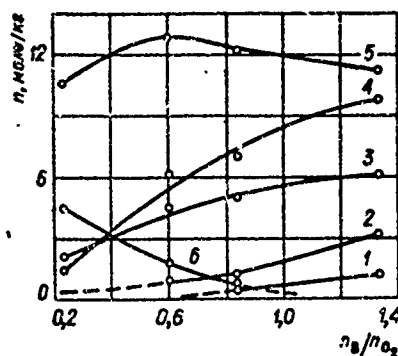


Fig. 3. EP composition of TEPN + boron mixture vs. metal content in mixture: 1. B<sub>4</sub>C; 2. BN; 3. B<sub>2</sub>O<sub>3</sub>; 4. H<sub>2</sub>; 5. CO; 6. CO<sub>2</sub>; 7. n, mole/kg

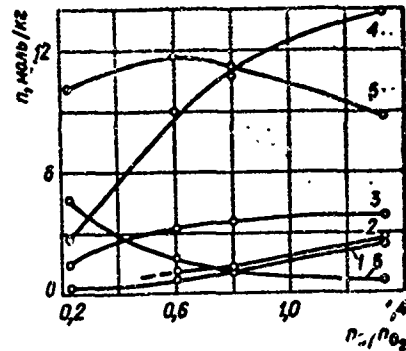


Fig. 4. EP composition of TEPN-o-borane mixture vs. metal content in mixture:  
 1. B<sub>4</sub>C; 2. BN; 3. B<sub>2</sub>O<sub>3</sub>;  
 4. H<sub>2</sub>; 5. CO; 6. CO<sub>2</sub>;  
 7. n, mole/kg.

For more complete oxidation of the boron, o-borane must be introduced into a mixture with an explosive with a higher oxygen balance than that of TEPN. The formation of a considerable amount of boron carbide in the EP (Fig. 4, 1) reduces the boron oxide content, which leads to a decrease in the explosion energy of the system TEPN + o-B, in comparison with the system TEPN + B. The decrease in explosion energy of the system TEPN + o-B is caused by the circumstance that a portion of the energy is consumed in breaking down the o-borane molecules during the explosion. The enthalpy of formation of the latter, equals  $\Delta H_f^0 = -43.3$  kcal/mole [10] or 300.5 kcal/kg.

The discussion presented above is illustrated graphically in Fig. 5. Curves 1 and 4 are the dependence of the heat of explosion of the TEPN-o-B and TEPN + B compound on metal content in the composition. Curve 2 is plotted on the assumption that the decomposition of the o-borane molecules takes place without expenditure of energy. In other words, the ordinate between curves 1 and 2 is the energy expended in breaking chemical bonds in the o-borane molecule.

Curve 3 is plotted on the assumption of equal boron carbide content in the EP, i.e., the function of the heat of explosion of the TEPN + o-B system would correspond to curve 3, if the boron carbide content in the EP of this system were equal to the content of the latter in the EP of the TEPN + B system. The ordinate between curves 2 and 3 corresponds to the energy losses in the TEPN + o-B system, caused by the flow of the energetically unfavorable boron carbide formation reaction. The difference in curves 3 and 4 is caused by the fact that the introduction of o-borane into the compound is connected with an increase in amount of hydrogen and carbon in the initial mixtures, in comparison with the TEPN + B system.

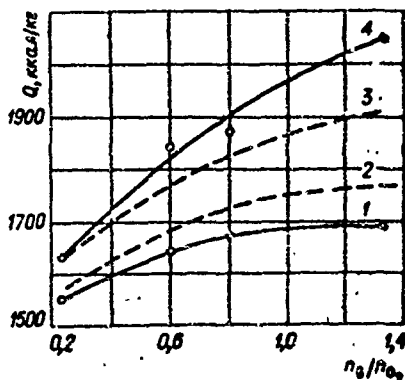


Fig. 5. Comparison of dependence of heat of explosion of TEPN + B and TEPN + o-borane compositions on metal content: 5.  $Q$ , kcal/kg.



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