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Study of TATP: Mass Loss and Friction Sensitivity During Ageing*)

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Abstract: Triacetone triperoxide (3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexoxonane; TATP) is one of the most frequently used improvised explosives, often misused worldwide. In our previous studies, we had observed that the kind of acid used to catalyse its formation has a significant influence on TATP's properties. TATP was prepared using five different acids that are often used in improvised conditions. All of the samples were subjected to natural ageing in both open and closed vials at laboratory temperature. During ageing, TATP sublimes and decomposes. The changes in crystal size and shape after ageing were documented by optical microscopy. The mass loss was monitored about every third day during ageing. Samples prepared using sulphuric and perchloric acids lose weight more quickly than the others due to chemical decomposition. The friction sensitivity was determined for all samples before and after ageing. Neither the type of acid used nor the influence of closing the vials had any significant influence on the friction sensitivity after ageing. The friction sensitivity of all tested samples of TATP was about the same − between that of lead azide and that of mercury fulminate.

Keywords: triacetone triperoxide, TATP, 3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexoxonane, friction sensitivity, mass loss

Introduction

Triacetone triperoxide (3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexoxonane, TATP) is one of the most commonly synthesized improvised explosives [1, 2].

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There are several reasons why TATP is so popular: simple synthetic procedure; knowledge of the synthesis is widely broadcast *via* the internet; raw materials for the synthesis are readily available in chemists' trade networks or DIY markets without any restrictions on the sale of such substances [3].

TATP is not a physically stable compound. It re-crystallizes spontaneously into larger, nicely formed, crystals and it quickly sublimes even at room temperature [4, 5]. Both these properties produce a change in the crystal morphology. The sensitivity of explosives in general strongly depends on the crystal size and shape. Therefore it can be supposed that the sensitivity of TATP can change during storage.

TATP is prepared by the reaction of acetone with hydrogen peroxide in an acidic environment. The acids published on web pages for the preparation of TATP for improvised explosives depend on the author of the procedure, his experience and also the local availability of the acids [6, 7]. A small amount of the acid used as the catalyst during TATP preparation remains in the crude product, as we have reported previously [8]. This acidic residue has a significant influence on the properties of the TATP produced (allotropic modification [9], thermal stability [8]; transformation of TATP to 3,3,6,6-tetramethyl-1,2,4,5-tetraoxacyclohexane − known under the acronym DADP [10, 11]; stability of TATP in solutions [12]).

We therefore carried out investigations on the influence of TATP ageing on its properties, particularly on the mass loss and the sensitivity to friction. Knowledge of friction sensitivity is very important for safe handling of primary explosives. The results of our article can be useful for anybody who handles TATP (primarily for EODs, criminal investigators or forensic analysts).

Material and Methods

Caution: TATP is a primary explosive sensitive to impact, friction, electrical discharge and flame − even when wet. The synthesis and handling of TATP are dangerous operations that require the standard safety precautions for handling primary explosives to be followed!!!

TATP synthesis

TATP was synthesized by the commonly used and well known procedures that are published in various modifications on web pages that deal with improvised explosives (e.g. Sciencemadness [6], Pyroforum [7]). Samples of TATP were prepared using five different acids. The molar ratio of acid to acetone was always 0.25. The sixth sample was re-crystallized TATP, used as a standard

for comparison.

Acetone (9 ml, 122 mmol) was mixed with 30% hydrogen peroxide (15.7 ml, 153 mmol) and placed in a glass beaker externally cooled by a water bath. The solution was stirred and the acid catalyst was added drop-wise with the temperature being kept below 20 °C. The concentrations and amounts of acid were as follows: 37% hydrochloric acid (2.56 ml, 30.6 mmol); 31% sulphuric acid (7.87 ml, 30.6 mmol); 65% nitric acid (2.12 ml, 30.6 mmol); 70% perchloric acid (2.65 ml, 30.6 mmol) and citric acid monohydrate (6.43 g, 30.6 mmol). Stirring was terminated immediately after the addition of the last drop of acid. The beaker containing the reaction mixture was covered with a watch glass and kept at laboratory temperature without stirring or cooling for 24 hours (except in the case of TATP from citric acid when the reaction time was extended to 14 days due to the slow precipitation of TATP). The resulting precipitate was collected by filtration, washed repeatedly with water until neutral, then twice with distilled water, and dried in the open air at room temperature. Re-crystallized TATP was prepared by crystallization from a hot methanol solution. The size and shape of the TATP crystals were documented by optical microscopy immediately after preparation.

Mass loss determination

The conditions of TATP ageing were chosen to be similar to those expected to be used for TATP storage by improvised producers. Twelve TATP samples (two samples from each acid and two samples of re-crystallized TATP; one sample from each acid was covered with a lid, the other was not covered) were placed into small plastic bottles (volume 20 ml, mouth diameter 17 mm, see Figure 1). The bottles with TATP were stored at laboratory temperature (from 22 to 25 °C). The weight of each sample was measured about every third day.

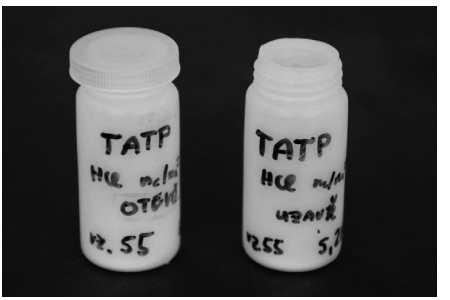

Figure 1. Ageing of the TATP samples was carried out in small plastic bottles (volume 20 ml, mouth diameter 17 mm, one being covered with a lid, and the other uncovered).

Friction sensitivity

Friction sensitivity was determined for the pristine and for the aged samples. Sensitivity to friction was measured using a small BAM type friction apparatus − FSKM-PEx. Porcelain plates type no. BFST-Pn-200 and porcelain plates type BFST-Pt-100S were used. The apparatus, porcelain plates and pegs were produced by OZM Research. The probit analysis was used to calculate the friction sensitivity curves of each sample.

HPLC analysis

The liquid chromatographic system and measuring conditions were used in an identical manner to that used in our previous study [13]. All samples were measured before ageing and after ageing (126 days).

Results and Discussion

The five types of TATP synthesized using different acids and one re-crystallized TATP were subjected to natural ageing (126 days, laboratory temperature). The mass loss of each sample was monitored during ageing and the friction sensitivity was determined before and after ageing.

The crystal sizes and shapes for un-aged and aged samples can be seen in Figures 2 and 3, respectively. In both figures, it is clear that the crystals of TATP prepared by using citric acid are the largest in comparison to all other samples. This is probably caused by the long reaction time for the preparation of TATP (14 days for citric acid, 24 hours for the other samples).

Changes of crystal size and shape were observed during ageing in the case of all samples. The smallest crystals visible in the un-aged samples disappeared during ageing. The increase in size of the crystals was not as high as was expected and as has been reported by us and other authors previously [4, 14].

Loss of mass was detected for all samples. Higher mass loss was observed for TATP samples aged in open bottles. This result was expected, due to the well known high volatility of TATP. The samples can be divided into two groups. The stability of TATP prepared using hydrochloric, nitric, or citric acid is about the same as the stability of TATP purified by re-crystallization; the samples prepared using sulphuric acid or perchloric acid were significantly less stable. This effect can be seen in Figure 4 (the loss of mass in the case of samples prepared from sulphuric and perchloric acids is much higher) and was also confirmed by HPLC analysis.

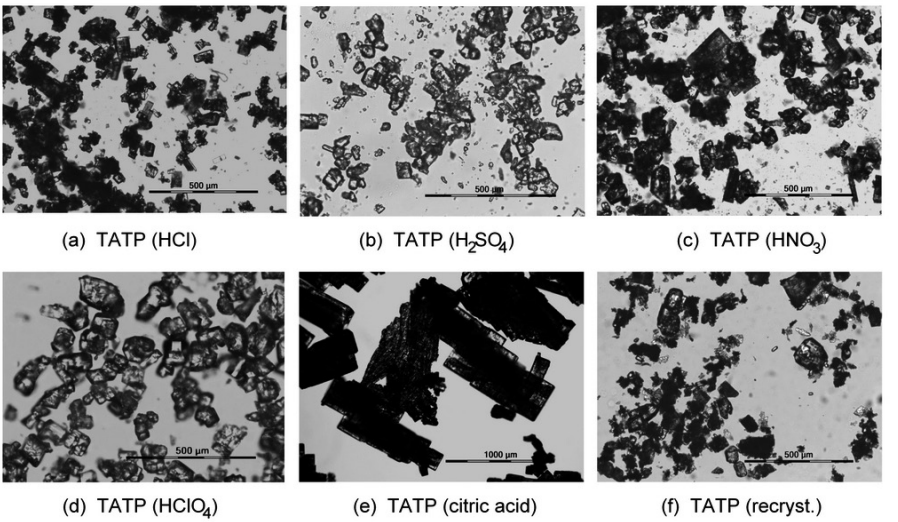

Figure 2. The crystal size and shape of un-aged TATP samples.

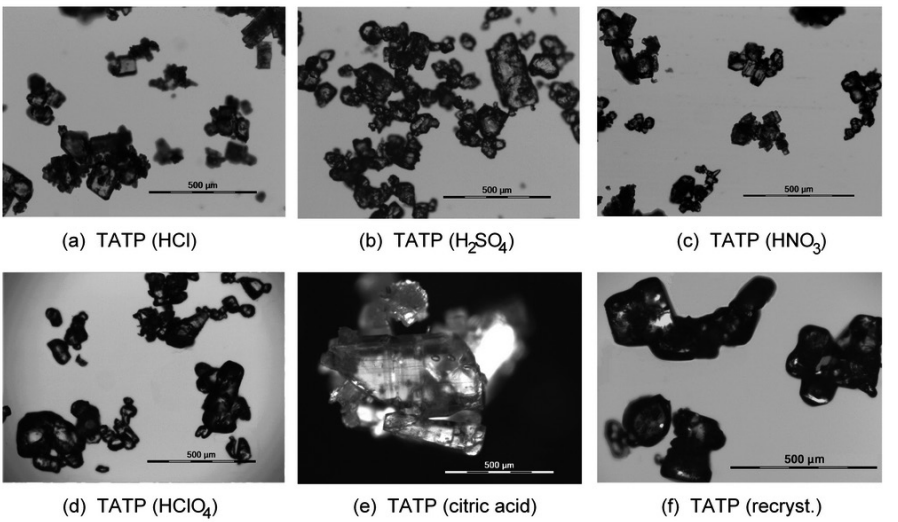

Figure 3. The crystal size and shape of aged TATP samples.

The HPLC chromatograms of all un-aged samples contained only two peaks, TATP and the side product; the same as in Ref. [13]. No change was observed in the chromatograms in the case of aged samples prepared using hydrochloric, nitric, or citric acid nor in the case of the aged re-crystallized sample. This

corresponds to [12], where it was reported that no chemical change of TATP prepared using hydrochloric acid occurred after 5 years in storage. However, several other compounds were detected by HPLC in the case of aged TATP samples prepared using sulphuric or perchloric acid. This fact corresponds to the low stability in solution of TATP prepared using sulphuric and perchloric acids [12]; the thermal stability of TATP prepared using sulphuric and perchloric acids is also poor [8].

Loss of mass for TATP prepared using hydrochloric, nitric, or citric acid is caused only by volatility and the samples are chemically as stable as the re-crystallized sample. On the other hand, the samples prepared using sulphuric or perchloric acid undergo chemical changes during ageing and these changes are also responsible for the higher mass loss observed in the case of these two samples during ageing.

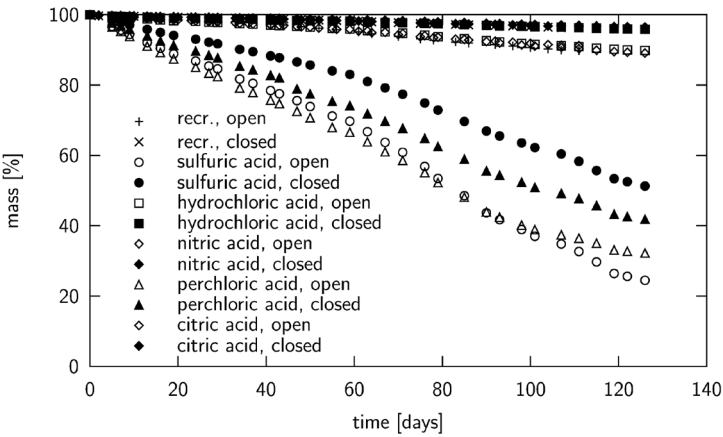

Figure 4. Influence on the mass loss of TATP of the acid used for TATP preparation (measured at laboratory temperature for 126 days). The lower lines are for TATP samples aged in open bottles; the upper lines are for closed bottles. The mass loss of the samples prepared using sulphuric or perchloric acid is significantly higher.

The friction sensitivity of TATP was determined for freshly prepared TATP (the day after preparation) and also for aged samples. The influence on the friction sensitivity of the acid used for TATP synthesis is demonstrated in Figure 5. The sensitivity of all samples is about the same. The acid used has almost no influence on the friction sensitivity of TATP, the differences between individual samples being within the limits of the methodology used [15]. The sensitivity of all samples is between that of mercury fulminate and that of lead azide.

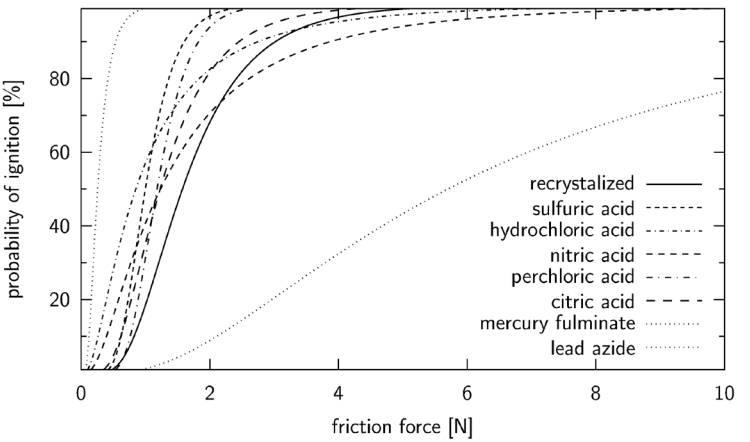

Figure 5. Friction sensitivity of freshly prepared TATP samples using various acids in comparison to re-crystallized TATP, mercury fulminate (right dotted curve) and lead azide (left dotted curve).

Neither the type of acid used nor the influence of closing the vials had any significant influence on the changes of the friction sensitivity during ageing. This is demonstrated in Figures 6 and 7 for TATP prepared by using hydrochloric and nitric acids respectively. The biggest change in sensitivity to friction was observed in the case of TATP prepared from sulphuric acid (Figure 8). The sensitivity to friction for this sample decreased during ageing.

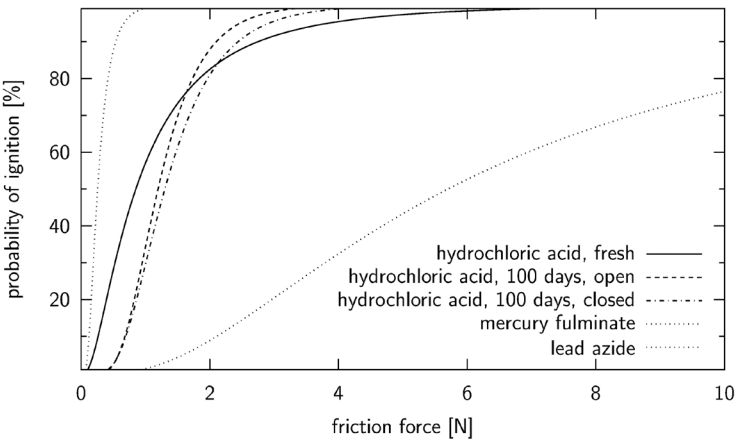

Figure 6. Friction sensitivity of fresh and aged TATP prepared by using hydrochloric acid in comparison to mercury fulminate (right dotted curve) and lead azide (left dotted curve).

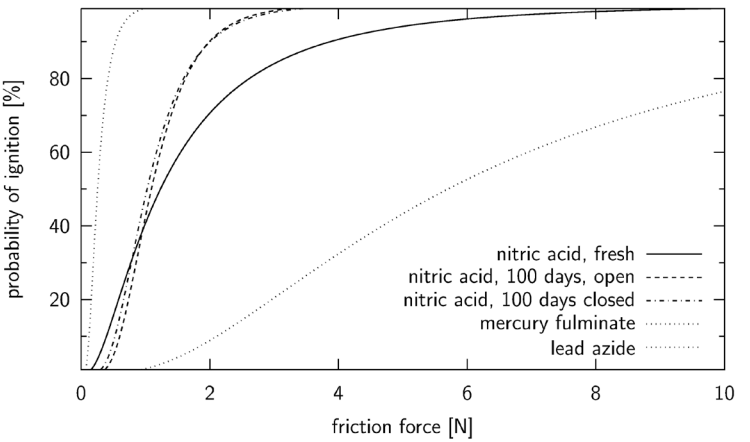

Figure 7. Friction sensitivity of fresh and aged TATP prepared by using nitric acid in comparison to mercury fulminate (right dotted curve) and lead azide (left dotted curve).

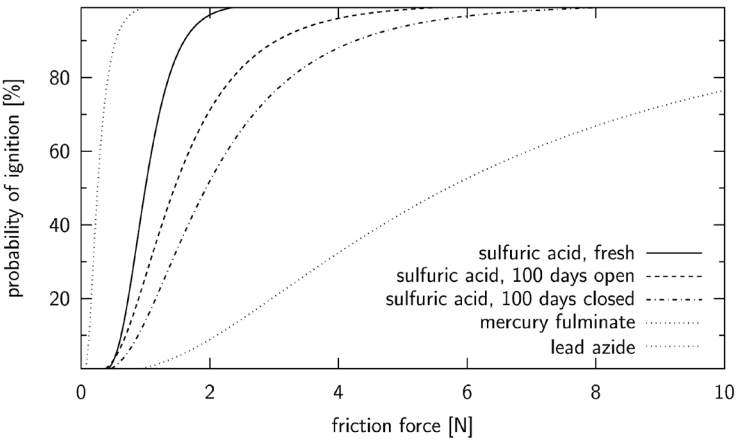

Figure 8. Friction sensitivity of fresh and aged TATP prepared by using sulphuric acid in comparison to mercury fulminate (right dotted curve) and lead azide (left dotted curve).

Conclusion

TATP was prepared using five different catalysing acids. Changes of crystal size and shape were observed during the ageing in the case of all samples. The

smallest crystals visible in un-aged samples disappeared during ageing. The mass losses during ageing of samples prepared with using hydrochloric, nitric and citric acid were similar to the mass loss of the recrystallized sample. The samples prepared using sulphuric and perchloric acids were significantly less stable. Neither the type of acid used nor the influence of closing the vials had any significant influence on the friction sensitivity during ageing.

Acknowledgements

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