1
Introduction to Pyrolants

Energetic materials are characterised by their ability to undergo spontaneous ($\Delta G < 0$) and highly exothermic reactions ($\Delta H < 0$). In addition, the specific amount of energy released by an energetic material is always sufficient to facilitate excitation of electronic transitions, thus causing known luminous effects such as glow, spark and flame. Energetic materials are typically classified according to their effects. Thus, they can be classified into high explosives, propellants and pyrolants (Figure 1.1). Typical energetic materials and some of the salient properties are listed in Table 1.1.

When initiated, high explosives undergo a detonation. That is a supersonic shockwave supported by exothermic chemical reactions [1–3]. In contrast, propellants and pyrolants undergo subsonic reactions and mainly yield gaseous products as in the case of propellants [4, 5] or predominantly condensed reaction products as in the case of pyrolants. The term *pyrolant* was originally coined by Kuwahara to emphasise on the difference between these materials and propellants [6]. Thus, the term aims at defining those energetic materials that upon combustion yield both hot flames and large amount of condensed products. Hence, pyrolants often find use where radiative and conductive heat transfer is necessary. Pyrolants also prominently differ from other energetic materials in that they have both very high gravimetric and volumetric enthalpy of combustion and very often densities far beyond 2.0 g cm^{-3} (see Table 1.1 for examples).

Pyrolants are typically constituted from metallic or non-metallic fuels (e.g. Al, Mg, Ti, B, Si, $C_{(gr)}$ and S_8) and inorganic (e.g. Fe_2O_3, $NaNO_3$, $KClO_4$ and $BaCrO_4$) and/or organic (e.g. C_2Cl_6 and $(C_2F_4)_n$) oxidizers or alloying partners (e.g. Ni and Pd). In contrast to propellants, they are mainly fuel rich and their combustion is influenced by afterburn reactions with atmospheric oxygen or other ambient species such as nitrogen or water vapour.

Pyrolants serve a surprisingly broad spectrum of applications such as payloads for mine-clearing torches ($Al/Ba(NO_3)_2/PVC$) [7, 8], delays ($Ti/KClO_4/BaCrO_4$) [9], heating charges ($Fe/KClO_4$) [10, 11], igniters (B/KNO_3) [12, 13], illuminants ($Mg/NaNO_3$) [14, 15], thermites (Al/Fe_2O_3) [16, 17], obscurants ($RP/Zr/KNO_3$) (RP, red phosphorus) [18], ($Al/ZnO/C_2Cl_6$) [20], tracers ($MgH_2/SrO_2/PVC$) [21], initiators (Ni/Al) [22] and many more. Recently, pyrolant combustion is increasingly used for the synthesis of new materials.

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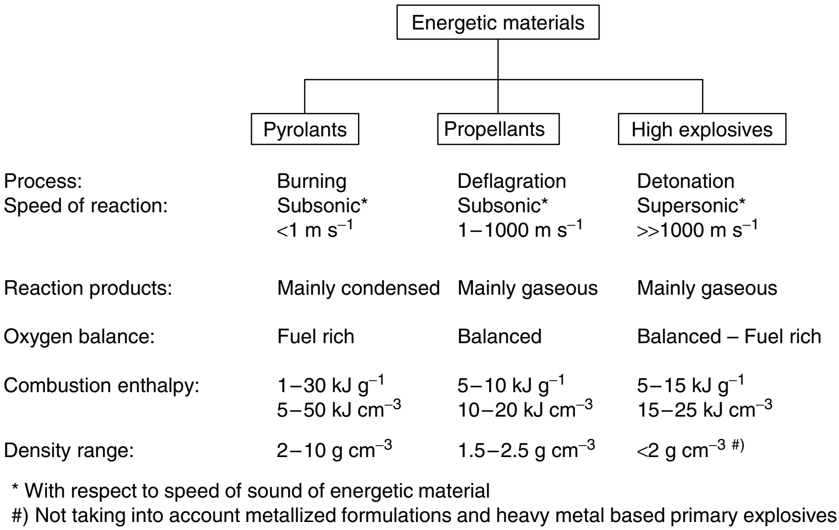

Figure 1.1 Classification of energetic materials.

Table 1.1 Performance parameters of selected energetic materials.

Class of energetic materials	Material, formula, weight ratio	ρ^a(g cm^{-3})	$\Delta_c H^c$ (kJ g^{-1})	$\Delta_c H^a$(kJ cm^{-3})	T_{ig}(°C)
High explosive	HMX, $C_4H_8N_8O_8$	1.906	9.459	18.028	287
	TNT, $C_7H_5N_3O_6$	1.654	14.979	24.775	300
	PETN, $C_5H_8N_4O_{12}$	1.778	8.136	14.465	148
	Nitroglycerine, $C_3H_5N_3O_9$	1.593	6.717	10.699	180
	Nitrocellulose[b], $C_6H_7N_3O_{11}$	1.660	9.118	15.135	200
Pyrolant	KNO_3/S_8/charcoal (75/10/15)	1.940	3.790	7.353	260–320
	Al/$KClO_4$(34/66)	2.579	9.780	25.223	446
	Fe/$KClO_4$ (20/80)	2.916	1.498	4.360	440–470
	Mg/PTFE/Viton (60/30/10)	1.889	22.560	42.616	540
	Zn/C_2Cl_6(45/55)	3.065	4.220	12.934	420
	Ta/THV-500[d] (74/26)	5.802	6.338	36.773	310

[a] At TMD = Theoretical Maximum Density.
[b] 14.4 wt% N.
[c] With liquid H_2O.
[d] THV-500 is copolymer of tetrafluoroethylene (TFE), Hexafluoropropene (HFP) and Vinylidene difluoride (VF_2) ratio: 60/20/20, $C_{2.223}H_{0.624}F_{3.822}$, $\rho = 2.03$ g cm^{-3}. PTFE, polytetrafluoroethylene.

An important group of pyrolants are those constituted from metal powder and halocarbon compounds [19]. The high energy density of metal–halocarbon pyrolants stems from the high enthalpy of formation of the corresponding metal–halogen bond (M–X). Thus, chlorocarbon but mainly fluorocarbon compounds are used as oxidizers.

On the basis of metal fluorocarbon combinations, pyrolants show superior exothermicity compared to many of the aforementioned fluorine-free systems [22]. This advantage is due to the high enthalpy of formation of the metal–fluorine bond not outperformed by any other combination of the respective metal. Thus, the exothermic step

$$M^w + wF \longrightarrow MF_w$$

is the driving force behind the reaction (w = maximum valence).

Owing to a great number of metallic elemental fluorophiles (~70), metal fluorocarbon pyrolants (MFPs) offer a great variability in performance. In addition, many alloys and binary compositions of fluorophiles may also come into play to further tailor the performance of the pyrolant: Mg_4Al_3, MgH_2, MgB_2, Mg_3N_2, $Mg(N_3)_2$, Mg_2Si and so on [23]. Very often MFPs find use in volume-restricted applications where other materials would not satisfy the requirements – see, for example, payloads for infrared decoy flares (see Chapter 10). Within the scope of this book, the following applications are discussed:

- agent defeat payloads
- countermeasure flares
- cutting torches
- heating devices
- igniters
- incendiaries
- material synthesis
- obscurants
- propellants
- reactive fragments
- stored chemical energy propulsion systems
- tracers
- tracking flares
- underwater flares.

This book focuses only on specialised pyrotechnic applications; thus, for a more generalised introduction to pyrotechnics, the interested reader is referred to the books by Shidlovski [24], Ellern [25], McLain [26], Conkling [27, 28], Hardt [29] and Kosanke *et al.* [30].

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