Expedient destruction of organic peroxides including triacetone triperoxide (TATP) in emergency situations

The destruction of organic peroxides particularly triacetone triperoxide (TATP) in emergency situations poses many challenges to emergency responders because of their inherent hazards and sensitivity to detonation. Incidents involving TATP have become more common in recent years as it has found widespread use as an explosive material in terrorism related incidents.

A new field portable approach using high temperature combustion has been developed and tested to destroy organic peroxides especially TATP. This approach provides a viable alternative to destruction of organic peroxides using explosives, or chemical neutralisation. The apparatus is made of commonly available parts, and does not require specialist expertise to safely operate. However, the handling of sensitive organic peroxides like TATP requires caution. Guidance is also offered about approaches to consider including risk control measures to effectively and safely mitigate risks associated with destroying sensitive organic peroxides in emergency settings.

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INTRODUCTION

Organic peroxides are a class of reactive organic chemicals[1,2] with application across a wide variety of industries and within the research environment. Their reactivity[3–6] arises from the oxygen–oxygen bond and is why they are prone to violently decompose due to heat, friction or mechanical shock. They can be accidentally formed during storage of typical laboratory solvents such as diethyl ether. Several explosions[3–6] within laboratories and workplaces have been attributed to the formation of these organic peroxides. Bretherick,[3] and more recently, Kelly[4] and others[5,6,13,16] have highlighted the hazards associated with these chemicals and their safe handling in occupational settings.

Their reactivity has also meant they have been investigated for use as explosives,[7–9] but their inherent instability precluded their widespread adoption by the military and industry. In recent years, organic peroxides[10–12] such as triacetone triperoxide (TATP) have found favour in terrorist and criminally inspired events as a primary explosive.

The friction sensitivity of organic peroxides[5,6,14] coupled with the circumstances in which it is often discovered at HAZMAT and terrorism-related incidents pose significant challenges to responders.[10–12] These include the amount present, and storage conditions, as well as the ability to sample and handle before its destruction.

The destruction of organic peroxides[17–23] can be achieved by a variety of approaches ranging from chemical neutralisation to thermal oxidation. In some circumstances they have been destroyed by detonation.[9,10] A common approach used and published by industry[15] has been to dilute the organic peroxide and burn the subsequent solution in a pan. However, this guidance includes significant caveats, and is not suitable in all situations. The challenge to select a suitable and safe destruction technique has been illustrated on a significant scale during the recent Texas floods[24] where the large volume of unstable organic peroxides was allowed to burn. Nonetheless, the approach[25,26] was subsequently criticised due to offsite impacts.

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The safe destruction of TATP and similar organic peroxides like hexamethylene triperoxide diamine (HMTD) used as illicit primary explosives also pose significant challenges. This includes identification, handling, and forensic attribution coupled with the amounts and circumstances of discovery. Consequently, there is great caution exhibited when handling organic peroxides like TATP based on historical incidents[9,27,28] where it detonated accidentally when handled. In some instances, it is assumed the material is present and the material detonated on site, or in a secure area immediately adjacent to the discovery. However, it takes time to safely prepare a site and the material for detonation. In addition, explosives are typically used to initiate detonation of the TATP. These challenges were aptly revealed during an incident in Escondido, California where it was decided to burn a house down[10] due to the presence of organic peroxides and the nature of their storage.

This paper will focus on describing a new approach using high temperature combustion to expediently destroy organic peroxides in industrial settings as well as illicitly made organic peroxides such as TATP in emergency settings. This approach provides a viable alternative to destruction of organic peroxides by detonation and overcomes the inherent limitations of the pan burning method commonly used by industry. The apparatus is made of commonly available parts and does not require specialist expertise to safely operate. Guidance is also offered about approaches to consider including risk control measures to effectively and safely use the apparatus and mitigate the incidents.

EXPERIMENTAL

TATP and HMTD was made following the methods reported by Oxley et al.[30,37] A risk assessment to determine safe working weights, storage and handling protocols and risk control measures to assure the safety of all personnel was undertaken prior to manufacture, handling, and testing of the destruction technique. The synthesised organic peroxides were characterised by Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR FTIR) to check their purity, in particular for the presence of any decomposition products such as Diacetone Diperoxide (DADP). The organic peroxides were stored and used within 72 h. Aliquots of the organic peroxide was added together to obtain the desired weight prior to testing of the destruction apparatus.

A schematic and photograph of the destruction apparatus are shown in Figures 1 and 2 respectively. The destruction apparatus comprised a propane burner coupled to a commercially sourced 9 kg propane cylinder incorporating flow control and other safety devices.

The organic peroxide (TATP) was dissolved in diesel within a non-reactive container. It was found the solubility of TATP in diesel is ca. 100 g/L and corresponds to an available oxygen content of ca. 4.9%. The dissolution of 10 g of TATP into 100 mL of diesel occurred over approximately 5 min with stirring and no increase of temperature. This indicated that there was no heat of dissolution and therefore no risk of accidentally heating the solution sufficiently to cause detonation of the TATP while being dissolved. Nonetheless, efforts should be made to prevent accidental contamination of the solution by transition metals or other materials.

The solution was drawn into a tube flowing air using the venturi effect. The solution was aspirated into the propane flame through an aspirating nozzle of a typical solvent degreasing gun. The air flow rate was controlled by pressure regulators attached to a 9.6 L air cylinder at 300 atmospheres. The air cylinder was a standard self contained breathing apparatus cylinder. After use the tubing was washed with diesel and the diesel was subsequently incinerated in the propane flame.

All the components necessary to build the apparatus were readily obtained from emergency response agencies, and local hardware stores.

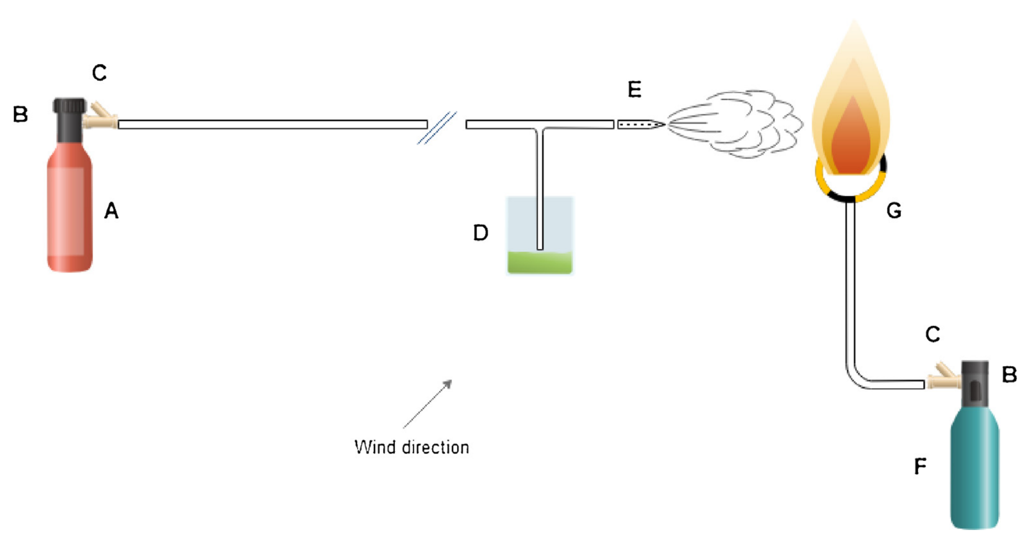

Figure 1. Schematic of organic peroxide destruction apparatus. A — air cylinder. B — pressure regulator. C — safety devices. D — peroxide solution and inlet tube. E — aspirator. F — LPG cylinder. G — propane burner.

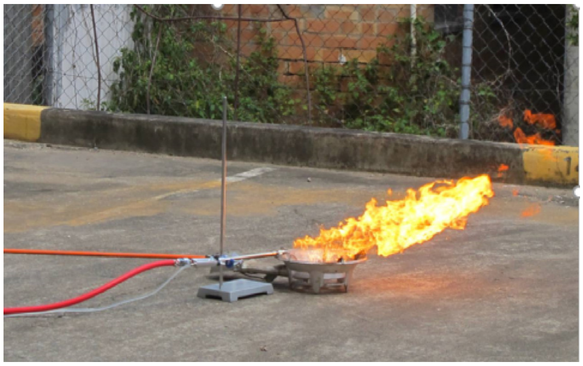

Figure 2. Operation of the field portable incineration apparatus.

The approach was successfully trialled on different organic peroxides, including HMTD, and TATP up to 20 g of threat material.

DISCUSSION

There are many potential approaches[6,9,18,20–23,30–32] to successfully destroy waste or unwanted organic peroxides including:

- detonation in place;
- thermal decomposition;
- acid based decomposition;
- catalytic decomposition; and
- dilution and subsequent burning.

However, the reactivity of organic peroxides has meant that the neutralisation reaction must be carefully controlled to prevent accidental deflagration, or detonation. For example: Oxley et al.[9] found concentrated sulfuric acid added directly to 1 g of TATP caused a detonation likely due to reaction rate and heat of reaction.

Historically, industry recommended[6,32] that waste and unwanted organic peroxides be diluted in a suitable organic solvent and burned in a pan. This method has been referred to as dilute and burn. However, they often noted the potential for detonation cannot be discounted especially for large amounts of organic peroxides.[32] This observed behaviour is readily explained if the properties of solvent, organic peroxide, and fire behaviour are considered. Unless the organic peroxide contributes significantly to the vapour above the solution the organic solvent will be preferentially consumed. Thus, eventually the solution will become saturated with the organic peroxide possibly causing crystallisation. The crystalline substrate will be readily heated by the radiant heat generated from the flame and the organic peroxide may deflagrate, or detonate.

In the case of TATP, its relatively low decomposition temperature and sensitivity to detonation precludes this approach on all but the smallest amounts (less than 1 g), and the effects of detonation pose little, if any risk to bystanders. Oxley et al.[9] reported the destruction of TATP using chemical neutralisation and catalytically assisted neutralisation. However, the processes often long periods of time, specific equipment, and reagents, and hence are not suitable for application in emergency settings where time may be at a premium and, reagents and technical expertise are not readily available.

TATP is readily soluble in a variety of organic solvents, such as toluene,[29] and diesel is relatively stable. HMTD is less soluble in many organic solvents, but is partially soluble in acetonitrile. An obvious advantage to dissolution and wetting these organic peroxide is that their sensitivity decreases.[14] Their solubility and solution stability provides an opportunity to develop a variation to the dilute and burn technique used by industry.

A two-step approach was developed that uses high temperature incineration of the solution through a propane flame. The two steps are:

- dissolve the organic peroxide and draw the solution into an air flow; and
- aspirate the organic peroxide solution directly into a propane flame.

The solution is obtained by firstly wetting the TATP and then dissolving with a suitable solvent. In this case diesel was used. It is recommended the TATP solution be kept below 5% available oxygen and ideally 1% available oxygen to reduce the potential of detonation.

The solution was continuously introduced into an air stream using the Venturi effect. Compressed air was sourced at low flow and pressure from a typical fire service air cylinder. The air flow and air pressure were controlled by a modified valve that is commonly available. The air stream containing the TATP solution was aspirated directly into the propane flame using an aspirator such as a commercially available solvent cleaning gun. Aspiration of the TATP solution generates a mist, or micro bubbles and assists with distribution within the flame and hence achieve complete combustion. In addition, diesel mist has lower flammability limit and flashpoint than diesel vapour,[39] and also assists combustion. This approach significantly reduced the potential for any accidental detonation of TATP during its destruction.

Incineration using a propane flame was chosen as propane (or liquified petroleum gas) was readily available to responders and they are usually familiar with its combustion behaviour and hazards. The burner and accessories can also be readily sourced from large hardware suppliers. The propane flame temperature[33] is ca. 1980 °C. The flame intensity was readily controlled via gas flow. Destruction of the TATP solution was complete within seconds to minutes depending on the air flow rate and solution volume. In addition, there is no waste products to subsequently manage.

The propane burner should be protected from the wind to prevent flame spread or accidental extinguishment. A thermal imaging camera and air monitoring for volatile organic compounds using a photo-ionisation detector were readily applied to confirm combustion performance.

Propane is readily combusted[40] and its major products are carbon dioxide and water. Diesel is also readily combusted[41,42] and the major products are carbon dioxide and water. However, incomplete combustion[41] leads to other combustion products such as polyaromatic hydrocarbons (PAHs), and volatile organic compounds like benzene, and acrolein.

The combustion of TATP and other sensitive organic peroxides has not been well studied,[34,36–38,42–44] since they readily detonate. However, published studies of the combustion of other organic peroxides[32,35] reported a range of combustion products may be generated including volatile organic compounds. Direct aspiration of the TATP solution mist into the propane flame assists uniform and complete combustion as illustrated in Figure 2.

The apparatus can be readily set up in most settings and readily scaled up to effectively destroy large quantities of TATP if required. The apparatus should be only applied outdoors where the heat and combustion products can be readily dispersed.

Consequently, the method has great appeal for emergency response and makes destruction safe and effective for a range of organic peroxides.

A challenge in emergency situations that requires the focussed attention of the responder (within industry, military, or public safety) is the handling and dissolution of the organic peroxide. These situations range from an assembled improvised explosive device (IED), closed and open containers to spillage on surfaces. It is essential the appropriate capabilities are available and subject matter expertise consulted before contemplating the handling of any sensitive organic peroxide so only prudent risk is adopted. The two highest risk activities are:

- handling sealed containers in particular glass and metal. A container includes an assembled improvised explosive device (IED); and
- dissolving any organic peroxide to make a stable solution.

To assist responders with potential actions an example decision making guidance flow chart is shown in Figure 3.

IEDs pose significant risks and they must be always managed in accordance with established procedures for rendering safe IEDs.

Containers also pose significant challenges for responders especially where organic peroxides are stored within sealed glass or metal containers. Glass and metal containers can generate significant penetrating fragments if they catastrophically fail. Moreover, it is well known metals readily contaminate organic peroxides causing sensitisation. Manipulating screw top lids or seals should be avoided. Several approaches can be applied to open closed containers such as hook and pull techniques, penetration using disruptors and other devices, or other piercing implements.[45,46,50] However, these techniques have not been widely reported and further validation is necessary to demonstrate all the potential approaches. Any responder considering applying such approaches must ensure they have the appropriate capabilities, access to Subject Matter Experts (SMEs) and practised these approaches before applying them in emergency situations. If the responder has doubts about their capabilities or access to SMEs then the container should be rendered safe like an IED.

Open containers and spilled organic peroxides pose less immediate risk. There are many approaches that can be applied to dissolve or mix the organic peroxide in a suitable solvent to prepare a stable solution. The suitability of these approaches depends on incident factors such as the organic peroxide properties, solvent, container, volume, and location. These techniques[3,6,11,47–50] have ranged from dissolving the organic peroxide directly in a suitable organic solvent to wetting the organic peroxide and then dissolving. The wetting technique and then dissolving has great

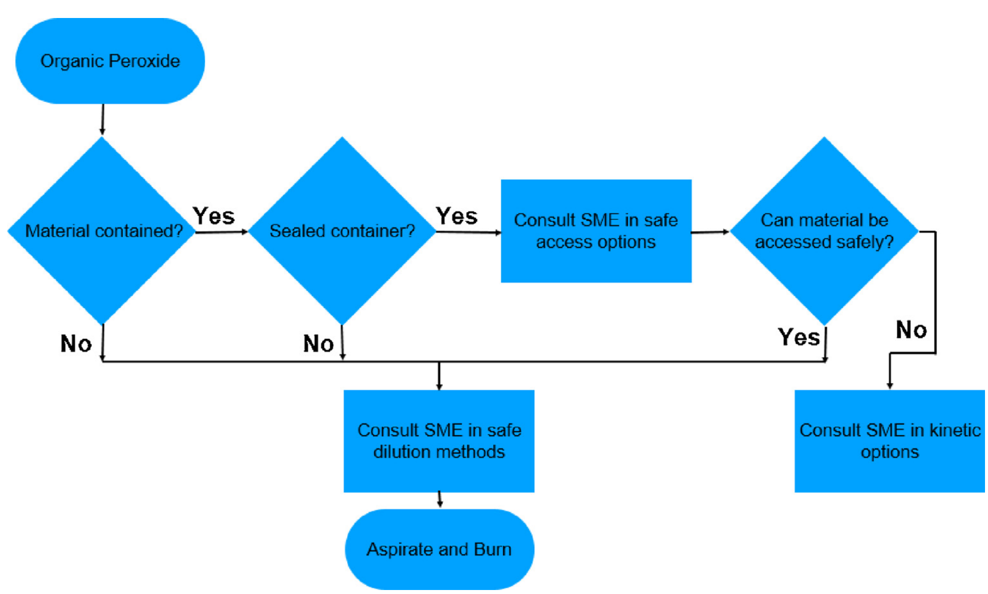

Figure 3. Example organic peroxide decision making guidance.

advantages in emergency settings. The solvent can be applied immediately adjacent to the organic peroxide and allowed to slowly wet followed by dissolution. Alternatively,[50] a mist of a suitable solvent can be applied to wet the peroxide and then dissolved. When wetting the organic peroxide using a misting approach sufficient wetting time must be allowed to dissipate any accumulated electrostatic charge. The solution can then be transferred to a suitable container if required using any number of common transfer methods. Any responder considering applying such approaches must ensure they have the appropriate capabilities, access to SMEs and practised these approaches before applying them in emergency situations.

Responders should follow established response principles when handling and destroying these sensitive materials that are also primary explosives. These include:

- risk assessment and incineration plan including criteria so only prudent risk is accepted;
- adopt appropriate risk control measures such as site isolation, personal protective equipment (fire protective clothing and respiratory protection);
- use only non-sparking and non-reactive tools for sampling, and handling TATP;
- select and apply appropriate handling techniques to dissolve the organic peroxide (TATP), such as carefully wetting the TATP prior to handling and dissolution;
- dilute the organic peroxide solution to less than 5% available oxygen and, ideally, less than 1% available oxygen;
- select a safe and secure are to establish the apparatus and ensure the area is isolated; and
- test the incineration method on a discrete TATP solution before scaling up destruction.

SUMMARY

A new field portable high temperature incineration apparatus and methodology was developed to destroy organic peroxides found in a variety of settings ranging from laboratories, and manufacturing facilities to emergencies like terrorism. The approach can be applied to a wide variety of organic peroxides including TATP.

This method works by directly aspirating an organic peroxide solution into a propane flame. The organic peroxide solution is quickly and completely consumed with no hazardous airborne contaminants generated, or waste to subsequently manage. This approach can be applied safely in a wide variety of situations ranging from industrial sites to urban areas with little, if any, risk to bystanders.

The apparatus is made of commonly available parts and does not require specialist expertise to safely operate. It provides a viable alternative to organic peroxide destruction using explosives and proven laboratory scale chemical neutralisation approaches. It also overcomes the limitations of the dilute and burn technique. Responders should always apply established response principles when handling and destroying sensitive organic peroxides. They should consider the guidance provided when developing and implementing a destruction plan.

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