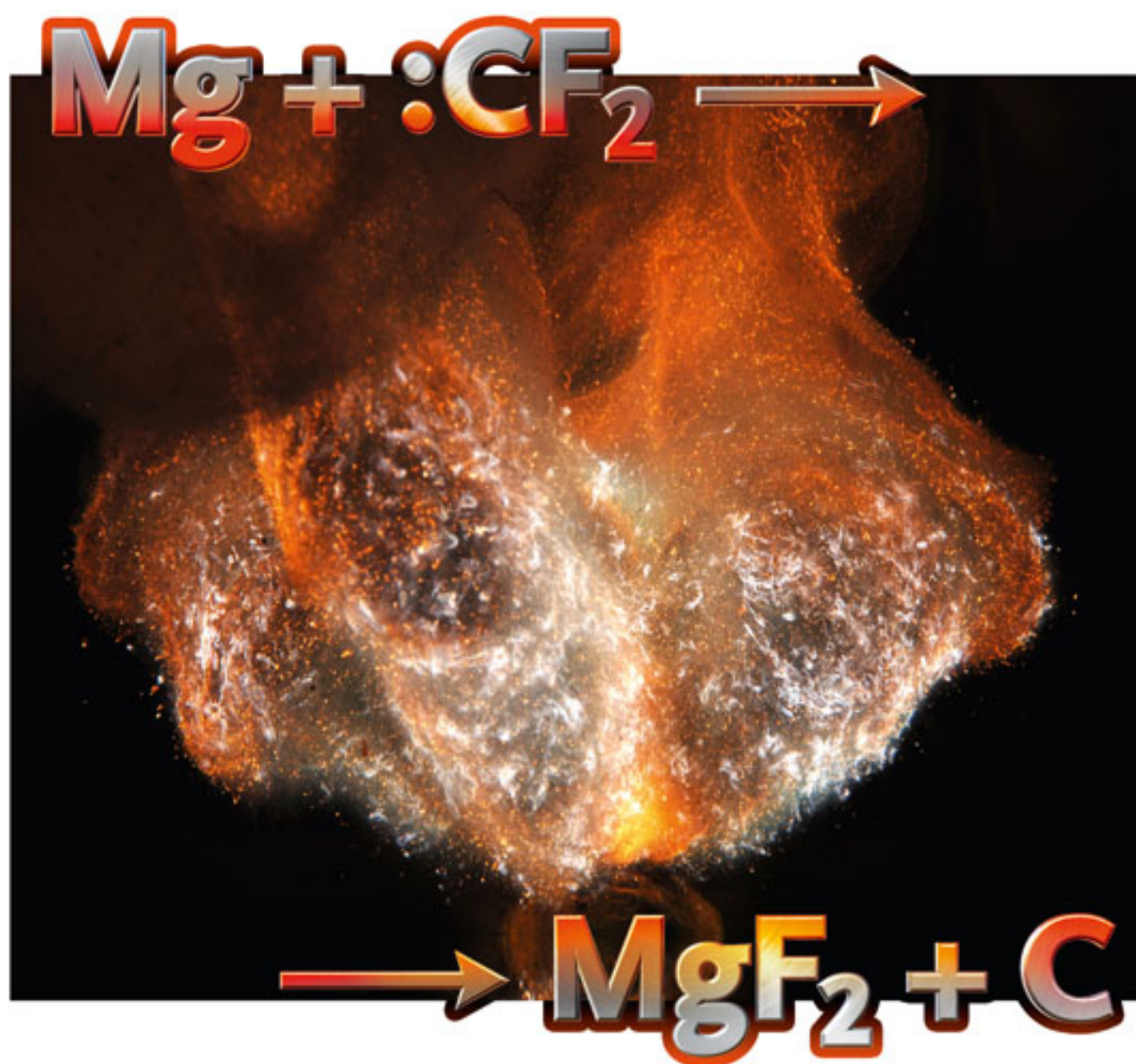


Metal-Fluorocarbon Based Energetic Materials



Ernst-Christian Koch

**Metal-Fluorocarbon Based
Energetic Materials**

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The Author

Dr. Ernst-Christian Koch

NATO Munitions Safety
Information Analysis Center (MSIAC)
Boulevard Leopold III
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Belgium

Cover

The cover picture depicts the combustion flame of Magnesium/Teflon TM/HycarTM strand (photographed by Andrzej Koleczko, Fraunhofer ICT, Germany) superimposed on the assumed main combustion step between difluorocarbene and magnesium.

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Dedicated to my family

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Foreword

We have known Dr Ernst-Christian Koch since meeting him during one of the International Pyrotechnics Seminar back in the 1990s. Even back then, we knew that he was more than just a research scientist interested in pyrolants and energetics. Dr Koch demonstrated a passion for pyrolants beyond that of a hobbyist or an employee. His enthusiasm is clearly demonstrated by the impressive number of his patents and publications. Therefore, it comes as no surprise that Dr Koch has channelled his drive for the dissemination of knowledge about pyrolants, and more specifically magnesium-Teflon-Viton (MTV) compositions into a clearly written book. Often, we will receive an email from Dr Koch that directs us to information about a new patent or publication about MTV. His ability to take a small amount of information and extrapolate beyond it is just one facet of his talent as a scientist. It is a pleasure to finally read a book that encompasses some (obviously, not all) of his knowledge in the field of pyrolants.

This book is unique in that its scope is limited to data about the MTV reaction, application of the reactions related to MTV, and metal–halogen reactions that might be substituted for the MTV reaction. The book provides the reader a single source for research results and data on all compositions related to MTV and the application thereof. The breadth of references, figures and tables demonstrate the vast and careful research Dr Koch undertook.

This book fills a void in the collection of pyrotechnic literature because it deals exclusively with research related to MTV-like compositions. Chapter 9 includes pictures that enable the reader to actually envision the combustion reaction of the different metal/fluoride reactions. Chapter 10 and 10.5 Operational Effects chapters are limited, only because of the availability and security constraints beyond the author's control. Chapters delving into previously unconsidered regions and Chapters 11 and 13 are of notable interest in the context of cyberwar and intellectual property disputes. Chapters 18 and 19 are a great compilation of the past and current practices. The history of the incidents involved with MTV manufacturing and the way processing has evolved to help mitigate explosive incidents is presented in a straightforward manner. Chapter 15 exemplifies Dr Koch's ability to look ahead. His citations in this chapter are abundant for a very limited field of research. Once again, the author illustrates his ability to take new information/ideas and to compile them in a useful and informative way.

No other known book documents MTV-like compositions in this depth. This book can be considered to be a textbook of everything associated with the MTV composition and, because of the extraordinary amount of documentation of data about MTV-like compositions, it will make an excellent reference book that all researchers of pyrolants and energetics must have.

*Dr Bernard Douda and Dr Sara Pliskin
Naval Surface Warfare Center,
Crane, Indiana, USA*

Preface

Metal/Fluorocarbon pyrolants, similar to black powder, are very versatile energetic materials with a great many number of applications. Over the last 50 years metal/fluorocarbon-based energetic materials have developed from secret laboratory curiosities into well-acknowledged standard payload materials for high-performance ordnance such as countermeasure flares and both strategic and tactical missile igniters. However, the long-lasting obligation to maintain secrecy over many of these compositions in most countries affected their further development and impeded personnel involved in becoming acquainted with the particular safety and sensitivity characteristics of these materials.

When I first dealt with Magnesium/TeflonTM/VitonTM (MTV) in the mid 1990s I became fascinated by these materials. However, trying to learn more about them was difficult because of the above mentioned classification issues. Thus my research aimed at exploring some of the fundamentals of MTV to have good basis to start further development on. Fortunately, in the meantime the Freedom of Information Act both in the United States and United Kingdom brought significant relief to this and has enabled access to formerly classified files. Still the information is not readily retrievable as the actual content of these files is not well documented. Thus, in order to establish a reference base for MTV, I have gathered documents from the public domain over the last 15 years. The present book now is the result of an attempt to present the most relevant information in a reasonable manner.

Even though carefully compiled, I preemptively apologize for any kind of technical errors and omissions which I am afraid cannot be completely avoided. However, I would be glad to receive your critical comments in order to improve future editions of this book.

I hope you enjoy reading the book as much as I enjoyed writing it.

Brussels and Kaiserslautern, October 2011

Ernst-Christian Koch

Acknowledgment

A book like this is never the achievement of a single individual. Thus I wish to express my sincere appreciation for the support I received during my research on metal fluorocarbon based energetic materials and while writing this monograph.

The late Dr. rer. nat. Peter Kalisch (†2010), retired technology and scientific director of the Diehl Stiftung/Nuremberg I gratefully acknowledge for his enduring, constructive and friendly support, and facilitating financial support for research on both combustion synthesis and obscurant properties of magnesium/graphite fluoride pyrolants.

I wish to thank the following individuals (in no certain order) for their advice both oral and written and/or their experimental support on this fascinating topic which has helped me in writing this book.

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Finally I wish to thank Dr. Bernard E. Douda for inviting me to become actively involved with the International Pyrotechnics Society. I thank him for his help and the friendly support he provided in response to the many questions I addressed to him over the years. I greatly appreciate his reviewing of parts of this book and his efforts to write a preface together with Dr. Sara Pliskin. It is his report on the “Genesis of IRCM” that has definitely triggered me to write this book.

Thank you Bernie!

Brussels and Kaiserslautern, October 2011

Ernst-Christian Koch

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, $\text{C}_{(\text{gr})}$ 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 $(\text{C}_2\text{F}_4)_n$) 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 ($\text{Al/Ba(NO}_3)_2/\text{PVC}$) [7, 8], delays ($\text{Ti/KClO}_4/\text{BaCrO}_4$) [9], heating charges (Fe/KClO_4) [10, 11], igniters (B/KNO_3) [12, 13], illuminants (Mg/NaNO_3) [14, 15], thermites ($\text{Al/Fe}_2\text{O}_3$) [16, 17], obscurants (RP/Zr/KNO_3) (RP, red phosphorus) [18], ($\text{Al/ZnO/C}_2\text{Cl}_6$) [20], tracers ($\text{MgH}_2/\text{SrO}_2/\text{PVC}$) [21], initiators (Ni/Al) [22] and many more. Recently, pyrolant combustion is increasingly used for the synthesis of new materials.

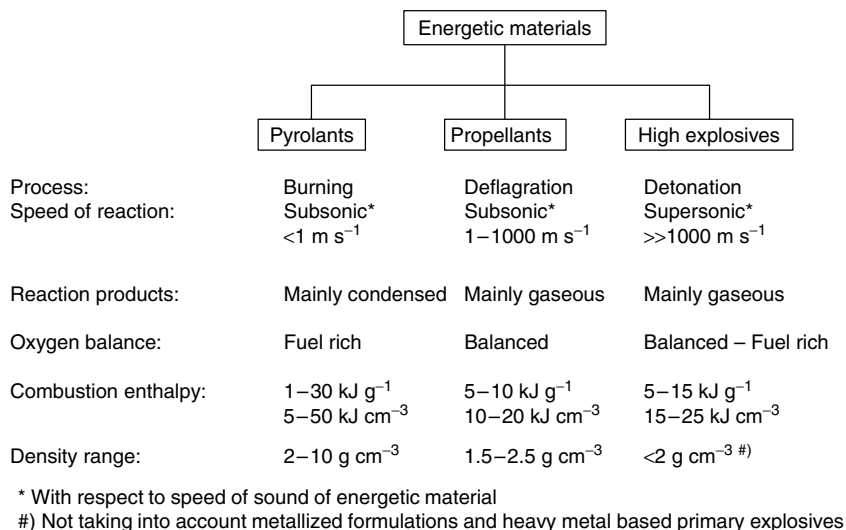


Figure 1.1 Classification of energetic materials.

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 ₄ H ₈ N ₈ O ₈	1.906	9.459	18.028	287
	TNT, C ₇ H ₅ N ₃ O ₆	1.654	14.979	24.775	300
	PETN, C ₅ H ₈ N ₄ O ₁₂	1.778	8.136	14.465	148
	Nitroglycerine, C ₃ H ₅ N ₃ O ₉	1.593	6.717	10.699	180
	Nitrocellulose ^b , C ₆ H ₇ N ₃ O 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 ₂ Cl ₆ (45/55)	3.065	4.220	12.934	420
	Ta/THV-500 ^d (74/26)	5.802	6.338	36.773	310

^aAt TMD = Theoretical Maximum Density.

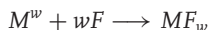
^b14.4 wt% N.

^cWith liquid H₂O.

^dTHV-500 is copolymer of tetrafluoroethylene (TFE), Hexafluoropropene (HFP) and Vinylidene difluoride (VF₂) 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



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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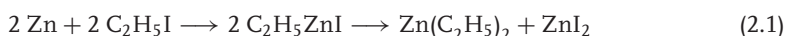
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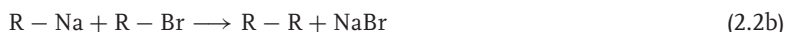
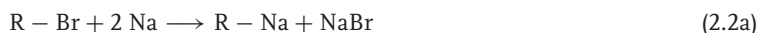
2 History

2.1 Organometallic Beginning

Although the unambiguous discovery of metal–fluorocarbon-based energetic materials did not occur until the mid-twentieth century, the way to these materials began nearly 100 years earlier. To begin with, in 1849, the British chemist Edward Frankland (1825–1899) (Figure 2.1), who was working with Robert Bunsen in Marburg/Germany, made attempts to isolate the ethyl radical, $\cdot\text{C}_2\text{H}_5$. Therefore, he treated iodoethane, $\text{C}_2\text{H}_5\text{I}$, with a surplus of zinc powder [2]. However, he did not get the radical but obtained a mixture of zinc(II) iodide and diethylzinc(0), $\text{Zn}(\text{C}_2\text{H}_5)_2$ (Eq. 2.1). This was the first ever reported reaction of an electropositive metal with a halocarbon compound:



In 1855, the Alsatian chemist Charles Adolphe Wurtz (1817–1884) observed the high reactivity of alkali metals with aliphatic halides (Eqs. 2.2a,b) and developed a C–C-coupling method that was later named after him [3]:



Wilhelm Hallwachs (not to be taken for the German physicist Wilhelm Hallwachs (1859–1920)) and Adalbert Schafarik in 1859 reported that magnesium undergoes fierce reaction with iodoethane to yield magnesium(II) iodide and a product of the unknown constitution, which was probably diethylmagnesium(0) (Eq. 2.3):



In the same paper, they also reported about the reaction of aluminium with iodoethane, yielding what they believed was “ethylaluminium Spontaneous combustion of this material in air yields brown-violet smoke, indicating the presence of iodine. Today, it is known that their reaction gave both diethylaluminium iodide and ethylaluminium diiodide [4] (Eq. 2.4):



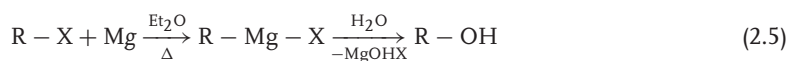


Figure 2.1 Edward Frankland [1].

Surprisingly, their report had no major impact on organomagnesium-chemistry and was not noticed in the scientific community until Barbier and Grignard's work (see below).

Although Antoine Lavoisier (1743–1794) had assumed the existence of a new element in hydrofluoric acid, it was not until 1886 when Henri Moissan (1852–1907) succeeded in synthesizing elemental fluorine. He electrolysed potassium fluoride dissolved in liquid hydrofluoric acid at -55°C in a platinum apparatus [5], and he was awarded the Nobel Prize for the same in 1906. As Moissan used graphite electrodes, the nascent fluorine reacted with carbon and produced a blend of perfluorocarbon compounds mainly containing tetrafluoromethane, CF_4 . Moissan noted that what he assumed to be pure CF_4 would fiercely react with sodium to give carbon and sodium fluoride [6].

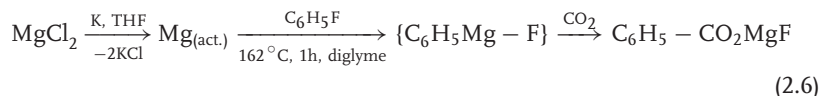
In 1898, Philippe Barbier (1848–1922) modified Saytzeff's alcohol synthesis by replacing zinc with the more reactive magnesium [7] (Eq. (2.5)). His student Victor Grignard (1871–1935) further developed this substitution [8] and was awarded the Nobel Prize for the same in 1912:



where $\text{X} = \text{I}, \text{Br} (\text{Cl})$.

After nearly 70 years, in 1972 Reuben Rieke showed that even kinetically inert alkyl fluorides reacts with activated magnesium – the latter is prepared by *in situ*

reduction of MgCl_2 with potassium sand [9] (Eq. (2.6)):



2.2

Explosive & Obscurant Properties

In 1907, Camille Matignon (1867–1934) who was exploring ways to make aluminium carbide, Al_4C_3 (which then was sought as a source for technical methane production), observed a very exothermic reaction between chlorocarbons and aluminium. Heating a mixture of hexachlorobenzene with aluminium in a test tube lead to ignition at 225°C and subsequent vigorous combustion to give both aluminium carbide and clouds of aluminium chloride ($T_{\text{subl.}}: 128^\circ\text{C}$) [10]:



This is the first documented record of a combustion reaction between a metal and halocarbon compound.

In 1913, the German chemist Hermann Staudinger (1881–1965) tried to synthesize illusive ethylenedione ($\text{O}=\text{C}=\text{C}=\text{O}$). Therefore, he aimed at abstracting the halogen atoms (X) from either oxalyl chloride and -bromide, $(\text{COX})_2$ by a reaction with potassium or its sodium alloy (NaK). He observed that mixtures of the reactants after some initial delay at ambient temperature would become highly sensitive to impact and would fiercely detonate if struck. Thus, he speculated about the formation of an unknown highly reactive intermediate [11].

Ernest E. F. Berger (1876–1934) (Figure 2.2) was appointed as a staff chemist at the chemical laboratory of the French artillery to work on explosives in 1908 [12]. In 1916, he proposed to use mixtures from metals and chlorocarbons to generate smoke. Being aware of the underlying chemical concept, he investigated a great variety of chlorine sources including also inorganic chlorine sources such as chlorides of antimony, lead, and iron (Table 2.1). However, the most famous ones are based on tetrachloromethane and zinc, which are widely known as *Berger's mixture*.

The following is an example of mixture taken from [13].

Berger mixture

25 wt% Zinc
50 wt% Tetrachloromethane
20 wt% Zinc oxide
5 wt% Diatomaceous earth



Figure 2.2 Photograph of Captain Ernest Edouard Frédéric Berger (1897). (Reproduced with kind permission by Bibliothèque de l'Ecole Polytechnique Palaiseau.)

Table 2.1 Claimed components of Berger's smoke mixtures [15, 16].

Chlorine sources		Fuels	Auxiliary components	
Name	Formula		Name	Formula
Tetrachloromethane	CCl_4	Al	Sodium chlorate	NaClO_3
Hexachloroethane	C_2Cl_6	CaSi_2	Sodium nitrate	NaNO_3
Tetrachloroethane	$\text{C}_2\text{Cl}_4\text{H}_2$	Ca	Naphthalene	C_{10}H_8
Trichloroethylene	$\text{C}_2\text{Cl}_3\text{H}$	Fe	Zinc oxide	ZnO
Pentachlorobenzene	$\text{C}_6\text{Cl}_5\text{H}$	Mg	–	–
Hexachlorobenzene	C_6Cl_6	Mn	–	–
Lead(II) chloride	PbCl_2	Na	–	–
Iron(III) chloride	FeCl_3	$\text{P}_{(\text{red})}$	–	–
Antimony(III) chloride	SbCl_3	Zn	–	–

The French forces applied these obscurants in the First World War with both navy and army in the so-called smoke generators. Later in the war, the Berger mixture saw widespread application with all belligerent countries. Berger was honored with the “Grand Prix de la Marine” in 1918 for his contribution to French warfare [14]. After the war, Berger reported that he had been in contact with Victor Grignard by early 1916 on these mixtures. Grignard had also proposed to him to use hexachlorobenzene as an alternative source of chlorine. In the same report, Berger also refers to Matignon’s work [14]. Thus, it is very likely that he was inspired to apply these highly exothermic reactions in pyrotechnic obscurant formulations [15].

In 1919, the US First World War veteran Richard Clyde Gowdy (1886–1946), a citizen of Cincinnati, invented a signal smoke mixture based on magnesium, hexachloroethane, and anthracene [17]. Although Berger had already proposed to use magnesium as a fuel, it was noted by him that these mixtures would burn almost too vigorously. Gowdy, a mechanical engineer, modified Berger’s mixture in that he applied anthracene both to cool down the combustion temperature and to generate soot that would turn the generated smoke black. It can be assumed that Gowdy learned about the Berger mixture in his military deployment to Europe.

Further refinements and modifications of Berger’s smoke mixture were successively undertaken by Metivier (1926) [18, 19] and Brandt (1937) [20] both in France.

In 1922, Staudinger reported about explosive reactions of alkali and alkaline earth metals with partially and perhalogenated solvents such as CH_2Cl_2 and CCl_4 . He intuitively assumed the formation of a very instable species on contact that would be very sensitive to mechanical impact and thus trigger an explosive reaction. However, he was unable to identify the actual species [21] but proposed to exploit these fierce reactions in detonating charges for ammunition [22, 23]. Staudinger was a visionary and he even tried to apply the explosive reaction between sodium and tetrachloromethane to make diamond [24]. He thought that both the high temperature and pressure from the explosion would enable to force the formed carbon soot to undergo phase transition to diamond. Although he was not successful with his experiment, about 60 years later nanodiamonds were isolated from TNT/RDX detonation soot and proved Staudinger’s basic idea that a detonation would furnish the necessary physical conditions for the formation of diamond [25]. Still 10 years after that (in 1998), a Chinese group reported about the successful nanodiamond synthesis based on the original Staudinger set up with sodium and tetrachloromethane in an autoclave [26].

2.3

Rise of Fluorocarbons

In the course of the electrolytic preparation of beryllium from molten $\text{KHF}_2/\text{BeF}_2$, in 1926, Paul Lebeau (1858–1959) and his collaborator Damien were able to purify and isolate tetrafluoromethane, CF_4 , by fractional distillation with a liquid air-cooled condenser. They observed vigorous combustion reactions of CF_4 with both sodium and calcium [27].