A review on gas-generants for application in exploding fire extinguisher balls

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Abstract. Fire is a highly exothermic reaction caused due to the rapid oxidation of a flammable substance. The mechanism of fire can be explained well with the help of a Fire Triangle comprised of the Source, Heat and Oxygen. Fire is complete and active only when all these three components are present simultaneously. There are numerous methods employed to extinguish fire, by depriving the fire of one or more of the components of the fire triangle. Recent technologies have emerged which makes use of a solid chemical mixture, placed inside a shell, which explodes when the chemical decomposes on being thrown into a fire and floods the fire surface with an inert gas which is a product of the decomposition. The chemical decomposes by absorbing heat from fire. Nitrogen or other non-toxic gases get released and puts out the fire by rapidly expanding and forming a blanket around the source of fire replacing Oxygen. The light weight, portability, easy and quick deployment and the release of non-toxic by-product are the advantages of the Fire Extinguishing Shells over the conventional ones. This paper presents a review of various chemicals that can be used can potentially be used in such fire extinguishing shells.

1. Introduction

Fire outbreak was ranked the third biggest risk to life and property by The India Risk Survey 2018 [1]. As per the latest Accident Deaths & Suicides in India (ADSI) report, a total of 11,037 cases of fire accidents were reported in the country resulting in 10,915 deaths during 2019 [2]. The cause-wise analysis of the incidents reveals that 58.0% of total deaths were reported in residential/dwelling buildings during 2019 which suggests that the failure/ignorance in deployment of the firefighting facilities right at the initial detection of outbreak must have led the fire to spiral out of control. The time delay between the detection of a fire breakout and its extinguishing is the most crucial parameter that decides the extent of damage caused. A fire can be neutralized with minimum resources if deployed in the initial stages. Conventional fire extinguisher requires training for deployment and may fail when handled by a panicked user. This calls for a technology that can be used by anyone irrespective of age and expertise, on detection of an undesirable fire, which can extinguish it or at least hold it under control till professional help arrives.

Collapsible fire extinguishing shells has recently surfaced in the market which uses a technology similar to that employed in safety airbags in automotive [3].

These shells, typically spherical in shape, encloses a mixture of chemical compound which picks up a thermal trigger and decomposes to form, among other by-products, high volumes of non-
inflammable gases that floods the surface of ignition, thereby cutting out oxygen supply and extinguishing fire momentarily.

2. **Comparison of potential gas generants for fire extinguishers**

2.1. Guanidine nitrate
Guanidine nitrate \((\text{CH}_5\text{N}_3\cdot\text{HNO}_3)\) appears to be a white crystalline solid that has low melting point of 216°C. It is soluble in water and no reactivity towards air in its normal state. It can act as an oxidizer (category 3) if it comes in contact with fire and may intensify fire. This substance contains no component considered to be persistent, bio-accumulative and toxic. It is harmful if swallowed. It can irritate our eyes moderately, skin severely and respiratory system if inhaled. It is carcinogenic to humans [3].

Large gas production and lower decomposition temperature is the reason for consideration of guanidine nitrate. Guanidinium nitrate (GN) being an energetic material shows the thermal decomposition behaviour in three possible routes: deprotonation, proceeding by dehydration and then resulting in an intermediate, ammonium nitrate. Studies have shown that GN undergoes thermal decomposition similar to that of a nitroguanidine (NQ), a dehydration product of GN. NQ was found to be relatively stable below its melting point of approximately 230°C, above which it decomposed to form solid products evolving ammonia and water vapour. The major intermediates identified during the decomposition of NQ were nitrous oxide, cyanamide, melamine, cyanic acid, cyanuric acid, ammeline and ammelide. These compounds, on further decomposition, yielded carbon dioxide, urea, nitrogen, hydrogen cyanide, cyanogen and other compounds about which no complete information is available, such as melem and melon probably containing condensed triazine rings. Most of the products reported during NQ decomposition have been observed for GN decomposition as well, indicating that NQ could be an intermediate during GN decomposition [14].

2.2. Aminotetrazole \((\text{CH}_3\text{N}_5)\)
5-Aminotetrazole is a white powder with a melting point of 205°C and is stable under normal temperature and pressure [6]. Tetrazoles have the highest potential in generating gases compared to other gas generants [6]. However, tetrazoles heretofore known and used produce unacceptably high levels of toxic substances upon combustion. The most difficult toxic gases to control are the various oxides of nitrogen (NOx) and carbon monoxide (CO). Reducing their levels is proven to be difficult. By altering the oxidizer/ fuel ratio, the NOx or CO levels can be reduced. Common combustion products to be expected from the tetrazoles are liquids and thus are difficult to filter out from the gas stream [7].

The fuel utilized in the non-azide gas generant is preferably selected from compounds that have high nitrogen content and regulate the carbon and hydrogen content thereof to moderate values. Tetrazoles compounds such as amino-tetrazole, tetrazole, 5-nitrotetrazole, 5-nitroaminotetrazole, bis-tetrazole, as well as triazole compounds such as 1,2,4-triazole-5-one or 3-nitro-1,2,4-triazole-5-one and metal salts of these tetrazoles and triazoles are those of interest as a gas generant. 5-aminotetrazole is generally used as the rocket fuel because of its cost, availability and safety [7]. 5-Aminotetrazole is promising energetic material with a high nitrogen content of about 82.3% and used in various gas generators. A mechanism of the thermal decomposition of 5-AT involving tautomeric forms of 5-AT, yields gaseous \((\text{HN}_3, \text{N}_2, \text{NH}_2\text{CN}, \text{NH}_3, \text{HCN})\) and condensed melamine and its forms. Formation of \(\text{HN}_3\) is due to the fragmentation of both the imino isomer (Fig 1 reaction (I)) and amino isomer (Fig 1 reactions (II) and (III)) of the 5-AT molecule. The decomposition of 5-AT yielding \(\text{N}_2\) is possible only for the amino tautomeric forms of 5-AT molecules (Fig 1 reaction (IV) for the 1-H isomer of the amino form) [7].
Seven products resulting from the thermal decomposition of 5-AT were identified: HN₃, N₂, NH₂CN, HCN, NH₃, melamine, and 5-AT vapor. Decomposition temperature was observed to be around 200°C. The table 1 shows the product mole fractions obtained at increasing temperature [7].

Table 1. Composition of the products (in mole fractions) of 5-AT thermal decomposition at the moment of maximum intensity of the nitrogen peak m/e = 28 at different initial temperatures. [7]

| T₀, °C | HN₃ | N₂  | NH₂CN | HCN  | NH₃ | 5-AT vapor |
|-------|-----|-----|-------|------|-----|------------|
| 195   | 0.49| 0.20| 0.05  | 0.09 | 0.08| 0.09       |
| 200   | 0.50| 0.29| 0.04  | 0.06 | 0.04| 0.07       |
| 155   | 0.48| 0.27| 0.12  | 0.04 | 0.06| 0.01       |
| 150   | 0.47| 0.28| 0.05  | 0.08 | 0.08| 0.04       |
| 160   | 0.50| 0.24| 0.08  | 0.07 | 0.07| 0.04       |
|       |     |     |       |      |     | Average Value 0.48±0.02 0.25±0.05 0.07±0.05 0.07±0.03 0.06±0.03 0.05±0.04 |

2.3. Azodicarbonamide (C₂H₄N₄O₂)
Azodicarbonamide is a yellow crystalline solid, soluble in water and insoluble in inorganic solvents and is characterized by a melting point of 225°C. It is highly explosive when it forms a dust cloud with air [8]. Characterized with low burning temperature and low concentration of toxic gases, the azodicarbonamide, basic cupric nitrate and 10% metal oxide (CuO, ZnO, MnO₂ or Fe₂O₃) gas-generating mixture is studied. Azodicarbonamide (ADC), which contains a –N=N– group in the molecule structure, has high nitrogen content (48.28 mass%) and gas production (220 mL g⁻¹). It is non-toxic and inexpensive. As such, azodicarbonamide (ADC) has the potential to be used as the gas-generating agents. Herein, the basic cupric nitrate (BCN) is introduced as an oxide in the gas-generating agents due to its high oxygen content (30%) and can reduce the combustion heat of gas-generating agents. In order to decrease the toxic gas content, the transition metal oxides are also introduced [9].
When thermal analysis of the pure ADC, ADC/BCN mixture and pure BCN at 10 K min\(^{-1}\) heating rates was studied, Pure ADC had three peaks corresponding to the three loss steps in its TG curve. The first stage is between 200 and 225\(^\circ\)C, and the second stage is happened from 225 to 245\(^\circ\)C, while the third stage ranges from 245\(^\circ\)C to about 285\(^\circ\)C. In the first stage, the \(\text{N}_2\) and amide group (–CONH\(_2\)) were produced by the homolysis of C–N bond, and the interaction of amide groups generated carbon monoxide and urea. Then the thermal decomposition of urea produced the isocyanic acid and \(\text{NH}_3\). Finally, the third stage was the cyclization reaction of bi-urea, which is generated by the breakage of N=N bond. There is a sharp endothermic peak from 190 to 264\(^\circ\)C in the DSC curve of BCN, with a mass loss of about 31% in the TG curve [9].

2.4. Sodium azide – potassium nitrate mixture (\(\text{NaN}_3/\text{KNO}_3\))

Sodium Azide has a melting point of 275\(^\circ\)C and that of potassium nitrate is 334\(^\circ\)C. It undergoes a violent decomposition around 300\(^\circ\)C and release nitrogen gas. It can be used in powdered as well as tablet forms. It is clear from the Figure 3 and 4 that its decomposition is different in various forms and environments showing different exothermic peaks for nitrogen and oxygen atmospheres [11].

In its tablet form sodium azide shows an intense exothermic reaction around 400\(^\circ\)C; the heat released by the small exothermic reactions accumulated and altogether causes a rapid reaction.

![Figure 2](image2.png)

**Figure 2.** TG-DSC curves of samples ADC/BCN. [9]

![Figure 3](image3.png)

**Figure 3.** DTA and TG curves of sodium azide in powder and tablet forms in air: (1) powder; (2) tablet [11]
resulting in a 5% weight loss. In powdered form it has more active area for reaction or heat transfer, it started decomposition by smaller exotherms at 400°C and reached a peak at 450°C. It causes a 60% weight loss of reaction mixture. Sodium azide shows high exothermic peak at elevated pressure, this is caused by the increased catalysis by sodium metal which was accumulated there due to higher pressures [11]. In nitrogen atmosphere, the sodium azide potassium nitrate on thermal analysis give traces of reaction around 130°C, as the orthorhombic structure of potassium nitrate was changing to trigonal structure around this temperature. Nitrogen atoms from azides and nitrates of potassium nitrate were interacting at around 220°C and causes the succeeding thermal event. The thermal analysis has two peaks, first corresponding to the decomposition of azide into nitrogen and sodium metal, in the range 330-400°C; the second broad peak in the range 620 -760°C indicates the reaction between sodium metal and oxygen from nitrates. In oxygen atmosphere (Figure 4), there was only one peak as the oxygen helps to oxidize it easily [12].

| Table 2. Comparison between the gas generators studied |
|-----------------------------------------------------|
| Sodium azide/ KNO₃ | Guanidine nitrate | Tetrazole | Azodicarbonamide |
| Toxicity | high | High | Very high | High |
| Comment | - | Oxidiser | Explosive | - |
| Decomposition temperature | 300-400°C | Around 200°C | Around 600°C using | Around 200°C |
| Heat of reaction | Exothermic | Less exothermic with suitable oxidiser | Endothermic | Less Exothermic using metal oxides |
| Gases evolved | N₂ (major gas), NOₓ (trace amt.) | NH₂, N₂O and NH₄(major), N₂, CO, CO₂, O₂ | N₂ (major), HCN, NH₂CN, and 5-AT vapour | N₂, NOₓ, CO (toxic gases are in large amount) |
| Gas: material ratio | 65 wt% of the NaN₃ is nitrogen | 49 wt% of the GN is nitrogen | 82.3 wt% of 5-AT is nitrogen | 48.28 wt% of it is nitrogen |
| Economics | ₹4.53/g | ₹0.75/g | ₹1800/g | ₹5.25/g |
3. Working of suggested gas generant filled fire extinguisher using sodium azide potassium nitrate mixture

Inside the airbag is a gas generator containing a mixture of NaN$_3$, KNO$_3$, and SiO$_2$. When the car undergoes a head-on collision, a series of three chemical reactions occur inside the gas generator. These reactions produce gas (N$_2$) to fill the airbag and convert NaN$_3$, a highly toxic substance, to harmless sodium and potassium silicate, a major ingredient of glass. Sodium azide (NaN$_3$) can decompose at 300°C to produce sodium metal (Na) and nitrogen gas. The signal from the deceleration sensor ignites the gas-generator mixture by an electrical impulse, creating the high-temperature condition necessary for NaN$_3$ to decompose. The nitrogen gas that is generated then fills the airbag. The purpose of the KNO$_3$ and SiO$_2$ is to remove the sodium metal (which is highly reactive and potentially explosive) by converting it to a harmless material like silicates [13]. The same concept can be implemented for a fire extinguisher, in which the mixture will be kept in a vessel and when thrown into the fire, heat transfer from the fire to the mixture can initiates the decomposition of the mixture and the follow up reactions, thereby producing large amount of N$_2$ gas in the vessel. This can result in a pressure built-up inside the vessel which in turn results in the collapse of the vessel, thereby releasing the large amount of N$_2$ gas with an increased velocity due to the sudden expansion, which can push away the O$_2$ gas near the fire and then results in flooding of the fire area. After the sodium azide decomposition, the sodium formed reacts with potassium nitrate to produce potassium oxide, sodium oxide (Na$_2$O), and additional N$_2$ gas. The N$_2$ generated in this second reaction also fills the vessel, and the metal oxides react with silicon dioxide (SiO$_2$) in a final reaction to produce silicate, which is harmless and stable [13]. These reactions are so fast that it completes the reaction in about 50 milliseconds. Since there are no side reactions in this, the expected gas product is merely N$_2$ gas.

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\begin{align*}
2\text{NaN}_3(s) & \rightarrow 2\text{Na}(l) + 3\text{N}_2(g) \\
2\text{KNO}_3(s) + 10\text{Na}(l) & \rightarrow 5\text{Na}_2\text{O}(s) + \text{K}_2\text{O}(s) + \text{N}_2(g) \\
\text{Na}_2\text{O}(s) + \text{K}_2\text{O}(s) + \text{SiO}_2(s) & \rightarrow \text{Na}_2\text{K}_2\text{SiO}_4(s)
\end{align*}
\]

4. Conclusion

In this review, we have studied some chemicals that may find application in fire extinguishers as gas generators. Guanidine nitrate, though the cheapest, releases moderate volumes of gas (N$_2$) while showing a tendency to oxidize itself and poses a threat of explosion. In terms of gas release on decomposition, 5-amino tetrazole offers a higher volume of inert gas while its high cost is prohibitive. Azodicarbonamide due to the emission of higher proportions of NO$_x$ and CO$_2$ compared to N$_2$ poses questions over the inertness of the gas released. As we have seen, Sodium azide –potassium nitrate mixture generates decent amounts of Nitrogen gas also has the advantage of low cost, coupled
with non-toxic gas emission. It can be concluded that sodium nitrate will effectively serve the desired purpose of the fire extinguishing shell as an easily affordable first level defence against domestic fire outbreaks.

The optimum dimensions and the material of construction of the fire extinguishing shells as well as the optimum quantity of the gas generant chemical to be filled has to be established through further research. An effective design of the shell ensures quick transfer heat from the fire to the chemical mixture initiating the decomposition reaction without any delay.

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