Research paper

SPONTANEOUS EXPLOSION OF AMMONIUM NITRATE IN A CONTACT WITH AN ACTIVE CLORINE-CONTAINING ORGANIC SUBSTANCE

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Abstract

Results of a complex investigation into behavior and consequences of chemical reactions between ammonium nitrate and an organic substance, disinfectant, sodium dichloroizocyanurate which is incompatible with ammonium nitrate are presented. This substance being dissolved in water releases active chlorine which easily enters into chemical reaction with ammonium nitrate. Interaction between ammonium ion and active chlorinated chemicals triggers a chain of chemical reactions at normal temperature, resulting in heating, formation of explosive gas NCl_3 and foaming. Chemical reactions which control the interaction rate, go at a rather low energy of activation, and their conversion level is restricted by attaining the temperature at which the released gas NCl_3 explodes (115°C). Under the most conditions, there are only local explosives observed which can not involve total mass of the mixture into the chemical conversion. So far as there are no conditions providing accumulation of explosive gas in rather large amount, its detonation can not involve ammonium nitrate into chemical conversion. Only the foam which contains solution of active reaction products and seems to have the higher propensity to initiating stimuli in comparison to the pure ammonium nitrate can support the buildup of explosive wave.

1. Introduction

The most destructive accidental explosions taking place in course of manufacturing and handling of explosive materials turn out to be connected with ammonium nitrate[1,2]. One can notice, however, an obvious contradiction between statistic of explosions which involved ammonium nitrate (AN) and its explosive properties determined with use of standard tests[3]. Pure AN does not burn under normal conditions and has very low susceptibility to common mechanical and thermal stimuli. There was no detonation observed in AN except of being initiated by direct action of detonation of other high explosive, and there was no well-grounded scenario proposed to connect explosion picture with conditions and properties of AN, even for the most famous explosions happened in Oppau and Texas-Sity[1].

The causes of accidental explosions having involved large masses of AN seem to be concerned to an unexpected change of its usual behavior. This change can be a result of various chemical or physical factors, in particular, of presence of active additives$^{4)}$. There are materials known$^{4)}$, which strongly reduce chemical stability of AN being in contact with it. Among these materials, some ones (mineral acids, sulfur, sulfides and several active chlorinated compounds) can initiate self-supporting chemical interaction with AN even under room temperature. These reactions have high exothermic effect and produce a real hazard of spontaneous explosion. The rules regulating safety during handling of AN require eliminating any contact with these substances.

Catastrophic explosion of a warehouse with 300-t off-grade ammonium nitrate at AZF plant in Toulouse, France took place on September, 21, 2001. The TNT equivalent was estimated 30–40 tons, 30 people were died, ~ 3 000 injured, 600 buildings were destroyed, the losses were estimated 2.1 billion Euro. The key idea connects this explosion with sodium dichloroizocyanurate (DCCNa, chemical formula is $C_3N_3O_3Cl_2Na$) which is a granulated disinfectant of the new generation. Some amount of this chemical seems to be brought during regular unloading together with defective portion of AN into the enter section of the warehouse. Really, DCCNa enters the group of chemicals recognized to be incompatible with AN due to hazard of spontaneous explosion. Contact at the AZF plant between DCCNa and AN could happen due to negligence and was a direct breach of the plant instructions. Before the Toulouse accident, there were no investigations into explosion in this pair; the same was also for the other dangerous compositions. After explosion, several papers have been published$^{5\text{-}7)}$ considering different aspects of explosive behavior.

The purpose of this work is to get the detailed information on the behavior and consequences of interaction between AN and DCCNa, which generates active chlorine in aqua solution. Results of investigation obtained shed light on mechanisms of interaction and spontaneous explosion and can be used to estimate hazard of contacts of AN with domestic chemicals.

2. Object and methods of investigation

French-fabricated industrial AN ~700 kg/m^3 in loose-packed density, consisting of porous spherical granules 1–2 mm in average diameter, and DCCNa as a polydisperse powder ~ 0.8 mm in the particle average size have been studied. Chemicals were used as supplied, or sieved after crushing into fractions with particles 0.63–1.25 mm and 0.25–0.63 mm in size. Before firings the chemicals were carefully dried up. Mixture was prepared at the mass fraction 1:1, that approximately corresponds to stoichiometric mixture. In the layer samples, chemicals were placed one over another by layers of identical thickness varied depending on the sample mass and sizes of the test vessel. Wetting the samples was implemented by different ways as follows. Water was injected directly into the ready dry sample using either a syringe or a special injector. Other way was when the chemicals, before the sample preparation, kept in moist air, and the amount of moisture absorbed by the sample was determined by the sample mass increment. The most part of procedures especially related to wetting the samples have been carried out remotely.

A number of techniques, common or specially designed, were used in this study. Kinetics of chemical interaction was analyzed with use of thermo-gravimetric, calorimetric and manometric devices. Reaction products were determined with use of mass-spectrometry, and release of explosive gases was simply visualized. The shock sensitivity was monitored by using the interface deceleration technique with electromagnetic device. Explosion of unconfined charges (up to 25 kg in mass) was studied visually and with use of thermocouples. Explosion and detonation properties of confined charges were studied using the closed-volume bomb, as well as the charge firings in steel and plastic tubes of different diameter equipped with photo, piezo- and contact gauges to monitor the wave propagation. Besides, to clarify physical details of explosion, numerical modeling has been involved.

3. Investigation results

3.1 Kinetics of chemical interaction

To avoid explosion hazard, we used only layer samples 300 mg in their maximum mass prepared from the components which were laid one on another as the separate layers. The samples of carefully dried components do not show visible traces of exothermic interaction, at least, during tests of several hours long under the temperature ranged from the room temperature up to 64°C.

Both components are hygroscopic materials, and at a common state they can contain 0.2 –2% moisture. Behavior of the small mass samples with this moisture does not differ from the dry samples. However under wet conditions the picture drastically changes. Samples exposed to air of 100% humidity absorb moisture rather fast. For instance, at 35°C, the 30-mg sample of AN increases its mass by 25 % for 3–4 hours, and the sample of DCCNa does the same for 16–17 hours. Visual observations and video filming show that wetting the samples results in release of gases, formation of a foam, change of the sample color and marked increase of the volume occupied with the sample. Heating recorded with use of thermocouples depends on a few factors, including the contact surface area of components, the sample mass, initial temperature, wetting way and amount of the injected water. In the case of the layer samples, heating due to the interaction does not exceed 25°C. In the case of mixture samples of small mass (2–5 g), injection of water in amount more than 5 wt. % results in the 40–70°C temperature increment. For the mixture sample 20 g and more in mass, injection of water causes the quick rise of temperature (during 30–70 sec) which reaches 100°C; thereafter an explosion happens being accompanied with destruction of the cup which contains the sample and discharge of the cup contains into the atmosphere.

The calorimetric study performed with the wetted 250-mg layer samples placed into the ampoule has shown that the heat release has a sharp rate peak at the first minutes after preparation of the wetted sample. Thereafter the heat release rate drops rapidly. In the open ampoules, chemical conversion ends long before the total consumption of chemicals. Experimental data on the maximum heat release rate, in spite of the marked scatter, demonstrate evident effects of the humidity and initial temperature. The highest values of the heat release rate are observed at 3–5 % of the water contents. With increase of initial temperature in a range from 20 to 74°C, the heat release rate grows following the Arrhenius plot with a low activation energy (30–65 kJ/mol) which is typically inherent in exchange or oxidation-reduction reactions.

Video filming of the process developing in the wetted mixture was conducted with chemicals of the 0.25–0.63 mm particle fraction. Samples ~ 2 g in mass were placed into a plexiglass cup 10 mm in diameter. The dry mixture is easily ignited by electrically heating coil placed at the top of the sample, and burns in a flameless combustion mode with the average rate ~ 0.6 mm/s, releasing a white smoke and leaving (after combustion) a grayish-white porous skeleton. If to wet the sample by injecting 0.2–0.3 g water, it initiates intensive generation of foam which results in extension of the volume occupied with the foamed material by 4–5 times. Expansion of the foam goes on 5–10 sec with an average rate 5 mm/s.

Foaming of the wetted mixture evidently occurs due to the gas release. If to place the heating coil at a distance 30–50 mm above the expanded foam top level and switch on voltage, it excites explosion in gas which produces the subsequent explosion in the foam and a series of the weaker local bursts–pops at the cup bottom. Though the cup after the test end more often remained intact, in a few tests explosion of the foam appeared to be much more powerful having caused the cup destruction and left a dent in the steel plate supporting the cup, at the place where at the explosion instant, according to the video filming, was the interface between gas and foam. In order to determine temperature at which explosion in the gas is initiated, we have carried out the same tests with the raised heating coil which the thermo junction was pasted in. These tests have shown that the gas released in the damped mixture is not ignited until the temperature of the heating coil reaches 115°C. At higher temperatures the gas decomposes with explosion.

The chemical mechanism of the interaction considered is very complicated and here we make only a few remarks concerning its key stages. In aqua solution, AN partially dissociates producing ammonium cation and anion of nitric acid, and hydrolysis of DCCNa produces a whole "bouquet" of active chlorinated substances. They include hypochlorides, chlorine, Cl_2O, etc. The following, most probable, step is interaction of chlorinated substances with ammonium ion, generating, as intermediate reaction products, a set of chloramines: NH_2Cl, $NHCl_2$ and nitrogen trichloride NCl_3. It is well known[8)] that chloramines are extremely active substances: mono-chloramine explodes at -40°C, and nitrogen trichloride which can be extracted as a liquid or vapor (at room temperature) decomposes with explosion following the branching chain mechanism at the temperatures over 100°C. Decomposition of chloramines accompanying with energy release, as well as generation of gaseous NCl_3, capable to be accumulated while the temperature of reacting substance does not exceed 100°C, enables us to give a rational interpretation of observations considered above.

In order to confirm this mechanism, we have implemented tests in which the powdery ammonium chloride substituted for AN. In aqua solution of ammonium chloride there is ammonium cation, but, obviously, no nitric acid anion presented. Thermogravimetric measurements and visual observation under behavior of dry and wetted mixtures of DCCNa with ammonium chloride have demonstrated that chemical interaction of this couple of chemicals do not almost differ from the mixture of DCCNa and AN. And in the contrary, in other series of tests, when sodium nitrate has been substituted for AN to exclude the presence of ammonium cation, but saving nitric acid anion, there was no interaction observed under considered conditions.

3.2 Shock sensitivity and detonability of dry AN + DCCNa mixture

Only dry mixture of components as supplied was studied in this series of tests. Shock sensitivity was studied with use of the contact boundary deceleration technique[9)]. The experimental assembly comprises the booster charge 80 mm in diameter that generates a plane shock wave, plate with an air gap 10–15 mm wide, paraffin disc 15–20 mm thick, and the charge of studied sample confined in a plastic casing 60 mm in diameter and 20 mm thick, with an electromagnetic gauge to monitor the contact-surface velocity. The intensity of the magnetic field was 340 Oe. The booster charge was fabricated of TNT or TNT/talc mixture, its composition and density were varied to provide the desired shock wave amplitude. The shock wave propagating through the plate with air gap and paraffin disc generates a rectangular profile at the paraffin/sample interface in time interval ~4–5 μs. The electromagnetic gauge monitored both the velocity of this interface and the wave velocity in the sample. Tests were conducted in a test field. If the sample tested does not react, the recorded signal is a horizontal line. In a reacting sample the contact-surface velocity reduces due to an exothermic reaction that evolves gaseous products and raises the pressure. It results in a decaying signal profile; the declination from a horizontal line starts the earlier the faster is the exothermic reaction.

Tests with the pure AN were used for comparison. It was shown that sensitivity of the AN + DCCNa mixture is less than sensitivity of pure AN and differs only a little from it. The shock wave 0.6 GPa in amplitude (the value determined in the paraffin disk) produces only tracks of reaction in AN and its mixture with DCCNa and seems to be near threshold of self-propagating reaction initiation. The shock 1 GPa or higher in amplitude triggers the marked exothermic reaction, and under the shock 1.5 GPa or higher in amplitude the samples violently decompose with a delay not exceeding 1.5–2 μs.

The detonation velocity of the mixture and pure AN (for comparison) was measured using electric contact gauges in steel and plastic tubes of various diameters. The length of tubes was no less than 7 tube diameters. Explosive mixture of loose-packed density detonating at velocity 5 km/s was used as the booster. The booster charge diameter was not less than diameter of the tested sample. The tests have shown that the mixture confined in steel tubes 80 and 146 mm in diameter (5 and 7 mm in wall thickness, accordingly) detonates steadily at velocity 2.6 and 3.1 km/s. In plastic tube 152 mm in diameter the mixture also demonstrates the steady detonation at velocity 2.1 m/c. For comparison, pure AN confined in steel tubes 146 mm in diameter detonates steadily at velocity 2.9 km/s. However, tests performed in steel tubes 80 mm in diameter demonstrate a scatter in behavior: the detonation was either decayed or leveled at the sample end at the velocity ~ 1.3 km/s. The same behavior of pure AN was observed in plastic tubes. There was no detonation observed in the tubes 152 mm in diameter and the process at the velocity ~1.3 km/s at the sample end was observed in the plastic 190-mm tube. So, the tests have shown that the mixture is more detonable than the pure AN due to participation of DCCNa in chemical conversion.

3.3 Explosion and detonation of the wetted mixture in confinement

The field tests were implemented with the wetted mixture samples up to 25 kg in mass placed into the 35-liter plastic tanks. Mixing was carried out by jet technique; the jets of components flowing out from separate containers have got the rotating mixer simultaneously with the sprayed water jet. In all tests wetting the mixture resulted in spontaneous exothermic reactions and heating. Consequences of these reactions differed from test to test without any regular trend, covering the range from a weakly developing process which begins as a pop and ejection of the white smoke cloud with the subsequent fusion of chemicals, and up to the vigorous explosion resulting in destruction of device, crushing of the plastic container walls into the fine fragments and the crater formation. There were no indications just before explosion, except of temperature which often increased up to 100^{o}C or slightly higher. However, a large mass of non-reacted material scattered by explosion and covering the ground in radius 25 m around the crater, as well as a moderate blasting effect of explosion indicate that there was no valid detonation.

Tests with monitoring the process were performed in steel or transparent plastic tubes. The mixture of 300 g in mass was prepared from the dry granulated components; water in amount of 10 or 20 g was introduced by injector through the closed bottom end of the tube. Plastic tubes were 35 mm in internal diameter with 12-mm walls and 260 mm long. Steel tubes 32 mm in internal diameter with 7-mm walls and 460 mm long had a few small orifices for the photo recording. In order to intensify luminosity of reacting products flowing out of the orifices they were filled with fine grained PETN. The tubes were set up in vertical position. All the tests manifested explosion after the water injection with a delay 30–70 s.

In the case of plastic tubes the brightly luminous process related to the chemical interaction arises at a point being away ~110 mm from the tube bottom and propagates forwards and backwards along the charge. The wave propagating forwards, to the open tube end, is a decaying low velocity detonation. Its initial velocity is ~ 1100 m/s, thereafter the velocity reduces, luminosity drops, mainly, due to destruction of casing. In the case of steel tubes low velocity detonation arises at a distance ~140 mm from the tube bottom and propagates steadily along the charge at velocity ~1500 m/s. Pressure in this wave recorded in a special test with use of the Kistler-type piezoquartz gauge is 0.5–0.8 GPa. Detonation has resulted in destruction of the casing into coarse elongated fragments specific of low velocity detonation in solids.

So, generation of explosive gas and formation of active foam are two factors which make the interaction really hazardous. But the role of explosive gas should not be overestimated. At least, we can conclude that the explosion of this gas, most likely, does not initiate decomposition of pure AN under normal conditions. An illustration is the results of two parallel tests performed with the mixture of ground chemicals (fraction 0.25–0.63 mm). The charges 70 mm long were placed in steel tubes 15 mm i.d. and 250 mm long with 4 orifices along the tube for the pressure gauges. The charge burning was initiated by igniter-cap mounted at the closed tube end. Difference between two tests was only that in one test the dry mixture was used, and in the other test a dry mixture was wetted by the water injection 30 sec before initiation of the mixture by the cap. During this 30-sec interval the interaction of wetted chemicals produces physical and chemical transformations drawing almost to self-ignition, and the purpose of these tests was to study effect of these transformations under conditions when due to the rather short length of the charge and possibility of generated gas to outflow through the open tube end this gas cannot accumulate in significant mass inside the reacting mixture.

As is seen from Fig. 1, in the case of the wetted charge the wave with very steep front is formed already at an initial phase of the process (see pressure record at the distance 40 mm). Parameters of this wave are evidently related to explosive decomposition of the active gas released. The pike pressure value is twice as much as the maximum pressure recorded at this distance in the case of dry mixture. However, at the distance 145 mm the difference vanishes, and the waves developed in two testes, become almost identical both on the front steepness and maximum pressure.

[Figure 1]

3.4 Numerical simulation

To shed light on this situation, we have involved numerical modeling. The computer code which used here for simulation was developed earlier in quasi-1D approximation to analyze the burning-to-explosion transition in porous solid materials [10]. The code has been modified to include the generation and explosion of active gas observed at wetting of the AN + DCCNa mixture. Considered is the charge of grained material 800 mm in length, confined in the closed cylinder casing. Behavior of the wetted mixture is reproduced at the charge section 200 mm in length where at the initial time instant the chemical reactions suppose to start on the grain surface generating the active gas and heat release. Active gas simulates properties of NCl_3, which, according to thermodynamic estimations, detonates at normal pressure with the velocity 1450 m/s, the detonation pressure and temperature are 4 MPa and 2500 K, respectively. The both values of active gas and heat release rates were selected approximately relayed upon calorimetric and thermo-gravimetric measurements with small mass samples described above. Due to the heat release the temperature of the grain surface and gas monotonously increases. The gas released can filtrate through the pores into the non-wetted section of the charge. The gas starts reacting when the temperature approaches 420 K, with the reaction rate following the Arrhenius formula at the activation energy 418 kJ/mole.

The calculation results are as follows. By the instant when the temperature at the wetted charge section has reached 420K and decomposition of the active gas begins, pressure of the gas filling the pores has approached 0.35 MPa. After ~ 16 ms a detonation-like pressure wave is generated in the gas. This wave propagates along the wetted section of the charge at the velocity ~870 m/s and along the other charge section at the velocity 710 m/s with the pike pressure ranged 3–4 MPa. However, transit of the wave produces only the 120–140 K increment of the grain surface temperature which turns out to be insufficient to initiate burning of AN even at the wetted charge section.

A real alternative, perhaps, is that the foam which contains a solution of active reaction products has the higher susceptibility to initiation as compared with AN. To simulate this alternative, the ignition temperature of the mixture is reduced from 800K to 550K. This has resulted in a drastic change of event shown in Fig. 2: the wave of gas explosion, propagating along the charge with the same parameters as in the previous case, has caused ignition of the mixture and followed (at some distance behind the primary front of the wave) by a vigorous pressure wave which amplitude quickly increased up to 250 MPa.

[Figure 2]

Conclusion

Thus, this investigation has clearly manifested that behavior and consequences of interaction inside the wetted mixture of AN and an organic disinfectant, DCCNa, which compose a couple of incompatible chemicals, considerably differ from usual properties of normal explosive mixtures. The main conclusions can be stated as follows.

Interaction between ammonium ion and active chlorinated chemicals produced in the course of dissolution of AN and DCCNa in water at normal temperature, triggers a chain of chemical reactions resulting in heating, formation of explosive gas NCl_3 and foaming.

Chemical reactions which control the interaction rate go at a rather low energy of activation, and conversion level is restricted by attaining the temperature at which the released gas NCl_3 explodes (115°C). Under the most conditions, there are only local explosives observed which can not involve total mass of the mixture into the explosive conversion.

So far as there are no conditions providing accumulation of explosive gas in rather large amount, its detonation can not involve AN into the chemical conversion. Only the foam which contains solution of active reaction products and seems to have the higher propensity to initiating stimuli in comparison to the pure AN can support the buildup of explosive wave.

The experiments in which ammonium nitrate was replaced by ammonium chloride have demonstrated that the reactions between ammonium ions and active chlorine triggering spontaneous explosion in the couple of ammonium nitrate + DCCNa can take place also in some other couples of substances resulting in almost the same consequences and making them potentially dangerous.

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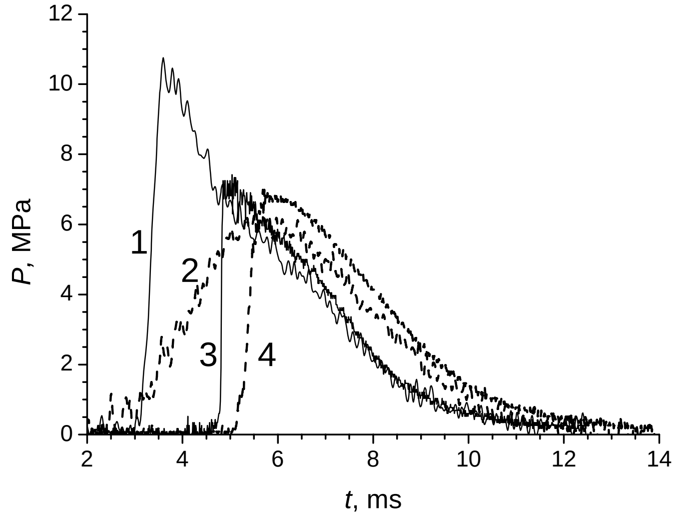

Fig. 1. Pressure–time profiles recorded at two points along the charge at a distance 40 and 145 mm from the closed charge end in two tests with the dry (curves 2 and 4) and wetted (curves 1 and 3) mixtures initiated by the igniter-cap.

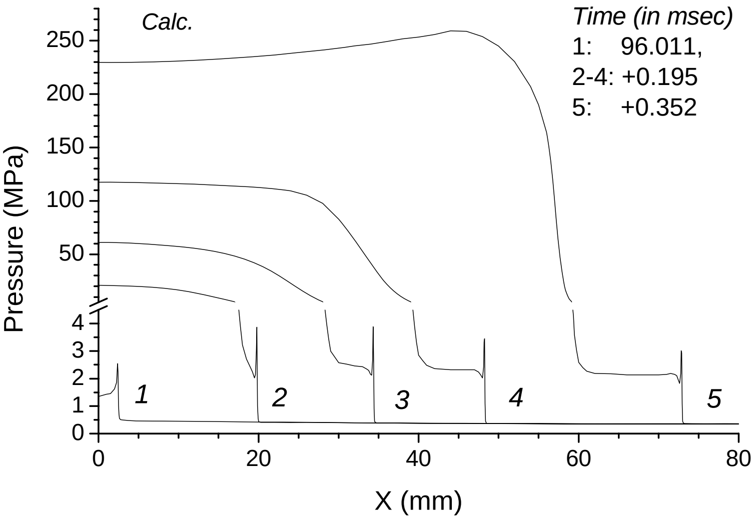

Fig. 2. Computation of explosion development in the wetted AN+DCCNa mixture with reduced ignition temperature of the mixture. Evolution in time of the pressure profile.