

Safety Concerns and Chemical Aspects of Improvised Explosive Devices and Homemade Explosives

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The continuous changes in socio-political scenarios of the last decades led to an impressive increase in terrorist events related to the use of improvised explosive devices (IEDs). The energetic material contained in them, representing the essential part of the apparatus, is object of intense investigation owing to the need of optimizing many variables, namely the chemical energy storage of the detonating compound, the availability of raw materials required for its synthesis, the ease of process synthesis by commonly used tools and the stability of the chemical energy carrier towards transport and handling. This critical analysis proposes a classification of the detonating compounds or mixtures according to their chemical, thermodynamic and ballistic properties that make them basic ingredients in IEDs and homemade explosives. The wide and always growing variety of ingredient combination poses a challenging problem of chemical identification, owing to an interference of signals in analytical data regression. Finally, a discussion on technical realizations of such improvised weapons is outlined in light of the recent protocols of process safety and disaster control.

1. Introduction

The synthesis of homemade explosives (HME) and the related production of IED represents a very serious threat to the social stability of many countries. Interesting reviews paper on the topic are available in literature (Doyle, 2013) and we refer the reader to the references quoted therein. Despite progressively stricter law enforcements against illegal use of exploding devices, the underground activity in the synthesis and preparation of exploding devices had a progressive growth in the last years, owing to their implications in suicidal purposes, terroristic or intentional operations and in unauthorized production of pyrotechnic materials. In the first group, several examples have been analyzed in detail. Some of them refer to suicide missions of "kamikazes", who lost their lives in suicide bombing (Kazim et al., 2008), and therefore these cases may belong both to the first and to the second group. In a different context, namely not related to killing third individuals, Sacco et al. (2020) surveyed a vast forensic literature pertaining to suicides carried out by use of domestic explosives spanning in a time gap of thirty years from 1990 to 2020. They observed that, in 21 cases of suicides considered, all of them refer to males, with average age under 40 years, whose deaths have been generally attributed to a severe barotrauma and fatal internal organs failure. However, as explicitly observed by the authors, pure suicidal events by IED are somewhat uncommon in literature.

The second case, namely related to terroristic or intentional operations, is sadly rich of a wider variety of examples in many countries. Bilukha et al. (2013). reported a distribution of incidents in Nepal in the years 2008-2011 and they classified the events according to different parameters, namely the type of devices used, the places of incident, the number of persons injured or killed, the age group and sex of the involved persons. Sotali and socket bomb were the devices preferably chosen, with explosions occurring with highest frequency in busy streets, shops or markets. Individuals exposed to a greater risk of injury were males in the age 20-39. Wolf et al. (2009) proposed an exhaustive classification of blast injuries into five different categories according to a causes of body damages. This classification is nowadays largely accepted by the scientific community in theme of blast safety science and medicine. While primary injuries were essentially ascribed to the effect of a

pressure wave on inner organs and tissues, secondary ones were attributed to debris and fragments thrown at high speed against the bodies of the victims as an effect of the energy released by detonation. Tertiary damages are due to injuries related to the shift of total bodyweight impacting against obstacles, while quaternary ones depend on the exposure of body and organs to thermal waves and to toxic compounds produced by the chemical reactions underlying explosions, such as carbon monoxide, cyanogen or nitrogen oxides. Finally, quinary damages are related to the aftereffects of an explosion, connected with the presence of infected, radioactive or otherwise noxious compounds intentionally dispersed by explosions and not related to the chemicals deriving from explosive reactions (Westrol et al., 2017). Unfortunately, long-term sequelae of blasts are recurrent and particularly insidious, as they may trigger infections, septic shocks and slow-healing illnesses of often unpredictable origin. In addition, quinary damages may worsen pre-existing pathologies, with an observed increased incidence of disturbances affecting the coagulation system. For these reasons, it should be noted that this classification does not necessarily mean a decreasing severity level. In particular, while some organs are selectively affected by specific damage categories, among the previously cited ones, there are other target organs suffering from damages related to all the aforementioned five causes of injuries. For example, eyes are typically subject to serious lesions deriving from all blast mechanisms, as pointed out by other authors (Scott et al., 2015), who analysed ocular lesions in several cases of blasts both in conventional war and in IED. When eyes are involved in blast consequences, the persons are subject to a very invalidating social life and, in case of permanent irreversible damage, psychological disorders and depression may heavily hit the affected person. It has been reported that severe ocular trauma is often associated with concomitant brain injury (Erdurman et al., 2011). Chaudhary et al. (2013) reviewed blast injuries in non-combat situation, namely in cases of explosions carried out among civilians out of a war context in India. They adopted a classification of blast injuries in four different categories, whose contents are essentially similar to the ones considered by the aforementioned authors. An extended investigation and data analysis on a large representative sample of terroristic bombing events has been carried out by Edwards et al. (2016), who collected the data taken from the Global Terrorism Database containing more than 58,000 bombing attacks over a period of 43 years. In this timespan, a geographical classification shows that the Middle East reaches the highest value at 21.5 % of the global number, followed by South Asia, South America and Western Europe in order of decreasing ranking. In blast injuries occurring at London in 2005 and Madrid, the greatest number of hospitalization was related to orthopaedic incidents, probably owing to the role of secondary and tertiary effects. Again, in the context of European blasting incidents, a report on fatal explosion injuries in Finland (Mäkitie and Pihlajamäki, 2006) from January 1985 to December 2004 evidenced that deaths by accidental origin occurred in 55 out of 68 total cases. It is interesting to observe that more than 90% of victims are represented by males, and this situation is statistically very frequent in many other case studies pertaining to general explosion accidents.

The third group, which pertains to pyrotechnics-related accidents, received a minor attention in the literature of blast injuries. This fact has been pointed out by Sandvall et al. (2017), who were among the first realizing a systematical analysis about lesions produced by fireworks of various types and assembly. Among them, HME, shells, mortars, rockets, firecrackers, sparklers and roman candles are analyzed as agents determining injuries of various gravity and localization. Among all cases considered, the first three listed species represent 62% of the total injuries considered and also they determined the major number of eye and hand damages with irreversible outcome. Rockets are particularly insidious as they may affect the nearby persons, as observed in a more recent study (Van Yperen et al., 2021). In fact, they are usually launched by soil using improvised supports that do not ensure a safe trajectory. Interestingly and dramatically, these authors pointed out that most lesions determining permanent impairment were ascribed to HME, causing amputations in even 77% of people using them.

In the present paper, the most recurrent types of explosives, technical realization and safety concerns pertaining to IEDs are analyzed. Additionally, some aspects concerning more recent trends in the choice of specific chemicals will be considered. This item is well relevant considering security aspects of chemical and process plants falling under the legislation known as Seveso Directives I-II-III and amendments, adopted in the European Union to regulate and prevent major industrial accident hazards, even though intentional acts and physical security attacks are considered in the national transposition of Seveso III only in some Countries (Laurent et al., 2021). In this regard, it is worth observing that process plants falling under upper tier classification of Seveso III framework may be less appealing for intentional attack, due to the most stringent safety and security burdens enforced, notwithstanding the higher hazardous material inventory compared to lower tier ones. Contrarily to common perception, lower tier, or non Seveso process plants may be exposed to a relevant degree of intentional risk, being possibly perceived as more easily vulnerable, thus needing as well the implementation of proper security measures. And further to technical and managerial measure, proper employees' awareness of establishment security procedures may strengthen or weaken the implemented security measures, thus requiring proper training sessions (Sas et al., 2021). The reminder of this paper is

divided as follows. In Section 2, a short overview about chemical composition of exploding materials and their classification according to the typically adopted recipes in IEDs is proposed. In Section 3, some considerations about design solutions and assemblies of IEDs, based on the personal activity of one of the authors in the Bomb Squad Operating Unit of the Police Department in Genova (Italy), are drawn. In Section 4, the conclusions are drawn and the direction for future works is traced.

2. Type of explosives and device configurations of IED

A thorough overview about the properties of explosive materials is beyond the scopes of this paper, but a simple summary of the most important aspects concerning selected explosives in IED is proposed.

2.1 Basic concepts and classification

Deflagration is defined as a chemical reaction having subsonic front speed propagation $v < v_0$, where v_0 is the sound speed in the material at standard thermodynamic conditions. Detonation occurs for $v > v_0$. In standard treatises on exploding materials, namely substances capable of releasing a sudden amount of heat by chemical reaction, they are primarily classified in primary and secondary explosives. The latter are generally used to obtain the desired destroying effect on the surrounding objects, while the former, generally being highly sensitive to heat and impact, supply the activation energy to trigger the decomposition of primary explosives. In an old terminology still adopted, low explosives have $v < 1000$ m/s, while high explosives have v spanning in a range 1,000-10,000 m/s. From a compositional point of view, explosives may be made of:

- (a) monomolecular compounds. In this case, the explosive properties are related to the rapid release of heat and (not necessarily) gases deriving from their dissociation. Organic peroxides are a typical example of this class of compounds.
- (b) mixtures where none of them has intrinsic explosive properties. In this case, the mixtures can be made of oxidizing (comburent) and combustible compounds whose mixing or reciprocal intimate contact may produce a blend capable to explode. An example is given by panclastite, in which liquid nitrogen tetroxide (N_2O_4) is mixed with hydrocarbons, where none of them has explosive properties.
- (c) Mixtures where at least one of them has intrinsic explosive properties. An example is given by aromatic nitrocompounds and ammonium nitrate AN (NH_4NO_3). This blending technique is adopted for economic motivations or even to obtain a synergic effect, namely to reach an effect that a single component, despite its intrinsic explosive nature, would not allow to reach.

All these classes of compounds/mixtures belong to the so-called class of "energetic materials" (Herweyer et al., 2021). Nanochemistry (Reverberi et al., 2017), traditionally focused on the synthesis of nanostructures or nanoparticles (Reverberi et al., 2018), has recently opened new frontiers in this topic: the term "nanoexplosive" is already part of the technical language in the sector (Gao et al., 2019).

It is interesting to stress that v is strongly dependent on the granulometry and compaction of the exploding material, and this property has been experimentally ascertained both for pure compounds (Bellitto et al., 2017) and mixtures. Within certain limits, both deflagration and detonation velocities grow for increasing apparent density ρ_p of the pressed explosive (Luebcke et al., 1995) or for decreasing particle sizes. As well known, the associated deflagration-to-detonation transition is still an open and challenging research field from a theoretical and experimental point of view (Tringe et al., 2021), and this phenomenon poses a serious safety concern in handling, disposal and dismantling of explosive devices.

Besides v and ρ_p , other important physico-chemical parameters characterizing an explosive compound or mixture are the sensitivity, the oxygen balance, the explosion enthalpy, the maximum ideal explosion temperature, the maximum explosion pressure attainable in a closed vessel, the equivalent in trinitrotoluene (TNT), the specific (per unit mass of explosive) volume of released gases in standard thermodynamic conditions and the same physical quantity at the explosion temperature (Akhavan, 2004).

2.2 Selected and typical explosives in IEDs

Statistics have shown that explosives adopted in IEDs may belong to all three aforementioned categories (a), (b) and (c), with a prevalence of (b) as preferential choice. In fact, bombers may supply themselves with energetic materials through an illegal market of civil or military explosives or by household manufacturing. In the latter case, explosives requiring complex and/or multistep process synthesis seldom appear in the realization of IEDs. For example, poly nitro derivatives of aromatic hydrocarbons like TNT or of polyalcohols like nitroglycerine (TNG), erythritol tetranitrate (ETN) and pentaerythritol tetranitrate (PETN) cannot be usually safely produced with a satisfactory yield or purity by handicraft equipment. Another motivation limiting the homemade production of certain species of explosives is the difficult availability of specific base reagents required for the synthesis. A typical example is offered by nitroamines as RDX and HMX, whose preparation

usually needs hexamethylenetetramine (hexamine) as reagent, today present on the free market only in some countries.

As for explosives of group (a), perhaps the top position is kept by organic peroxides (Türker, 2021), like the sadly known triacetone triperoxide (TATP). It is largely adopted by terrorists owing to its easy of preparation from commonly widespread reagents, namely acetone, sulphuric acid and hydrogen peroxide. In unconfined state, it acts as a combustible provided its mass m is lesser than 2 g, but it shifts to a detonating regime for $m > 2$ g. It is very sensitive to impact and friction, and it has a remarkable vapor pressure at room temperature, a thing that greatly increases the risks of unpredicted explosions while opening the containers where it is stored, owing to the presence of its crystals deposited by sublimation around the plugs of containers themselves.

Another peroxide-based explosive, hexamethylene triperoxide amine (HMTD), can be formed by reaction between hexamine and hydrogen peroxide. It is believed to be even more friction-sensitive than TATP and therefore its handling calls for particular caution (Yeager, 2012). It is statistically less chosen than TATP.

Many other shock and heat sensitive primary explosives used in IEDs belong to subset (a). Among them, it is worth mentioning:

- Metal azides $X(N_3)_n$, namely salts of hydrazoic acid with $X = Ag, Hg$ and usually Pb , are heat and shock sensitive toxic primary explosives sometimes used in IEDs. Their synthesis needs using alkali azides or hydrazine compounds, which is toxic reagents usually subject to legal controls.
- Metal fulminates $X(CNO)_n$, where $X = Hg, Ag, Cu$, can be more easily synthesized by a relatively simple process relying upon metal nitrates and ethanol. They have impact and heat sensitivity close to metal azides.
- Metal acetylides, that is compounds where hydrogen(s) of acetylene (C_2H_2) is/are replaced by $X = Cu$ and Ag , have the unusual properties of exploding without releasing gaseous products. Like metal fulminates, they can be easily synthesized using gaseous acetylene and soluble metal salts of the corresponding cation. Their high shock sensitivity in dry state poses a high risk both for the bomber and for the sapper during disarm operations.
- Urea nitrate (UN), or better uronium nitrate ($(NH_2)_2COHNO_3$) is a typically easy-to-made IED (Tamiri et al., 2009), whose identification in blast residues is has been object of scientific investigations and often represents a challenging problem in analytical and forensic chemistry. However, its limited stability towards water discourages its uses.

Explosives of group (b) in IEDs are generally represented by intimate mixtures of an oxidizing agent (comburent) with a reducing one (combustible), in equal or different phases. The choice of them spans over a surprisingly wide variety of compounds, present in different goods often destined to domestic uses, from which they can be extracted with relative ease or directly used as they are. As for oxidizers in solid phase, nitrates like alkali metals or calcium nitrate ($Ca(NO_3)_2$) are commonly used as fertilizers, but laws require that they are sold mixed with inert solids in order to hinder their criminal use. Chlorates, perchlorates and more rarely permanganates are typical salts used in various blends. It should be noted that the corresponding ammonium salts are themselves intrinsic explosives and hence they can be considered as belonging also to group (a), but they are not generally used alone, as some of them, like ammonium nitrate (NH_4NO_3) are rather insensitive to activation. The reductants mixed with them are generally powdered metals like Al, Mg, Zn and powdered charcoal, sugars and wood saw. Liquid and pasty materials are also adopted, like fuel oil, paraffinic hydrocarbons and waxes. A typical example is given by homemade mixtures of NH_4NO_3 with fuel oil (ANFO), a well known civil explosive that many bombers try to realize by improvised techniques (Figuli et al., 2018).

Explosives of group (c), namely combination of intrinsic deflagrating/detonating agents, are seldom encountered in IED, as their manufacture is generally more impractical as it requires components whose commercial availability may become more difficult. However, there are exceptions: among them, it is worth mentioning the terroristic attack at the Delhi court in 2011, where AN and PETN were used (Corbin and McCord, 2013). Another typical recipe is based on a mix of AN with nitromethane NM (CH_3NO_2) in order to enhance the detonation speed (Zygmunt and Buczkowski, 2012). For this reason, NM, commonly used as propellant in rocket model aircrafts, is nowadays in the hotspot as a precursor for IEDs and it seems advisable a stringent limitation of free market policy, even if the restriction is currently envisaged only by some national legislations.

3. Design solutions and assemblies in IEDs

Usually, IEDs are made by explosives of the aforementioned three types, in contact with a likewise improvised detonator. It is often realized with a thin tube of plastic or other materials, containing a highly pressed primary explosive physically connected with a fuse or with an electrically heated metal filament wired to a battery and lightened by a remote control. In more rudimentary devices, the detonator is absent and it is replaced by a wire dipped in the primary charge and short-circuited by a remote switch operated by the bomber. The outer

container is generally metallic, of varying shape, but other materials have been also adopted for mimetic purposes. An example of an actual IED containing powdered AN with Al is reported in Fig.1.

IEDs may be used to cause direct injuries to humans or to damage chemical plants and containers of toxic or pressurized gaseous hydrocarbons, leading to dramatic scenarios with fireballs and BLEVE with even catastrophic consequences (Milazzo et al., 2009). In case of continuous or nearly-instantaneous release of toxic chemicals in the environment as an effect of damages produced by IEDs, the relevant consequence area may be estimated by semiempirical expressions (Vianello et al., 2016). Indeed, a thorough identification and evaluation of physical attack scenarios still require theoretical detailed procedures and research efforts, extending the well known QRA methodologies derived from process plants, e.g. CCPS (Center for Chemical Process Safety, 2003). A basic reference point in terms of ammunition management is the International Ammunition Technical Guideline (IATG 01.80, 2016), providing effect and damage prediction relations. Vehicle-borne improvised explosive devices (VBIED) are another cause of dramatic fatality scenarios. A risk assessment method for explosive blasts related to VBIEDs has been recently proposed by Marks et al. (2021), who combined a blast CFD software with a Monte Carlo technique in order to account for charge mass, location and other parameters subject to uncertainties in an urban environment.



Figure 1: Panel (a): image of an IED, made of a metallic box containing a mixture of NH_4NO_3 and powdered Al, equipped with a homemade detonator, found in Liguria (Italy) and defused by one of the authors (F.C.). Panel (b): image of the same author dressing a safety equipment, during an inspection of a suspicious baggage.

4. Conclusions

A short survey on IEDs has been proposed. Some technical aspects pertaining to chemical composition and manufacture of these devices have been analyzed on the basis of the direct field experience of one of the authors. A future development of this work will be focused on explosion and effect modelling of different actual IEDs, in order to better assess the likely physical damage scenarios for chemical and process Seveso plants and better integrate safety and security practices minimizing the risk of injuries to humans and damages to industrial sites.

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