REACTION ZONES IN DETONATIONS OF DENSE EXPLOSIVES

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The data of experimental studies concerning diamond synthesis in detonation are analyzed. The new results of electrical conductivity diagnostics in TNT and TNT/RDX compositions are discussed. For the heterogeneous explosives like TNT/RDX the mesoscale processes are studied experimentally and numerically. All this information allows one to suggest the following reaction course in dense explosives: liberation of the over-equilibrium quantity of carbon in the shock wave in a diamond later in non-diamond form, oxidation of excess carbon, and in heterogeneous compositions – simultaneous interaction of components, including mixing.

INTRODUCTION

At present time different opinions exist about reaction zone thickness in detonations of high explosives (HE), as well as about the chemical processes within this zone and its general structure. The present paper analyzes the data to draw certain conclusions. The good indicator of a reaction course is the amount of free carbon, including diamond phase. In this connection the results of three lines of research treating this process are discussed:

- ultradisperse diamond synthesis, including experiments with isotope labels;
- electrical conductivity in detonating carbon-rich explosives;
- hydrodynamic interactions between the components of the heterogeneous explosives.

HIGH PRESSURE REACTION ZONE CHEMISTRY

The method of labeled atoms gives direct and unique information about the mechanism of the explosive detonation decomposition. All HEs contain carbon. In detonation of carbon-containing explosives, or shock-wave (SW) decomposition of carbon-containing compounds the carbon may be released in the diamond and non-diamond phase. The different carbon phases give additional information about the phenomenon, so the method may be quite successful.[1,2]

A stable isotope of carbon ^{13}C was introduced into the methyl group of TNT molecules. TNT was mixed with fine-grained RDX (smaller than 50 μm) in the first test and with coarse-grained (larger than 120 μm) HMX in the second one. Free charges were detonated in the explosive chamber (2 m^3) filled by gaseous helium. After detonation gaseous products were separated gradually by the condensation up to liquid helium temperature (4 K). The solid detonation products were separated chemically. ^{13}C atoms concentration in the detonation products was measured by the mass-spectrometry method.[1,2]

The main characteristics of the explosive charges and the distribution of ^{13}C atoms for the HE components and detonation products are given in Tables 1, 2.

Experimental results provided in Tables 1, 2 and data for the yield of diamond and non-diamond carbon forms for different explosive compositions[3,4] make it possible to calculate the distribution of carbon released from explosive components among the gaseous products, diamond and non-diamond carbon soots.[6] Results of calculation are given in Table 3.

TABLE 1. CHARACTERISTICS OF THE ORIGINAL EXPLOSIVE CHARGES AND SOOTS.

Test No.	***Explosive charges***					***Detonation soots***	
	HE composition		*Size of HE particles, μm*	*Mass of charge, g*	*Mass of booster, g*	*Condensed carbon, g*	*Diamond content, %*
	HE	*Content, %*					
1	*TNT* *RDX*	40 60	<50	35	4,5	3,3	61
2	*TNT* *HMX*	40 60	>120	31,14	9,67	2,6	45

TABLE 2. DISTRIBUTION OF ^{13}C ATOMS FOR HE AND DETONATION PRODUCTS.

Test No.	$^{13}C/C_\Sigma$, %						
	HE		***Detonation products***				
	TNT	*HE with booster*	*Condensed carbon*	*Diamond*	*CO*	CO_2	CH_4
1	9,23	5,7	5,5	6,8	4,2	4,6	3,9
2	9,23	5,03	5,94	8,05	4,94	3,78	-

TABLE 3. EXPERIMENTAL AND CALCULATED DISTRIBUTION OF CARBON FOR DETONATION SOOTS.

Test No.	***HE component***	***Detonation soots***				
		Yield of free carbon for HE component, %	*Part of HE carbon separated in free forms, %*	*Diamond content for individual HE soot, %*	***Diamond content in common soot, %***	
					Experimental	*Calculated by (1), (2)*
1	*TNT* *RDX*	12,3 5,2	33,0 32,5	79,4 50,0	67±5	69,2
2	*TNT* *HMX*	12,2 2,0	33,0 12,0	65,0 27,0		69,2

The results obtained may be explained as follows. The *Part of HE carbon separated in free forms* for TNT and fine-grained RDX is the same (≈33,0-32,5 %), so it is possible to conclude that during detonation explosive components are mixed before the complete formation of carbon particles and the start of the carbon oxidation process. A result of this is a reduction in the amount of TNT carbon transferred into the free form and an increase in the yield of carbon from RDX comparing with pure TNT and RDX explosives. In the case of coarse-grained explosive different levels of conversion of TNT and HMX carbon into free condensed forms are obtained (33,0 and 12,0 %). This result points to formation of carbon particles or oxidation of them to a marked level before mixing of carbon from explosive components.

Hence, in mixed fine-grained explosives the carbon is almost entirely mixed during the main detonation decomposition reactions. However, the *Diamond content for individual HE soot* for TNT and RDX is markedly different (79,4 and 50,0 %). This contradiction may be resolved as follows. It was found that behind the front of even quite strong SW the hydrogen is chemically bound with carbon or other heavy atoms.[5] It follows from these results and[3,4] that the initial stage of conversion of carbon-containing compounds in an SW may be the release of carbon in the diamond phase and methane:

$$C_7H_5N_3O_6 \rightarrow (23/4)C + (5/4)CH_4 + \ldots \quad (1)$$

for the case of TNT;

$$C_3H_6N_6O_6 \rightarrow (3/2)C + (3/2)CH_4 + \ldots \quad (2)$$

for the case of RDX (for HMX similarly).

At the next stage methane hydrogen oxidizes and carbon is released in the non-diamond phase since the physical and chemical parameters of the medium have changed. Then a part of the free diamond and non-diamond carbon released is oxidized by the remaining oxygen from the surface of formed carbon conglomerates.

Above assumptions explain precisely, in particular, the content of diamond in the decomposition products of many explosives and organic compounds explored.[3,4] In more detail this mechanism is discussed in[6].

Alternative hypothesis which explain the results obtained by means of labeled atoms do not contradict the individual facts but they do not describe the whole mechanism of carbon release and the experimental data on diamond synthesis.

CONDUCTIVITY IN TNT

Additional information supporting this hypothesis is given by the electrical conductivity measurements in detonation. The conductivity is an important physical parameter which, in principle, depends not only on the physical conditions (pressure, temperature, etc.) but also on the medium composition directly. In SW physics the conductivity tests are widely used, but several attempts to exploit the approach to study the reaction zone in HE had not led to a definite success. To our opinion, the perspectives of this method in detonation were retarded because of two reasons: the difficulties in the interpretation of the results and the insufficient level of the experiments. Nevertheless, the recent developments gave way to use electrical diagnostics to extract the valuable physical information about the detonation zone.

We will discuss mainly the case of TNT which produces a lot of free carbon. In this HE the conductivity behind the detonation wave is known to be remarkably high, but in earlier works a large scattering of data was observed: from ~ 4 $(\Omega\ \mathrm{cm})^{-1}$ in[7] to ~ 100 $(\Omega\ \mathrm{cm})^{-1}$.[8] Even more diverse results were reported later.

Recently more accurate measurements were done which can resolve this controversy. Our experiments gave about 25 $(\Omega\,\text{cm})^{-1}$ in cast TNT.[9] This large value explains part of the dispersion of literature data. The resistance of the experimental cell is quite low and can be easily masked by parasite inductance and/or resistance. The latter can be unexpectedly high because in short-time explosive tests the skin effect in metallic leads and cell materials is quite strong. In our experiments we used coaxial copper cell and a constant current scheme,[7] see Figure 1.

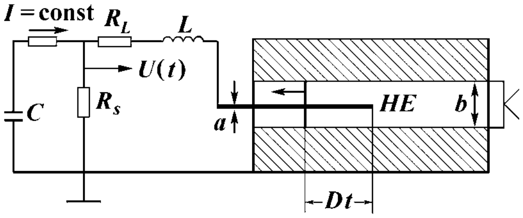


FIGURE 1. EXPERIMENTAL CONFIGURATION.

Typically the charge diameter b was around 10 mm and central electrode diameter a was 2 mm. For these dimensions the spatial resolution is 2 – 3 mm.[9] So this cell was used to study the conductivity profile behind the detonation front over the distance of several cm. The correction for the cell deformation under the detonation pressure was introduced. For this a dynamics of the explosion confined in a thick copper case was simulated. The recorded voltage $U(t)$ across the reference shunt R_S is affected by the parasitic impedance of the connecting line shown in Figure 1 as L and R_L. These distortions were removed numerically. Finally the conductivity is expressed as follows:

$$\sigma(x) = \frac{\ln(b/a)}{2\pi}\frac{f(x)}{D}\frac{d}{dt}\left(\frac{1}{R(t)}\right).$$

Here $x = Dt$ and $R(t)$ is the cell resistance,

$$R(t) = \left(\frac{R_S U(t) + L dU/dt}{U(0) - U(t)} - R_L\right).$$

$f(x)$ is the correcting factor for cell deformation. For example, if one has the composition TNT/RDX 50/50 and b/a = 10/2, then this correcting function is

$$f(x) = 1.019 + 0.035x,$$

x is supposed to be in centimeters.

Figure 2 demonstrates an example of experimental results. Due to experimental noise and variations of the charge density, the calculated $\sigma(x)$ profile is liable to considerable fluctuations. These errors are much less pronounced for the integral conductance:

$$Y = \int_0^{Dt} \sigma dx,$$

which is also shown in Figure 2.

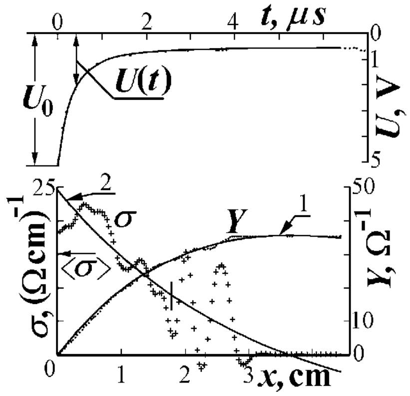


FIGURE 2. EXPERIMENTAL RECORD *U(t)* (TOP) AND THE CALCULATED CONDUCTIVITY PROFILE $\sigma(x)$ (BOTTOM) FOR CAST TNT.

Considering the essentially integral nature of the method, one should regard Y to be the net experimental result. As to conductivity, it is reasonable to estimate its general characteristics, namely the maximal value and the effective profile width. To that purpose the $Y(x)$ dependence was approximated by the simple smooth function using least squares method (see line 1 in Figure 2), and the smoothed conductivity by definition is the derivative of that function (line 2, Figure 2). This line follows the general trend of the data but does not reflect the irregular variations. The negative values of the smoothed conductivity at $x > 3.6$ cm is caused by the decrease of the fitting $Y(x)$ function in this interval while the data points give zero value. This deviation is within ≈ 10 % of the maximal conductivity and the total error in the recovered conductivity is ≈ 20 %. A quantity of interest is $<\sigma>$, i.e., the conductivity averaged over certain distance; in Figure 2 the arrow pointing to $15\ (\Omega\ \mathrm{cm})^{-1}$ marks the conductivity averaged over the interval from 0 to 2 cm behind the detonation front. The vertical mark on the σ profile shows the effective width of the conducting zone (e-fold decrease of σ). Note that the maximal conductivity found by this procedure is in fact a value averaged over the resolution limit (2 – 3 mm) and should not be confused with the σ maximum found by high-resolution method reported below.

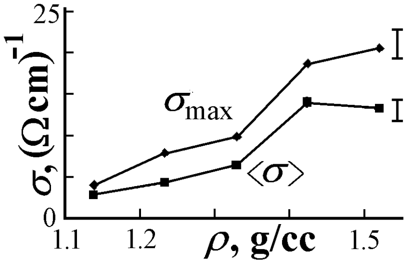


FIGURE 3. CONDUCTIVITY IN PRESSED TNT. $<\sigma>$ IS AVERAGED OVER THE 1 CM INTERVAL AND σ_{MAX} IS AN ESTIMATED MAXIMAL CONDUCTIVITY. VERTICAL BARS REPRESENT THE RANGE OF DATA SCATTERING.

The conductivity vs. initial density in pressed TNT was measured in a similar way, the minor modification was that the central electrode was fixed in an dielectric plug which confined the explosive. The results are shown in Figure 3.

The maximum of the $<\sigma>$ at 1.43 g/cc is not significant as compared with the errors. Thus we conclude that the conductivity increases with the initial density, approaching the value found in cast TNT. This differs from the results[10] where the minimum resistance was found around 1.35 – 1.4 g/cc. Apparently the difference was produced by the reflected shocks in the cell used in[10]. In our experiments this effect was also observed when the detonation wave met the dielectric plug at the end of the charge (Figure 4).

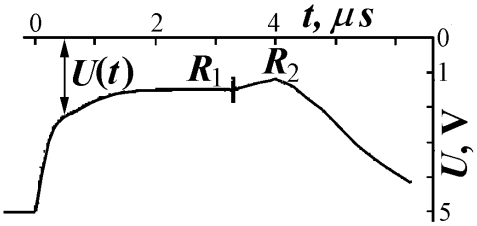


FIGURE 4. THE RECORD FOR TNT. ρ = 1.25 G/CC, R_1/R_2 = 1.42.

In Figure 4 a vertical bar at 3.2 μs marks the end of detonation. After that the voltage drop continues and the minimal resistance R_2 (affected by the shock reflected from the plug into the detonation products) is markedly less than R_1 reached just before the detonation ends. This post facto extremum appears at virtually the same densities (1.25 – 1.35 g/cc) as the resistance minimum.[10] Apparently this minimum was spurious.

The results reported above perhaps mark the limit that can be reached using conventional schemes of electrotechnical level. To extend the range of measured conductivity and/or resolution, new approaches are needed.

The scheme having about an order of magnitude better resolution and at least two orders of magnitude higher limit of conductivity[11] is described in a companion paper.[12] The chief idea was to place the reference shunt directly into the explosive thus minimizing parasite effects. The technique was applied to resolve the structure of the conducting zone in TNT. The high conductivity of about 30 (Ω cm)$^{-1}$ was found within centimeters behind the detonation front confirming the results of low-resolution method reported above. And it turned out that immediately behind the wave front there is a peak of even higher conductivity ~ 250 (Ω cm)$^{-1}$, about 1 mm wide. Note that the coaxial scheme described above can not resolve this peak because of insufficient resolution.

The discovery of the peak combined with the results reported above allow one to understand all known TNT conductivity data. For example, Hayes's records[8] were only 20 ns wide, i.e., confined to the peak zone which explains the highest conductivity reported in the literature. Most other works had much worse resolution (several mm) and could not recover the conductivity peak. To measure moderately high conductivity ~ 30 (Ω cm)$^{-1}$ serious problem is the parasite impedance which can easily simulate low conductivity. Part of the data scattering can be attributed to the density effect. Finally, some of the values reported are simply not reasonable, as 0.07 (Ω cm)$^{-1}$ in[13] though the origin of errors may not be clear in every case.

Earlier the conductivity peak was found in more oxygen-balanced explosives: PETN and RDX though the corresponding values were much lower.[14] There exist different opinions about the nature of conductivity in explosives in general, but for TNT the consensus is that high conductivity is the result of the free carbon release. In line of the view argued in the previous section the peak conductivity may be regarded as the manifestation of elevated (well over equilibrium) concentration of free carbon in conductive phase at early stage of chemical reaction.

INTERACTION OF COMPOSITE HE COMPONENTS

Most HEs are mixtures (the typical example is TNT/RDX composition). It is generally agreed that the structure of composite HEs is important during initiation. But for normal detonation the heterogeneous effects are usually neglected and the mixture is regarded as effectively uniform explosive with average properties. The mesoscale phenomena, e.g., interaction between the RDX grains and the TNT matrix, had not attracted much attention.

But these meso-processes certainly are important in detonation synthesis. Particularly, an interesting problem is the mixing of the components. The mixing can proceed either faster or slower than the main chemical reaction, or else mixing and reaction may evolve in parallel affecting each other. One approach to this problem is the analysis of detonation products described in the first section of present paper.

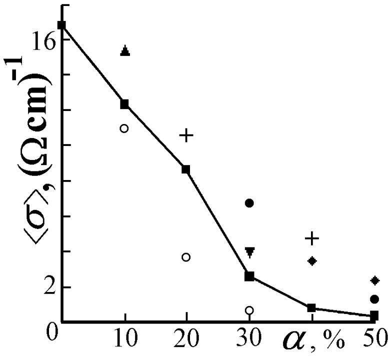


FIGURE 5. CONDUCTIVITY VS RDX FRACTION α IN CAST TNT/RDX COMPOSITIONS.

The independent experimental method potentially sensitive to meso-processes in real time is the electrical conductivity diagnostics. The recent results[9] demonstrate that the conductivity in TNT/RDX compositions falls down regularly when RDX content increases (Figure 5). This can be explained naturally by the lower carbon content and by the increase of nonconducting diamond phase yield when detonation parameters increase.

In Figure 5 the line is drawn through data points obtained for commercial RDX (0.2 mm grain size). The decrease of conductivity takes place at the same RDX concentrations which are needed to produce appreciable diamond yield according to data.[4]

The essential effect of RDX grain size is also found: the coarse-grained composition has higher conductivity, in some cases for an order of magnitude. In Figure 5 the solid points above the line represent coarse-grained (~ 1 mm) RDX, and open circles correspond to fine-grained (5 μm) RDX. The characteristic decay time of conductivity is also sensitive to grain size.

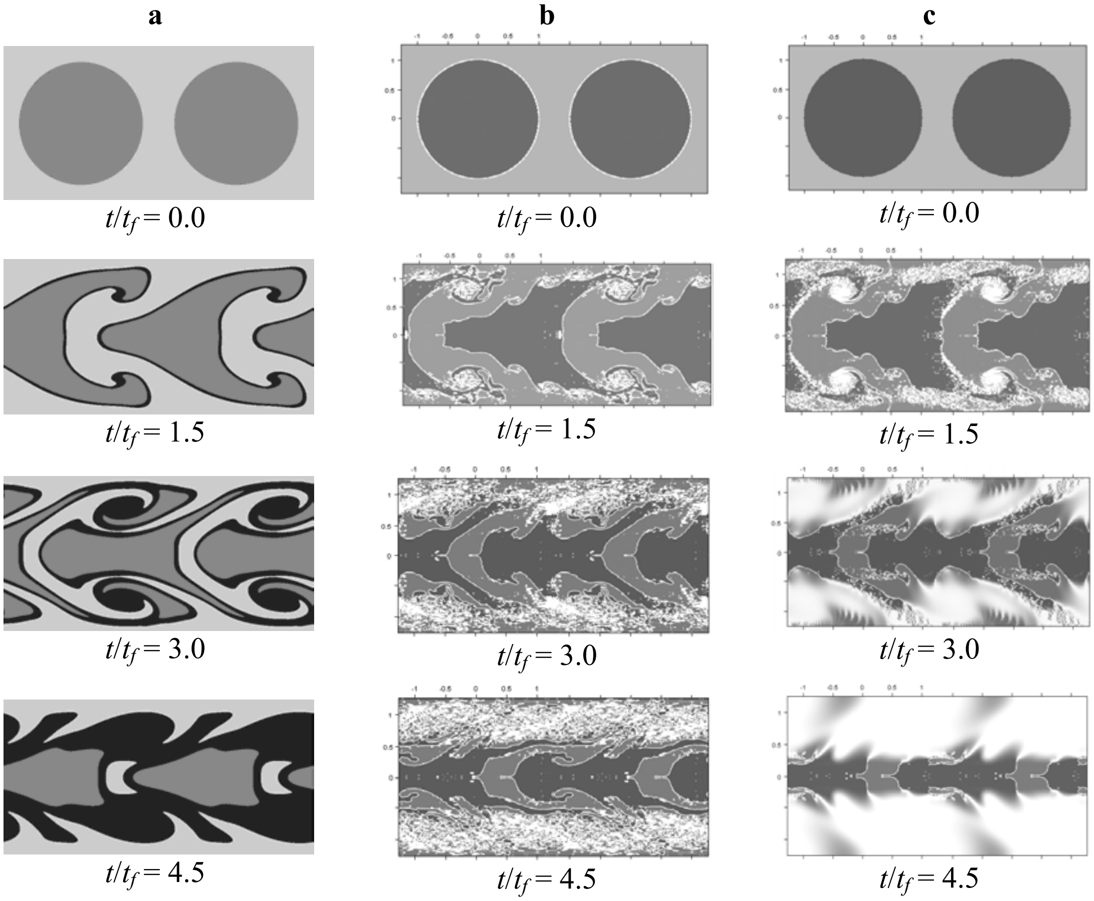
In the two-component medium the current flows predominantly through the good-conducting net formed by the TNT detonation products. The diffusion is significant only at micron scale. But the components (TNT and RDX) have different densities, and behind the detonation front they acquire the different velocities. So there exist a relative velocity Δu of about 200 m/s as estimated by Titov and Mitrofanov.[15] The hydrodynamic interaction of the components leads to the distortion of current channels, possibly up to their blocking, and to the partial dispersion of large inclusions when the flow instability develops at the grain interface.

Two-dimensional simulations of the heterogeneous flow were performed to understand the effect of hydrodynamics on the mixing. Initially a velocity Δu was imparted to a globule of gas (representing the RDX grain) immersed in the different gas (TNT) while the other parameters were uniform. The volume ratio was 50/50, and conditions at the boundaries of the calculation region were periodic. An example of such a flow is shown in Figure 6. The left column displays the results of lattice Boltsmann equation (LBE) method similar to that described in[16] at Reynolds number 1600; the middle and the right column show the conventional finite-difference gas-dynamic simulations[17–18] without viscosity. Simulations shown in right column incorporate the $k–\varepsilon$ turbulence model. The times by which the rows in Figure 6 are labeled are expressed in units of the characteristic flow time $t_f = d/\Delta u$, d being the grain diameter. The results of all methods at $t/t_f = 1.5$ are in good agreement. Later the difference in the matter properties inherent to each method manifests itself. LBE method incorporates diffusion and viscosity and may be recommended to simulate small grains (e.g., $d = 32$ μm for $\Delta u = 200$ m/s and viscosity of 0,04 cm^2/s; $t_f = 0{,}16$ μs) while the conventional gas dynamics is more suitable for large grains.

The significant distortion of the bubbles takes place about $(1 - 2)t_f$. The mixed boundary layer at $t = t_f$ is estimated to be about one tenth of the grain diameter. The calculations of the effective conductivity of two-component medium (low-conductive RDX bubbles in high-conductive TNT environment) revealed the same time scale. Similar calculations with polygonal grains and asymmetric initial configuration gave somewhat faster development of instabilities as well as faster conductance drop. In general, there was a qualitative agreement between the experimental conductivity decay time and the calculated one.

So, for the typical grain size of 0.2 mm the characteristic time of such processes is around 1 μs. The fine-grained (~ 5 μm) RDX is mixed within tens of nanoseconds while the mixing of millimeter-sized grains can last for several microseconds.

The results described in first section agree with these estimates for large particles, but for < 50 μm grains the agreement is at best qualitative. In fact, such a material should be called medium-grained. The characteristic time t_f in this case is of order of 100 ns and the expected degree of mixing during the chemical reaction time is modest while our interpretation of the isotope experiments assumes substantial mixing. Probably the coincidence of the reaction and mixing time scales requires more detailed analysis since these processes can affect each other. For example, apart of relative movement, the pulsation of bubbles caused by the different reaction rate in RDX and TNT may play a role leading to faster mixing. Authors plan to consider these problems in future research.



$t/t_f = 0.0$ $t/t_f = 0.0$ $t/t_f = 0.0$

$t/t_f = 1.5$ $t/t_f = 1.5$ $t/t_f = 1.5$

$t/t_f = 3.0$ $t/t_f = 3.0$ $t/t_f = 3.0$

$t/t_f = 4.5$ $t/t_f = 4.5$ $t/t_f = 4.5$

FIGURE 6. DEVELOPMENT OF INSTABILITIES AND MIXING IN FLOW AROUND CYLINDER. a – SIMULATION BY THE LBE METHOD, b – DIRECT GAS-DYNAMIC SIMULATION WITHOUT THE TURBULENCE, c – GAS-DYNAMIC SIMULATION WITH TURBULENCE.

CONCLUSIONS

Thus, the analysis presented allowed to suggest the following structure of the detonation zone. At an early stage of the reaction the considerable part of the carbon, bound in explosive molecule, is released. Then during ~ 100 ns the carbon and hydrogen are oxidated. In heterogeneous explosives the mesoscale processes may take additional ~ 1 μs (for standard grain size). At this stage the secondary reactions are possible due to the shift of the chemical equilibrium when the components are mixed.

ACKNOWLEDGEMENTS

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