



## Forensic Investigation of Some Peroxides Explosives

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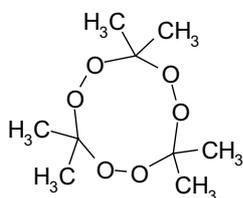
**Abstract:** Some of peroxides: triacetoneperoxide (TATP), hexamethylenetriperoxidediamine (HMTD) have been used recently as “irregular” explosives for delinquency and international terrorism purposes. The intimate knowledge of properties and methods of analysis of these substances is necessary for experts. Forensic investigations of some peroxides explosives: triacetoneperoxide (TATP) and hexamethylenetriperoxidediamine (HMTD) were carried out in this work. The detonation process of peroxides initiation by means of pyroxylin layer ignition was investigated, velocity of detonation at apparent density ( $\rho_{\text{HMTD}} = 0.38 \text{ g/cm}^3$ ,  $\rho_{\text{TATP}} = 0.47 \text{ g/cm}^3$ ) was measured by means of a Russian fotoregister GFR-3. These data were compared with literature detonation velocity values that had been measured at larger densities. The values of detonation velocities complement each other rather well, linear dependencies of  $D$  vs.  $\rho$  found at densities  $\rho = 0.35\text{-}1.2 \text{ g/cm}^3$ . The high sensitivity of the investigated analytical methods, that were applied ( $10^{-5}\text{-}10^{-8} \text{ g}$ ) facilitate the determination of possible times for finding traces of TATP after an explosion. Time  $t = 6$  hours after explosion is the critical time for finding peroxides traces of TATP on a metal surface by means of analytical methods used in this work.

**Keywords:** peroxide, methods of analysis, traces, volatilize, detonation

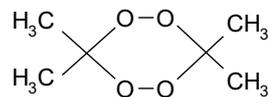
## Introduction

A number of organic peroxides are applied in chemical, polymer, pharmaceutical and some other branches of industry. Some of peroxides are produced in fair quantities. Explosion properties of benzoyl peroxide, cyclohexanone peroxide and cumene hydroperoxide were investigated in preceding papers and were discussed at NTREM seminars [1, 2]. Unfortunately, some of peroxides: triacetoneperoxide (TATP), diacetonediperoxide (DADP), and hexamethylenetriperoxidediamine (HMTD) have been used recently as "irregular" explosives for delinquency and international terrorism purposes. The intimate knowledge of properties and of methods of analysis of TATP and HMTD is necessary for experts.

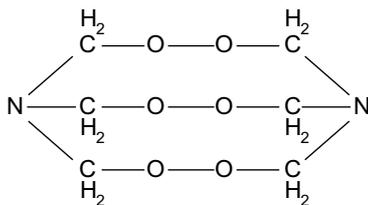
Chemical formulas of acetoneperoxides and HMTD are:



Triacetoneperoxide



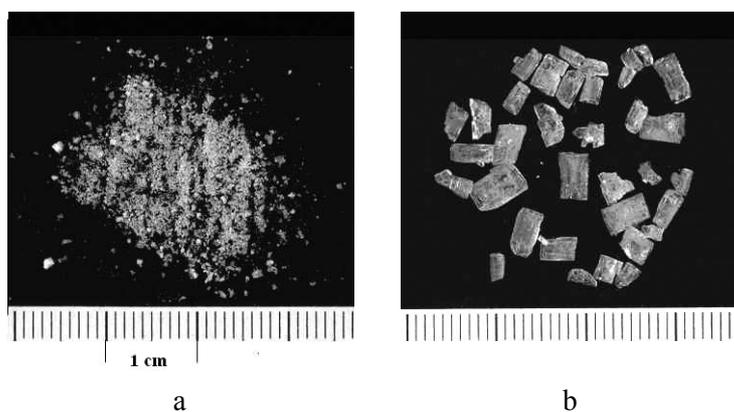
Diacetonediperoxide



Hexamethylenetriperoxidediamine

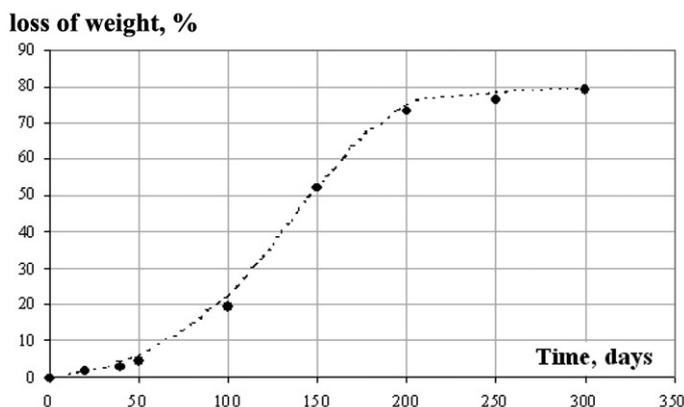
The literature data about these explosives and physicochemical characteristics of TATP and HMTD were summarized [3, 4]. TATP is rather volatile substance: 6.5% of the sample volatilized at  $T = 14-18\text{ }^{\circ}\text{C}$  after 48 hours.

There is growth of crystals at TATP stored in desiccator due to sublimation (Figure 1).



**Figure 1.** Growth of crystals of TATP stored in desiccator. a – TATP crystals immediately after production, b - TATP crystals after storage for 30 days.

The curve of loss of weight of HMTD stored vs. time has a form of a letter “S” that indicates self-catalyzed HMTD decomposition (Figure 2).



**Figure 2.** Loss of weight of HMTD stored at  $T = 50\text{ }^{\circ}\text{C}$ .

The main explosive properties of these peroxides were described [3-5]. The experimental value of the heat of explosion of TATP is  $Q_v = 2803\text{ kJ/kg}$  in extruded and cast charges [4]. The heat of explosion of HMTD is given as  $Q_v = 5079\text{ kJ/kg}$  [7]. Apparently this last value is too large. Some chemical characteristics, safety properties and explosive performances of TATP and HMTD have been investigated by M.H. Lefebvre et al. [8].

## Experimental and Results

TATP, DADP and HMTD were synthesized according to reported methods [5]. All reagents were of analytical grade. The structure and purity of the peroxides samples were thoroughly controlled by means of:

1. Infrared spectroscopy (complex, consisting of IR microscope "Continuum" – IR- Fourier spectrometer "Nexus" ("Termo Nicolet");
2. Mass spectrometry "Polaris Q" ("Termo");
3. Gas Chromatography («Agilent 6890» with MSD (mod. 5975). GC capillary column type «HP-5MS», length 30 meters, diameter 0.25 mm, and film thickness 0.25  $\mu\text{m}$ ).

Next methods were developed for analyzing of trace amounts of TATP, DADP and HMTD.

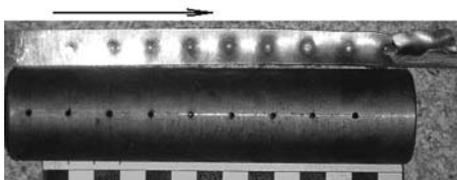
4. High Performance Liquid Chromatography (Chromatographic systems: «Hewlett Packard 1100» with DAD (Diode Array Detector) G1315A on the column «Symmetry Shield RP18 3.5  $\mu\text{m}$ » 2.1 x 150 mm; «Waters Alliance» with mass-selection detector «TMD» and diode array «996» on the column «Symmetry C18 3.5  $\mu\text{m}$ » 2.1 x 150 mm). Sensitivities of the peroxides under investigation are  $10^{-7}$ - $10^{-8}$  g for DADP and  $10^{-5}$  for HMTD.
5. Thin Layer Chromatography (TLC). Plates: «Sorbfil» (Russia) PETPh UV-254 100x100; «Merck» (Germany) HPTLC Fertigplatten Kieselgel 60 F<sub>254</sub> 100x100, DC-Plastikfolien Kieselgel 60 F<sub>254</sub> 200x200, DC- Alufolien Kieselgel 60 F<sub>254</sub> 200 x 200; «Silufol UV-254» (ChSSR) 150 x 150 were used. Development was carried out by means of spraying of plates with solution of diphenylamine (2%) in ethanol under ultraviolet radiation. Sensitivity of this method with reference to HMTD and to TATP is  $10^{-7}$  and  $2 \times 10^{-6}$  g, respectively.
6. Gas Chromatography (Chromatographic systems: «Hewlett Packard 5890 series II Plus» with ECD (electron capture detector); «Agilent 6890N» with MSD (mod. 5975); «Termo Electron Focus» with FID (flame ionization detector). GC capillary column type «HP-5MS», and «HP-1 Ultra» length 12-30 meters, diameter 0.25 mm, film thickness 0.25  $\mu\text{m}$ ). Sensitivity of this method with reference to TATP and to DADP is  $10^{-8}$ - $10^{-7}$  g.

Standard solutions for investigation of the sensitivity of these chromatographic methods to the substances under investigation were prepared by means of step-by-step dilution of their solutions in acetonitrile. All the above sensitivities of these methods with reference to the peroxides were determined.

Detonation process of peroxides was initiated by means of pyroxylin layer ( $m \sim 0.5$  g), velocity of detonation at apparent density ( $\rho_{\text{HMTD}} = 0.38$  g/cm<sup>3</sup>,

$\rho_{\text{TATP}} = 0.47 \text{ g/cm}^3$ ) was measured by means of Russian fotoregister GFR-3. Charges had glass (diameter  $d = 12\text{-}14 \text{ mm}$ , wall thickness  $\delta \sim 1 \text{ mm}$ ) or steel ( $d = 10 \text{ mm}$ ,  $\delta = 13 \text{ mm}$ , length  $l = 250 \text{ mm}$ ) confinements. Radial holes were drilled in the steel wall. The photorecording procedure of detonation in the steel tubes was the same as that described in earlier work [1].

Charges were fastened to metal witness-plates. If photorecording in steel tubes was not carried out, the witness-plate was fastened to the radial holes of the tube. The detonation was propagated in both confinements in all runs. The steel tubes were not destroyed. Deformation of the witness-plates is demonstrated in Figures 3 and 4.



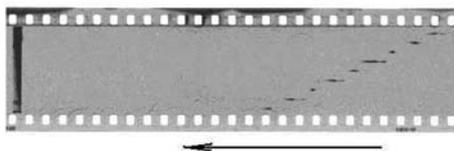
**Figure 3.** Steel tube and witness-plate after detonation of TATP charge without photorecording. Arrow shows direction of detonation propagation.

One can see the increased depth of dents on the witness-plate that were made by products of explosion, which flowed from the radial holes. In other words, the process accelerated after ignition.



**Figure 4.** Deformation of witness-plate after detonation of HMTD charge in a glass tube.

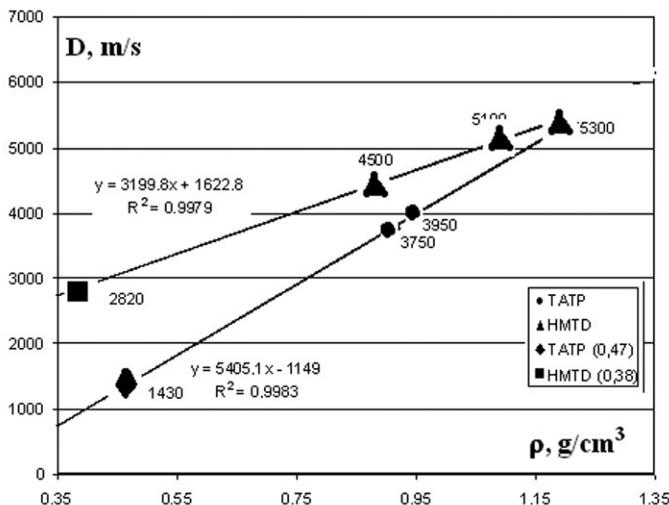
Photographic record of detonation propagation of HMTD in a steel tube is shown in Figure 5.



**Figure 5.** Photographic record of detonation propagation of HMTD in a steel tube.

The constant slope of the line, that connects points of luminescence of detonation in radial holes, testifies to the stability of the process in the tube. The average value of detonation velocity of HMTD was at  $\rho = 0.38 \text{ g/cm}^3$   $D = 2820 \pm 200 \text{ m/s}$ , and of TATP at  $\rho = 0.47 \text{ g/cm}^3$   $D = 1430 \pm 80 \text{ m/s}$ .

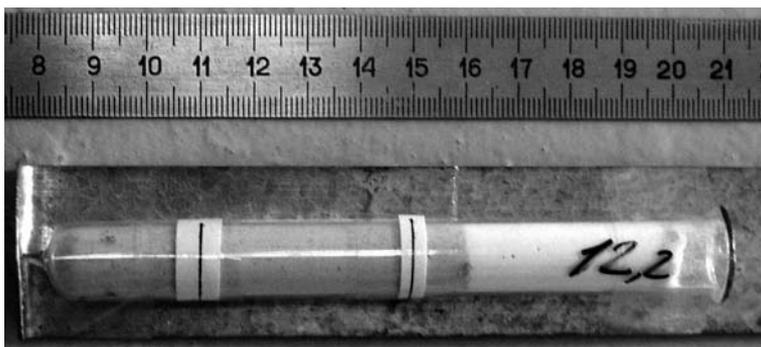
These data were compared with literature [3-5] detonation velocity values that had been measured at larger densities (Figure 6). One can see that the values complement each other rather well, linear dependencies of  $D$  vs.  $\rho$  are found over a density range  $\rho = 0.35\text{-}1.2 \text{ g/cm}^3$ .



**Figure 6.** Comparison of detonation velocities at apparent density with literature  $D$  values measured at larger densities.

To check for initiation of detonation of a high explosive by means of a HMTD booster, the following was carried out. Half of the length of a glass tube ( $d = 12.2 \text{ mm}$ ) was filled with well-milled TNT ( $\rho \sim 0.9 \text{ g/cm}^3$ ), HMTD was placed in a top part of the tube (Figure 7). Initiation of HMTD was accomplished

as usual by means of burning. Stable detonation of all parts of the charge propagated ( $D = 3100$  m/s).



**Figure 7.** Photograph of charge for initiation of TNT by means of detonation of HMTD.

The high volatility of TATP causes difficulty in finding traces of it at sites of occurrence. The high sensitivity of the investigated analytical methods (see above) allowed us to determine the possible period for finding traces of TATP after an explosion. TATP was placed in a steel cup ( $d = 25$  mm,  $\delta = 6.5$  mm,  $L = 125$  mm), a cap was closed with a brass cover ( $\delta = 13$  mm) with a screw; there was a hole in the cover for placing a detonator. The charge with TATP after premolding ( $\rho = 0.86$  g/cm<sup>3</sup>) was evacuated for 2 hours, and then it was initiated in a blasting chamber. Fragments of the confinement (Figure 8) were separated into three parts with approximately equal surfaces. The masses of groups of fragments were  $m_1 = 243$  g,  $m_2 = 209$  g, and  $m_3 = 208$  g. The first group of fragments after exposure to air during 2 hours at room temperature was placed in a hermetic vessel with 100 ml acetone. The same procedures were carried out with the second and third groups of fragments after exposure to air during 6 and 8 hours, respectively.



**Figure 8.** Photograph of steel confinement take and of its fragments after detonation of TATP.

Samples of acetone from the extractive vessels were filtered and were evaporated at room temperature. Solid residues were immediately dissolved in acetonitrile (1 ml). Identification of TATP was carried out by means of methods 3 and 6. It was established that traces of TATP could be found in the second group of fragments (after exposure to air during 6 hours), but TATP could not be found in the third group of fragments (after exposure to air during 8 hours). Hence, time  $t = 6$  hours after explosion is the critical time for finding peroxides traces by means of the analytical methods 3-6 used in this work

It should be noted, that materials with adsorbant surfaces (paper, rubber, wood, textile etc.) retain traces of TATP much longer.

## Conclusion

Forensic investigations of some peroxides explosives: triacetoneperoxide (TATP) and hexamethylenetriperoxidodiamine (HMTD) were carried out in this work.

The detonation process of peroxides initiation by means of pyroxylin

layer ignition was investigated, velocity of detonation at apparent density ( $\rho_{\text{HMTD}} = 0.38 \text{ g/cm}^3$ ,  $\rho_{\text{TATP}} = 0.47 \text{ g/cm}^3$ ) was measured by means of a Russian fotoregister GFR-3. These data were compared with literature detonation velocity values that had been measured at larger densities. The values of detonation velocities complement each other rather well, linear dependencies of  $D$  vs.  $\rho$  found at densities  $\rho = 0.35\text{-}1.2 \text{ g/cm}^3$ .

The high sensitivity of the investigated analytical methods, that were applied ( $10^{-5}\text{-}10^{-8} \text{ g}$ ) facilitate the determination of possible times for finding traces of TATP after an explosion. Time  $t = 6$  hours after explosion is the critical time for finding peroxides traces of TATP on a metal surface by means of analytical methods 3-6 used in this work.

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