Central European Journal of Energetic Materials, **2013**, *10*(2), 263-275
ISSN 1733-7178

Decreasing the Friction Sensitivity of TATP, DADP and HMTD*)

Robert MATYÁŠ*, Jakub ŠELEŠOVSKÝ and Tomáš MUSIL

Institute of Energetic Materials, Faculty of Chemical Technology, University of Pardubice, Studentska 95, 532 10 Pardubice, Czech Republic
**E-mail: robert.matyas@upce.cz*

Abstract: The influence of water and WD-40 oil content on the sensitivity to friction of three primary explosives, triacetone triperoxide (TATP), diacetone diperoxide (DADP) and hexamethylene triperoxide diamine (HMTD), has been investigated. All of these explosives belong to a group of improvised explosives. The possibility of desensitization of these explosives by the addition of other substances was studied. Sensitivity curves were obtained for the solid organic peroxides with various liquid contents. The sensitivity decreases significantly with only a small quantity of liquid − up to about 20% of the liquid. Further increase in the liquid content has a negligible further impact on the sensitivity to friction. Water and WD-40 oil were compared as desensitizating agents.

Keywords: primary explosive, TATP, HMTD, sensitivity to friction, desensitization

Introduction

Organic peroxides with a high peroxide group content belong to a group of explosives that are highly sensitive to mechanical impulses. The ease of preparation of these compounds together with the availability of the starting materials [1] and a well understood fabrication method are reasons why these explosives are often prepared under improvised conditions [2-4]. Thus organic peroxides are frequently the subject of disposal procedures performed by EODs

*) Part of this work was presented at the *38th International Pyrotechnic Seminar*, held 10-15 June 2012, Denver, USA.

worldwide. These procedures entail several risks due to the high sensitivity of these compounds, and due to the possibility of unexpected explosion during handling.

Triacetone triperoxide (chemical nomenclature: 3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexaoxonane, 3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexaoxacyclononane, generally known as TATP) and hexamethylene triperoxide diamine (chemical nomenclature: 1,6-diaza-3,4,8,9,12,13-hexaoxabicyclo[4,4,4] tetradecane, known as HMTD) belong to a group of highly brisant primary explosives with high initiating efficiency [5-7]. These organic peroxides fall into the most often prepared improvised explosives around the world.

Diacetone diperoxide (chemical nomenclature: 3,3,6,6-tetramethyl-1,2,4,5-tetraoxane; 3,3,6,6,-tetramethyl-1,2,4,5-tetraoxacyclohexane DADP) shows significantly lower initiating efficiency compared with TATP [8], thus its misuse for improvised detonating fuse preparation is unlikely. For this reason DADP is rarely prepared under improvised conditions. Nevertheless, under specific conditions, DADP is present as a product in the same reaction mixture as that used for TATP preparation. A mixture of TATP and DADP or DADP alone can be the result of the reaction [9, 10]. Another possibility for DADP formation under amateur conditions is the spontaneous transformation of TATP to DADP [11, 12]. Thus DADP can become an unwanted by-product or even the main product of an improvised preparation of TATP. This is the reason why DADP can also be something EODs can expect. For example, during a terrorist outrage in Casablanca in 2003, traces of both TATP and DADP were detected on post-explosion debris [13]. This fact can be considered to be good evidence for the misuse of a TATP/DADP mixture.

All of the organic peroxides discussed above belong to a group of compounds which are highly sensitive to mechanical impulses [5-7, 14]. Friction sensitivity of explosives is one of the basic 'sensitivity' parameters. Friction occurs in practically any type of manipulation of the compound (when transferred, when stirred, when stroked, etc.). Thus friction occurs during the deactivation of the explosives and the subsequent disposal process performed by EODs [**)]. Because of this, it is highly desirable to be able to reduce the friction sensitivity, thus minimizing the risks when handling these compounds. That is why our work

**) Several methods for the disposal of organic peroxides have been published. Bellamy recommended burning a toluene solution of TATP. TATP is very soluble in toluene; burning of this solution is safe and without risk of explosion [15]. This method is suitable for TATP but not for HMTD and DADP (both have low solubility in toluene). Other published methods are based on chemical decomposition by the action of chemical agents [15-17]. However, the decomposition of larger amounts of organic peroxides is hazardous and not recommended, as it is exothermic. The heat liberated during decomposition could possibly ignite any remaining organic peroxide (especially when a large amount of peroxide is decomposed). On the other hand, safe methods of decomposition take a long time and are not suitable for field conditions.

is aimed at studying the possibility of reducing the friction sensitivity of TATP, DADP and HMTD.

It is generally well known that the presence of water causes a reduction in the sensitivity of explosives to mechanical impulses. Similar behaviour can be observed for other substances having lubricating capabilities (*e.g*. oils) [18, 19]. In order to study the potential reduction in friction sensitivity, two easily obtainable liquids with low viscosity were chosen − water and WD-40 oil. Water is available almost everywhere; WD-40 oil is commercially available and can be applied by spraying. Nowadays WD-40 oil is used for the disposal of sensitive explosives by EODs in several states (*e.g*. by the police force of the Czech Republic).

Material and Methods

Caution: TATP, HMTD and DADP are primary explosives sensitive to impact, friction, electric discharge and flame, even when wet. Indeed wet TATP can detonate with up to 25% of water content [6]. The synthesis and handling of TATP, DADP and HMTD are dangerous operations that require adherence to standard safety precautions for handling primary explosives!!!

Synthesis of primary explosives

TATP and HMTD were synthesized by procedures that are published in various modifications on web pages that deal with improvised explosives; DADP was synthesised according to Dubnikova procedure [20].

Triacetone triperoxide (TATP)

Triacetone triperoxide (3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexaoxonane; 3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexaoxacyclononane; TATP) was prepared by the standard route from acetone and hydrogen peroxide (30%) catalyzed by hydrochloric acid according to the procedure already published in our previous works (the molar ratio of catalyst to acetone was 0.25, the molar ratio of acetone to hydrogen peroxide was 1.25). TATP was not purified by crystallization, but was used in its raw, as prepared state. The crystal size and shape (which have an impact on sensitivity) were determined by optical microscopy and were published in our previous paper [14]. The measurement of friction sensitivity of the TATP mixtures with water and oil WD-40 was carried out during the three days following preparation.

Diacetone diperoxide (DADP)

Diacetone diperoxide (3,3,6,6-tetramethyl-1,2,4,5-tetraoxane; 3,3,6,6,-tetramethyl-1,2,4,5-tetraoxacyclohexane; DADP) was prepared by transformation of TATP in a dichloromethane solution in the presence of *p*-toluenesulfonic acid [20]. Raw DADP was purified by crystallization from methanol. The crystal size and shape were determined by optical microscopy and have been published in our previous paper [14]. The measurement of friction sensitivity of the DADP mixtures with water and oil WD-40 was carried out during the three days following preparation.

Hexamethylene triperoxide diamine (HMTD)

Hexamethylene triperoxide diamine (3,4,8,9,12,13-hexaoxa-1,6-diazabicyclo[4,4,4]tetradecane; HMTD) was prepared according to the well known Girsewald procedure from hexamethylene tetramine, hydrogen peroxide (30%) and citric acid (the molar ratio of hydrogen peroxide to hexamethylene tetramine was 4, the molar ratio of citric acid to hexamethylene tetramine was 1). HMTD was not purified by crystallization, but was used in its raw, as prepared state. The crystal size and shape were determined by electron microscopy and have been published in our previous paper [14]. The measurement of friction sensitivity of the HMTD mixtures with water and oil WD-40 was carried out during the week following preparation.

Preparation of mixtures with water and oil WD-40

The dry primary explosive (about 0.4 g) was carefully mixed with a predetermined amount of water or oil WD-40. The amount of liquid is expressed as mass percentage of the liquid in the mixtures. In the case of water, a drop of detergent was added to the water for better wettability of the TATP and DADP crystals. The friction sensitivity of the mixtures was measured immediately after preparing of the mixtures.

Determination of sensitivity to friction

The sensitivity to friction was determined using an FSKM-PEx (OZM Research, Czech Republic) friction sensitivity tester. This is a modernized version of a standard BAM small-scale friction tester. The single side roughened ceramic plates (type BFST-Pt-100S) and porcelain pegs (type BFST-Pn-200) were provided by OZM Research, Czech Republic. Every peg was used once from each side, the plates were used three times at different places. The linear speed of a plate was 46.7 mm/s. The sample size was 10 mm^3 and the reaction of the sample was assessed by human ear (explosion, crackling). Probit analysis was used to evaluate the friction sensitivity of all samples [21]. Five levels of friction force and 15 trials at each level were used. The measuring details were the same as in the previous study [14].

Results and Discussion

The sensitivity curves for the organic peroxides lubricated with water and oil are shown in Figures 1-6. A decrease in sensitivity to friction after the addition of a liquid was observed in all cases (except in the case of the addition of 5% of liquid to TATP, in which case the sensitivity remained similar to that of the dry sample). The sensitivity to friction decreases up to the level of about 20% liquid. Further addition of liquid above this level has a negligible further impact on the sensitivity to friction.

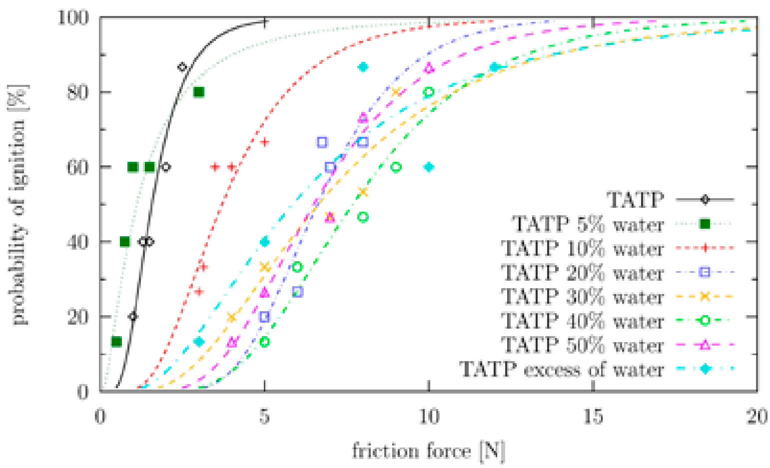

Figure 1. Sensitivity to friction of TATP with water.

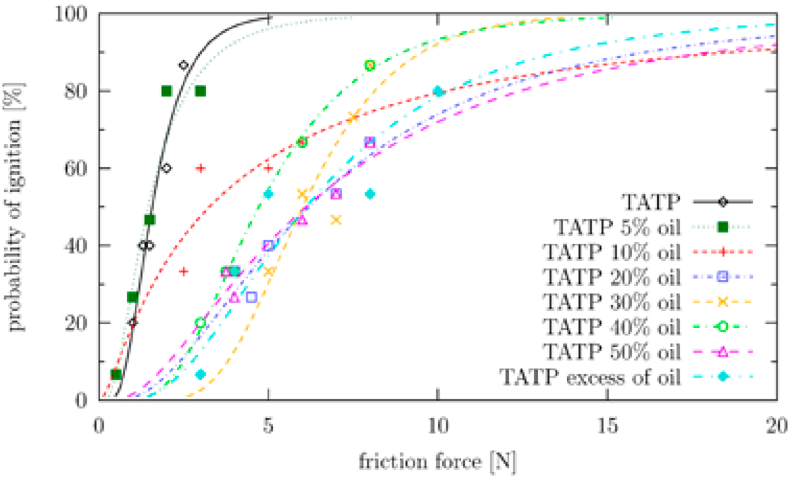

Figure 2. Sensitivity to friction of TATP with oil WD-40.

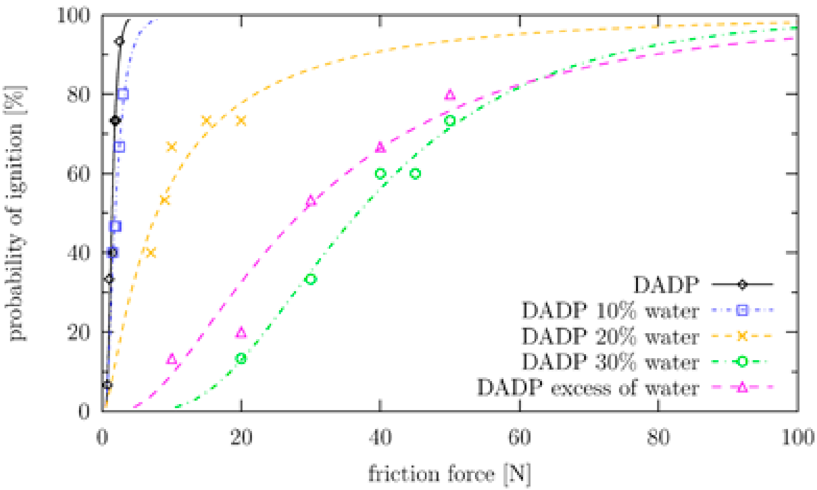

Figure 3. Sensitivity to friction of DADP with water.

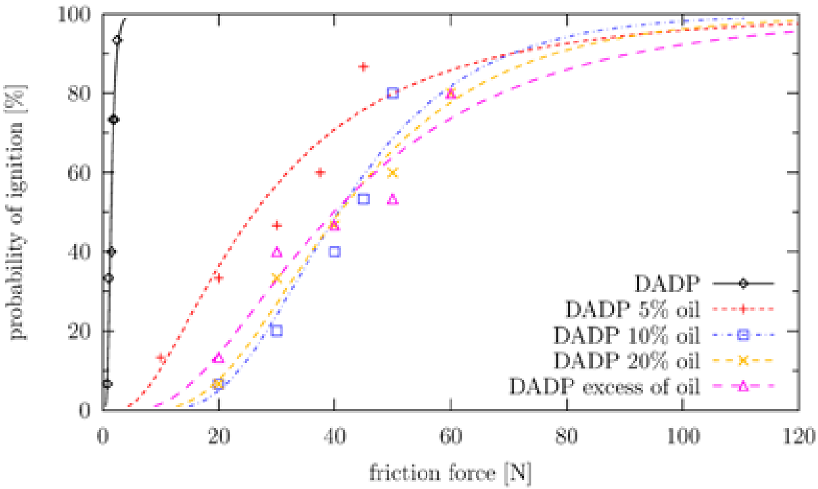

Figure 4. Sensitivity to friction of DADP with oil WD-40.

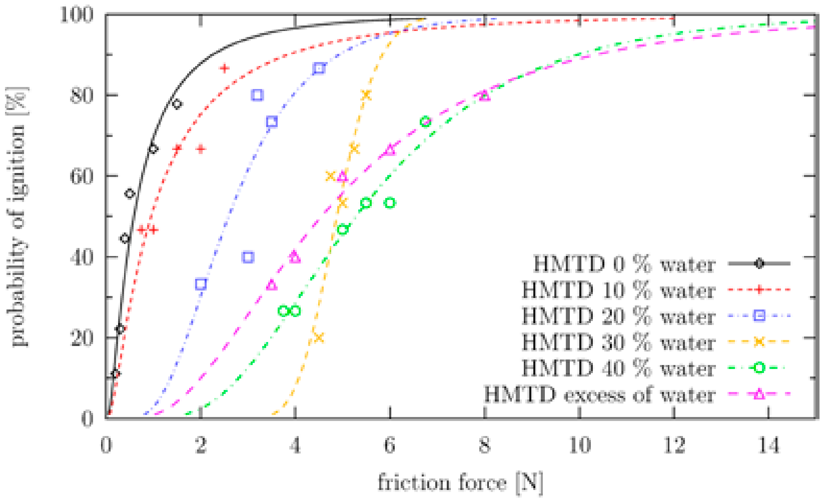

Figure 5. Sensitivity to friction of HMTD with water.

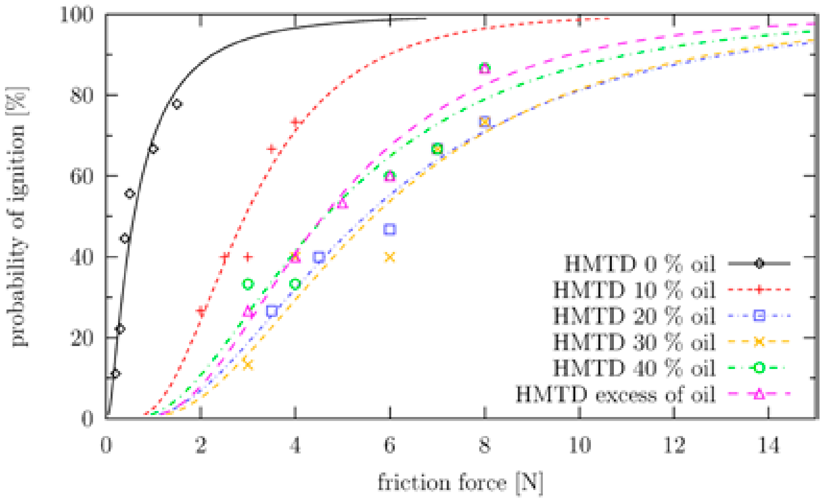

Figure 6. Sensitivity to friction of HMTD with oil WD-40.

In the cases of a small quantity of liquid with HMTD and DADP, *e.g*. up to 10%, the oil reduces the sensitivity to friction significantly more than water (see Figures 8-9). This effect was not observed for TATP (Figure 7).

Table 1. Sensitivities to friction (F_{50}) of dry samples and of samples with an excess of water or oil

	F_{50} [N]		
	TATP	DADP	HMTD
Dry sample	1.57	1.40	0.59
Excess water	5.86	28.6	4.56
Excess oil	6.11	39.9	4.60

If the liquid was added in excess, there was no noticeable difference between water and oil. Excess liquid means that the sample is fully immersed in the liquid (as in Figure 10a). The sensitivities to friction (expressed as F_{50}) for the dry samples and for samples with an excess of water or oil are given in Table 1. The sensitivity to friction for the dry samples is in a typical range for the more sensitive primary explosives: the sensitivities are between that for dextrinated lead azide (LA, F_{50} = 0.26 N) and mercury fulminate (MF, F_{50} = 7.47 N). The sensitivities to friction for HMTD and TATP after the addition of an excess of liquid are close to the friction sensitivity of mercury fulminate. DADP in an excess of water or oil is less sensitive than 2-diazo-4,6-dinitrophenol (DDNP,

F_{50} = 22.0 N), however it is still more sensitive than dry PETN (F_{50} = 80.8 N). The values of F_{50} for the standard explosives were read from the sensitivity curves in [14]. These curves were obtained using the same method, apparatus and conditions.

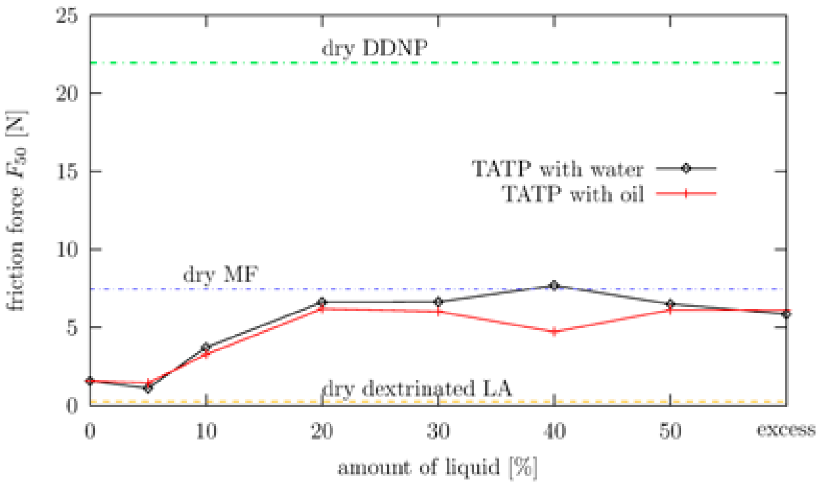

Figure 7. Decrease in the sensitivity to friction (F_{50}) of TATP (LA – lead azide, MF – mercury fulminate, DDNP – 2-diazo-4,6-dinitrophenol).

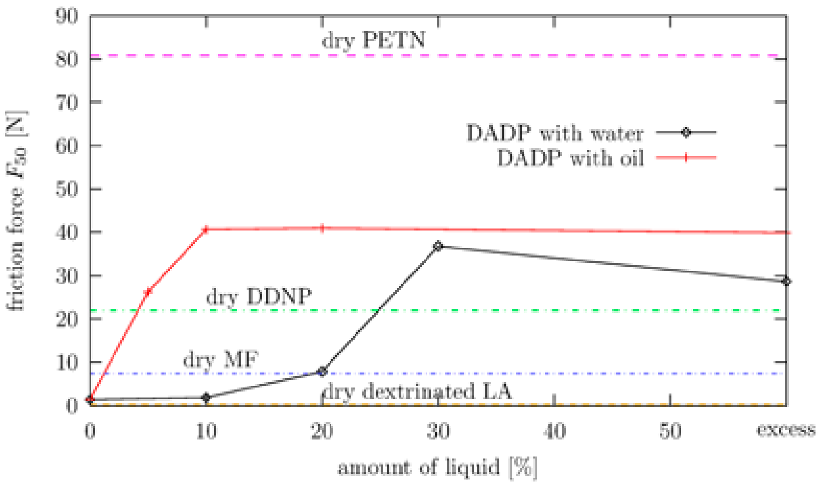

Figure 8. Decrease in the sensitivity to friction (F_{50}) of DADP (LA – lead azide, MF – mercury fulminate, DDNP – 2-diazo-4,6-dinitrophenol, PETN – pentaerythritol tetranitrate).

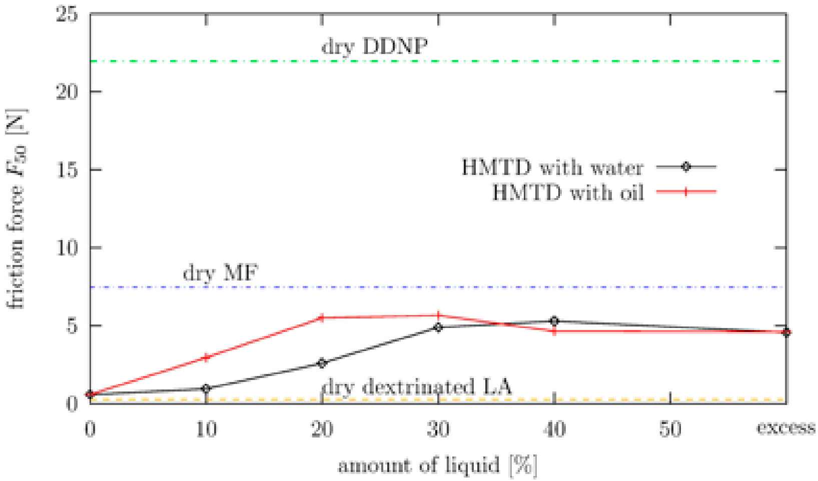

Figure 9. Decrease in the sensitivity to friction (F_{50}) of HMTD (LA – lead azide, MF – mercury fulminate, DDNP – 2-diazo-4,6-dinitrophenol).

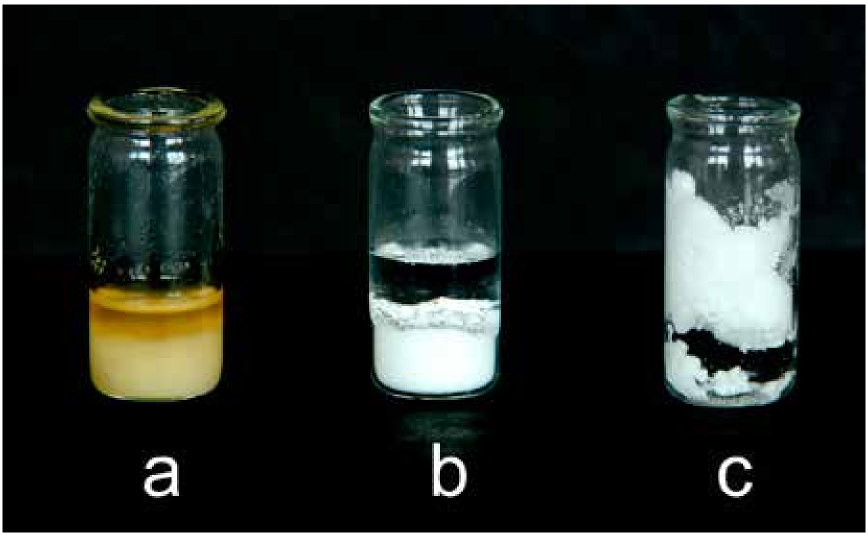

Figure 10. The addition of an excess of liquid to TATP: (a) TATP with oil WD-40 (just sprayed, without mixing), (b) TATP with water just after the addition, water does not penetrate the layer of TATP, (c) TATP with water during mixing, the TATP and water phases are still separated.

There is no strong reason to choose between water and oil for decreasing the sensitivity to friction when disposing of any organic peroxide found. The pros and cons for both possibilities are summarized in Table 2. If one wants to decrease the sensitivity only, the better choice is oil, if it is available. The contamination of a sample with oil however makes further analysis of the sample more difficult. Water does not contaminate the sample, and is as suitable as oil for decreasing the sensitivity to friction, if used in excess. The great advantage of water is its availability and nonflammability.

However, the problem with water is its poor penetration into the sample. Figure 10 shows three vials with TATP. Vial (a) contains TATP with oil, where the oil has fully penetrated into the TATP powder without any mechanical mixing. The similar situation for TATP with water is shown in vial (b). The water and the powder are fully separated; the water does not penetrate into the sample, and a small portion of TATP floats on the surface. Vial (c) shows the same situation during mixing. The water and TATP are still separated, at least partially. Careful and intensive mixing is necessary in this case. Such mixing is a disadvantage for using water in the field. The situation in the case of DADP is similar; in the case of HMTD this problem was not observed.

From a practical point of view, when disposing of any organic peroxide found, probably the best way to decrease the sensitivity to friction is to use an excess of low viscosity oil. The complications for any further analysis are more than balanced by the safety aspects. If oil is not available, using excess water will do a similar job. However the most misused organic peroxide is TATP and problems with the penetration of water into the sample can occur.

Table 2. Pros and cons for using water and oil to decrease the friction sensitivity of organic peroxides

	Water	Oil WD-40
availability	everywhere	limited
further analysis of sample	possible	limited
decrease in sensitivity in case of small addition	lower	higher
'miscibility' or penetration into the material	limited	good
flammability	nonflammable	flammable

Conclusions

The sensitivity to friction of commonly misused organic peroxides (TATP, DADP, HMTD) was measured to evaluate the effect of adding a desensitizing liquid (water, oil). When adding small quantities (up to about 10%), oil reduced the sensitivity to friction more than water. The decrease in the sensitivity to friction continues up to *ca*. 20% of an added liquid. If the liquid is added in excess, the decrease in sensitivity will not be further changed significantly. In the case of the disposal of organic peroxides, probably the best way to decrease the sensitivity to friction is by the use of an excess of a low viscosity oil, due to the problems associated with mixing TATP and DADP with water.

Acknowledgements

This work was performed as a part of the Ministry of the Interior of the Czech Republic, Project No. VG20102014032.

References

[1] Dudek K., Matyáš R., Dorazil T., DIEPE – Detection and Identification of Explosive Precursors and Explosives, *New Trends Res. Energ. Mater.*, *Proc. Semin., 14th*, Pardubice, April 13-15, **2011**, 595-601.
[2] Yeager K., Dangerous Innovations, in: *Trace Chemical Sensing of Explosives* (Woodfin R.L., Ed.), John Wiley & Sons, New Jersey, **2007**, pp. 43-67.
[3] Marshall M., Oxley J.C., *Aspects of Explosives Detection,* Elsevier, London, **2009**, pp. 12-20, 49-50.
[4] Oxley J.C., What's Special about Liquid Explosives? *Proceedings of the NATO Advanced Research Workshop on Detection of Liquid Explosives and Flammable Agents in Connection with Terrorism*, St. Peterburg, **2007**, pp. 27-38.
[5] Bagal L.I., *Khimiya i tekhnologiya iniciiruyushchikh vzryvchatykh veshchestv* (in Russian), Mashinostroenie, Moskva, **1975**, pp. 406-415.
[6] Fedoroff B.T., Sheffield O.E., Kaye S.M., *Encyclopedia of Explosives and Related Items*, Picatinny Arsenal, Dover, **1960**, vol. 1, pp. A42-A45; **1975** vol. 7, pp. H83-H84.
[7] Matyáš R., Pachman J., *Primary Explosives*, Springer, Heidelberg, **2013**.
[8] Egorshev V., Sinditskii V., Smirnov S., Glinkovsky E., Kuzmin V., A Comparative Study on Cyclic Acetone Peroxides, *New Trends Res. Energ. Mater.*, *Proc. Semin., 12th*, Pardubice, April 1-3, **2009**, 113-123.
[9] Fitzgerald M., Bilusich D., Sulfuric, Hydrochloric, and Nitric Acid-catalyzed Triacetone Triperoxide (TATP) Reaction Mixtures: An Aging Study, *J. Forensic Sci.*, **2011**, *56*, 1143-1149.
[10] Matyáš R., Pachman J., Study of TATP: Influence of Reaction Conditions on Product Composition, *Propellants Explos. Pyrotech*., **2010**, *35*, 31-37.
[11] Matyáš R., Pachman J., Ang H.G., Study of TATP: Spontaneous Transformation of TATP to DADP, *Propellants Explos. Pyrotech*., **2008**, *33*, 89-91.
[12] Matyáš R., Pachman J., Ang H.G., Study of TATP: Spontaneous Transformation of TATP to DADP, *Propellants Explos. Pyrotech.* **2009**, *34*, 484-488.
[13] Stambouli A., El Bouri A., Bouayoun T., Bellimam M.A., Headspace-GC/MS

Detection of TATP Traces in Post-explosion Debris, *Forensic Sci. Int.*, **2004**, *146S*, S191-S194.
[14] Matyáš R., Šelešovský J., Musil T., Sensitivity to Friction for Primary Explosives, *J. Hazard. Mater.*, **2012**, *213-214*, 236-241.
[15] Bellamy A.J., Triacetone Triperoxide: Its Chemical Destruction, *J. Forensic Sci.*, **1999**, *44*, 603-608.
[16] Oxley J.C., Smith J.L., Jiaorong H., Wei L., Destruction of Peroxide Explosives, *J. Forensic Sci.,* **2009**, *54*, 1029-1033.
[17] Matyáš R., Chemical Destruction of Triacetone Triperoxide and Hexamethylenetriperoxidediamine, *New Trends Res. Energ. Mater.*, *Proc. Semin.*, *6th*, Pardubice, April **2003**, 164-173.
[18] Kaye S.M., *Encyclopedia of Explosives and Related Items*, Picatinny Arsenal, vol. 10, Dover **1983**, pp. W14, W26-W28.
[19] Avrami L., Hutchinson R., The Sensitivity to Impact and Friction, in: *Energetic Materials 2. Technology of the Inorganic Azides*, (Fair H.D., Walker R.F., Eds.), Plenum Press, New York, **1977**, pp. 140, 152-155.
[20] Dubnikova F., Kosloff R., Almog J., Zeiri Y., Boese R., Itzhaky H., Alt A., Keinan E., Decomposition of Triacetone Triperoxide is an Entropic Explosion, *J. Am. Chem. Soc.*, **2005**, *127*, 1146-1159.
[21] Šelešovský J., Pachman J, Probit Analysis in Evaluation of Explosive‘s Sensitivity, *New Trends Res. Energ. Mater.*, *Proc. Semin.*, *13th*, Pardubice, April 21-23, **2010**, pp. 662-668.