

THE CHEMICAL REACTION MECHANISM IN THE DETONATION OF EXPLOSIVES

A. Ya. Apin and L. N. Stesik

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It is known that in liquid explosives the detonation front is nonuniform. The reaction does not occur over the entire cross section but in individual centers formed by the collision of oblique shock waves [1, 2].

In [3] an investigation was made of the influence of powders of certain inorganic compounds (BaSO_4 , HgO , and others) on the transition from a low-velocity to a high-velocity detonation in gelatin dynamite, which is a continuous homogeneous explosive. It was found that the presence of inhomogeneities in the charge — particles of a foreign powder — considerably facilitates the transition from a low to a high-velocity detonation, if the specific weight of the particles exceeds 2.8 g/cm^3 . This phenomenon was explained as follows. The shock front of the detonation wave is reflected at the foreign particles. At the points of collision between waves reflected from adjacent particles there is an increase in pressure and temperature which leads to rapid decomposition at these points and then propagates to the adjoining volume of explosive.

In this study we investigated the influence of powder admixtures on the critical diameter of the detonation of a solid, continuous and homogeneous (from the macroscopic point of view) explosive. As such explosives we selected ballistite powders (plasticized nitropolymers) of the NB and N types. NB powder contains 40% nitroglycerine; N powder contains 28% nitroglycerine and 11% dinitrotoluene.

For creating inhomogeneities in the explosive we used inorganic powders, whose density $\rho (\text{g} \cdot \text{cm}^{-3})$ and particle size $\delta (\text{cm})$ were as follows:

	CaCO_3	MgO	Bi_2O_3	PbO	HgO	W
$\rho, \text{g} \cdot \text{cm}^{-3} =$	2.71	3.2—3.7	8.2—8.9	8.0—9.5	11.14	19.3
$\delta, \text{cm} =$	$3 \cdot 10^{-4}$	$3 \cdot 10^{-3}$	$5 \cdot 10^{-4}$	$3 \cdot 10^{-4}$	$3 \cdot 10^{-4}$	$5 \cdot 10^{-4}$

The size of the chalk particles was determined most reliably; this was measured by two methods: filtration of gas through the powder and measurement under the microscope. The results were found to be in good agreement.

The explosive charges were cylindrical rods 25-30 cm in length. Detonation was initiated using an auxiliary detonator of cast TNT-RDX 50/50. The propagation of the detonation was recorded by a SFR high-speed photorecorder; the detonation velocity was measured at the same time. In order to obtain a clearer trace of the detonation on the photographic film the charges were wrapped in a single layer of cellophane.

Compositions prepared from two different batches of NB powder were used. Table 1 gives the results of experiments made with compositions prepared from the first batch (NB-1).

Table 2 gives data obtained for compositions prepared from the second batch of NB powder (NB-2) and for compositions prepared from N powder. Tables 1 and 2 give the densities of the charges $\rho_1, \text{g} \cdot \text{cm}^{-3}$, and the densities of the powder $\rho_2, \text{g} \cdot \text{cm}^{-3}$, corresponding to the given charge densities. In addition, the tables give the concentrations n, cm^{-3} , of the particles of the admixture and the detonation velocity $D, \text{m} \cdot \text{sec}^{-1}$. The detonation velocities were averaged for charges of different diameters. Such averaging is entirely possible because the detonation velocity of ballistite powders is not dependent on the diameter of the charge [4].

In charges of ballistite powders, even with diameters less than the critical value d^- , the detonation is propagated without change of velocity, but after traveling some distance it is abruptly interrupted.

No interval of smooth deceleration is noted. * The arithmetic mean error of measuring detonation velocity is $\pm 0.5\%$.

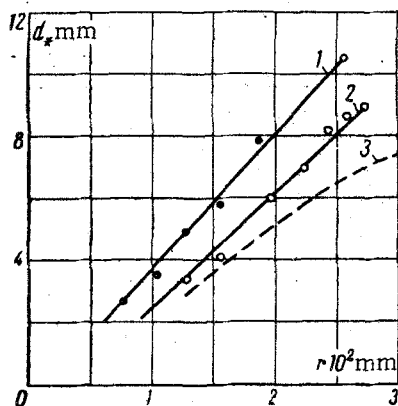
*The observed facts are of theoretical interest. The pressure in the detonation wave on the axis of the charge obviously remains constant until the detonation attenuates. The abruptness of attenuation is probably related to the peculiarities of the mechanism of detonation in continuous explosives in which inhomogeneities are evenly distributed.

Tables 1 and 2 give two values of the charge diameter: the diameter d_*^+ at which the detonation was propagated stably in all the experiments (three experiments), and the diameter d_*^- at which the detonation was damped in all the experiments (two-three experiments). The figure shows the mean values for d_*^+ and d_*^- .

NB-1 + admixture	$\rho_1, \text{g/cm}^3$	$\rho_2, \text{g/cm}^3$	n, cm^{-3}	d_*, mm		D, m/sec
				d_*^+	d_*^-	
0%	1.630	1.630	—	10.5	10.0	7420
1% PbO	1.660	1.647	—	4.0	—	7420
1% HgO	1.654	1.640	—	4.0	—	7420
1% Bi ₂ O ₃	1.654	1.641	—	4.0	—	7450
1% MgO	1.657	1.648	—	9.0	8.0	4740
0.2% CaCO ₃	1.644	1.642	$0.86 \cdot 10^8$	8.2	7.1	7490
0.5% CaCO ₃	1.652	1.648	$2.16 \cdot 10^8$	6.2	5.0	7490
1% CaCO ₃	1.657	1.646	$4.32 \cdot 10^8$	5.1	4.5	7440
2% CaCO ₃	1.660	1.636	$8.66 \cdot 10^8$	3.7	3.2	7450
5% CaCO ₃	1.680	1.634	$21.9 \cdot 10^8$	3.2	2.0	7440
1% W	1.651	1.636	$1.64 \cdot 10^8$	8.9	7.6	7450
7% W	1.725	1.604	$1.20 \cdot 10^7$	7.0	6.1	7460

NB-2 and N + admixture	$\rho_1, \text{g/cm}^3$	$\rho_2, \text{g/cm}^3$	n, cm^{-3}	d_*, mm		D, m/sec
				d_*^+	d_*^-	
NB-2 + 0%	1.621	1.621	—	8.85	8.50	7580
0.02% CaCO ₃	1.620	1.620	$0.085 \cdot 10^8$	8.50	8.15	7570
0.05% CaCO ₃	—	—	$0.211 \cdot 10^8$	8.10	7.70	7580
0.1% CaCO ₃	—	—	$0.422 \cdot 10^8$	6.90	6.60	7560
0.2% CaCO ₃	1.610	1.608	$0.844 \cdot 10^8$	6.10	5.50	7550
0.5% CaCO ₃	—	—	$2.11 \cdot 10^8$	4.04	—	—
1% CaCO ₃	—	—	$4.22 \cdot 10^8$	3.60	3.00	—
H + 0%	1.590	1.590	—	28.0	27.0	—
0.5% CaCO ₃	—	—	$2.08 \cdot 10^8$	11.6	11.3	—
1% CaCO ₃	—	—	$4.15 \cdot 10^8$	8.2	7.7	—
2% CaCO ₃	—	—	$8.30 \cdot 10^8$	7.0	6.4	—
5% CaCO ₃	—	—	$20.75 \cdot 10^8$	5.6	5.2	—

Tables 1 and 2 show that the introduction of inorganic admixtures into the powder appreciably reduces the value of the critical diameter d_* . PbO, HgO, and Bi₂O₃ bring about the greatest reduction in critical diameter. Experiments with chalk admixture revealed that d_* decreases with increase in the concentration of admixture particles in the powder. An initial analysis of the results of the first series of experiments with NB-1 powder revealed that d_* is linearly dependent on the mean distance between admixture particles. This indicates the following mechanism of the chemical reaction in a detonation wave propagating through a powder charge with foreign particles. The chemical reaction in the detonation wave is initiated in individual centers, whose concentration, in the first approximation, is proportional to the concentration of the foreign particles. Then the reaction is propagated into the adjacent layers of powder. Accordingly, the reaction time has two parts: the time for the reaction to develop in the center (delay time t_0) and the time of propagation of the reaction from the centers to the adjacent layers of powder ("burning" time t_p)



$$t = t_0 + t_p = t_0 + \frac{r - \delta}{2u} \quad (1)$$

Here r is the mean distance between reaction centers, δ is the characteristic dimension of the center; u is the mean velocity of propagation of the reaction in the powder. The quantity r can be expressed in terms of the concentration of reaction centers:

$$r = N^{-1/3} \quad (2)$$

If it is assumed that d_* is proportional to the time of the chemical reaction, we can write

$$d_* = B + C(r - \delta) = B + C(N^{-1/3} - \delta) \quad (3)$$

However, formula (3) is not applicable for a very small content of admixture in the powder, if N is identified with the concentration of foreign particles. For this reason it was of interest to measure d_* for small concentrations of foreign particles. In this case the form of the dependence of d_* on N must be determined to some degree by the mechanism of chemical reaction during the detonation of the pure powder.

If the reaction in the pure powder is homogeneous (simultaneous over the entire layer of powder compressed by the shock wave) the introduction of inhomogeneities into the charge essentially changes the mechanism of the chemical reaction. A heterogeneous reaction occurs which competes with the homogeneous reaction. The influence of the heterogeneous reaction on d_* is first felt when the time of this reaction becomes less than the time of the homogeneous reaction, that is, when the distance between the centers becomes less than a certain value. In this case the dependence of d_* on the mean distance between particles will be linear.

However, if the reaction in the pure powder is heterogeneous, i. e., if the powder contains reaction centers with some concentration n_0 , the introduction of an admixture does not change the reaction mechanism; there is a change only in the concentration of reaction centers in the powder. In this case the concentration of centers will be equal to the sum of the concentration n_0 of the initial centers and the concentration n of particles of the admixture

$$N = n_0 + n.$$

Then d_* must be a linear function of $(n_0 + n)^{-1/3}$; however, n_0 may be relatively small and important only in the case of a small content of admixture. For this reason we carried out experiments with a second batch of powder (NB-2), the chalk content of which was varied from 0.02% to 1%.

Detailed analysis of the results revealed that a linear dependence of d_* on the mean distance between centers applies only when the presence of reaction centers in the pure powder is assumed. On the basis of the experimental results we computed values of the concentration n_0 of initial centers in three batches of powder: $6.0 \cdot 10^7 \text{ cm}^{-3}$ for NB-1, $5.0 \cdot 10^7 \text{ cm}^{-3}$ for NB-2, and $1.2 \cdot 10^7 \text{ cm}^{-3}$ for N. The figure shows the dependence of d_* on the mean distance between reaction centers, with the initial centers taken into account: curve 1 for NB-1 and curve 2 for NB-2. The experimental results are well described by a linear dependence. The broken line in this same figure shows the dependence of d_* on the mean distance between chalk particles for samples from the second batch of NB powder. In this case the dependence deviates appreciably from the linear.

Thus, the results give one a definite basis for asserting that in a pure ballistite powder there are inhomogeneities that form centers for the development of a reaction during the passage of a detonation wave.

The concepts developed above of the focal mechanism of initiation of a chemical reaction in the detonation of powders can also be applied to the detonation of any other single or mixed explosives (solid, cast, molded, powdered).

The formula describing the dependence of d_* on the concentration of foreign particles assumes the form

$$d_* = B + C[(n_0 + n)^{-1/3} - \delta]. \quad (4)$$

If the delay time t_0 and the characteristic dimension δ of the center are neglected, (4) assumes the simpler form

$$d_*^3 N = \text{const.} \quad (5)$$

On the basis of the established cubic law, each individual explosive can be characterized by its own constant. The minimum initiating impulse necessary for exciting a stable detonation in a charge of explosive near d_* will obviously be proportional to the critical volume $V_* = d_*^3$. The greater V_* , the less sensitive should the explosive be to the excitation of a detonation by an initiating impulse. Therefore, the reciprocal of the critical volume will serve as a measure of detonation sensitivity dependent on the chemical properties and the physical homogeneity of the substance

$$V_*^{-1} = AN. \quad (6)$$

According to the adopted model, d_* is determined by the concentration of reaction centers and the velocity of propagation of the reaction through the substance. The latter is dependent on its chemical nature. Comparing the experimental results for N and NB powder, we see that n_0 for N powder is several times less than for NB powder. On the other hand, at a 5% chalk content, when n_0 can be neglected, d_* for N powder is approximately twice the value for NB powder. Therefore, the velocity of propagation of the reaction from centers in N powder is approximately half as great. The lesser value of n_0 and the propagation velocity determine the high value of the critical diameter for N powder.

Charges from different batches of NB powder have different values of d_* . Apparently, the principal reason for this is the deviation of the composition of specimens of the powder from the nominal composition, which is confirmed by the different values of the detonation velocity. NB-2 powder detonates with a great velocity, attributable either to the high

nitroglycerine content or the use of nitrocellulose with a high nitrogen content.

With respect to the nature of the reaction centers in the pure powder, it may be postulated that these are microscopic air bubbles or inclusions of nitroglycerine and trinitrocellulose due to incomplete gelation. If this is, in fact, the nature of the inhomogeneities, it should be possible to vary their concentration by varying the technique for producing the powder mass and thereby modifying the detonation capacity of ballistite powders.

The influence of temperature and the kinetics of the chemical reaction on d_* is considered in [5-7]. In the case of a heterogeneous reaction, a change in initial temperature affects the time of development of the reaction in a center, the velocity of propagation of the reaction from a center into the adjacent layers of explosive, and the probability of formation of new centers.

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