Chapter 1
Introduction to Initiating Substances

Initiating substances (primaries) are chemical compounds/mixtures used in igniters or detonators to bring about burning or detonation of energetic material. The vocabulary regarding initiators is rather vast, often divided by the type of input and output of the element or its application. In general, igniters (containing a priming composition) are used to provide flame, while detonators (containing the primary explosive) are designed to create a shock wave which starts the detonation reaction in a secondary explosive. Combinations of both are seen, for example, in detonators in which the igniter is first initiated and the resulting flame starts the detonator [1].

The successful initiation of explosives begins with a small external stimulus called the simple initiating impulse (SII). The SII is a nonexplosive type of impulse such as flame, heat, impact, stab, friction, electric spark, etc. The choice depends on the type of material to be initiated and on the desired output effect. The energy provided by this impulse is sufficient enough to initiate the burning of a priming mixture—a sensitive mixture sometimes called prime (in pyrotechnics the term prime is used for the first layer enabling successful ignition). The energy from the combustion of the priming composition needs to be magnified or delayed by a sequence of elements, such as delay, transfer, and output charges. The entire sequence is called an explosive train and is simplified in Fig. 1.1.

The term primer in Fig. 1.1 represents the first element in the explosive train with flame as a desired output (e.g., percussion primer, pyrotechnic prime, electric fusehead, safety fuse, etc.). It needs to be stressed here that consistency in terminology does not exist regarding the term primer which is often used for primary explosives and boosters, but also for a charge consisting of detonating cord, detonator, and transfer charge made of secondary explosive, for detonator fused booster charges or more commonly for percussion-sensitive pyrotechnic mixtures loaded in small metal caps used in ammunition cartridges. Regarding Fig. 1.1, the primer is, as stated, the first element in the explosive train sensitive to the SII. All such elements contain a priming composition, which is typically a pyrotechnic mixture designed specifically for each particular application from a variety of substances (the topic is briefly described in later parts of this chapter). The transfer

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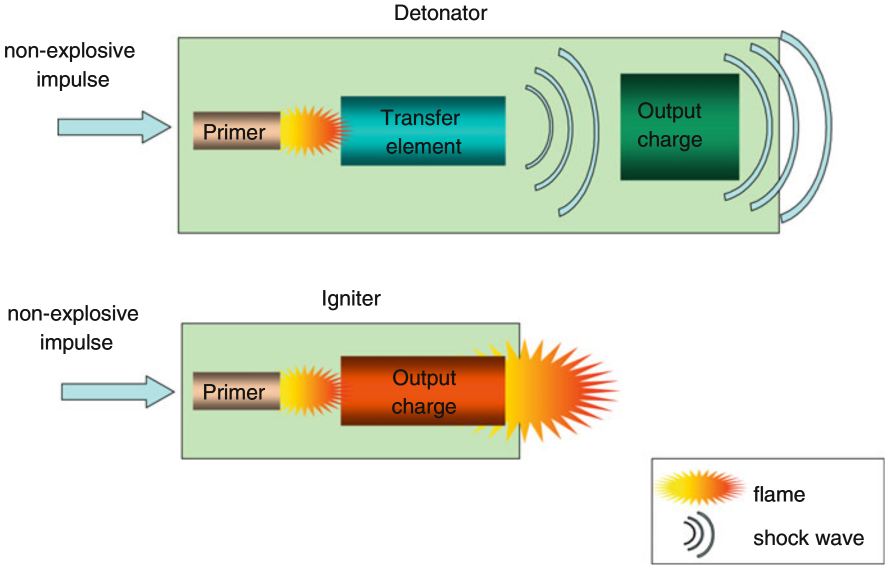

Fig. 1.1 Schematic representation of the two most common types of explosive trains

element in Fig. 1.1 represents any element used in the detonation train to augment or delay the initial impulse. The materials for such an element may range from a primary explosive (column of lead azide or 2-diazo-4,6-dinitrophenol—dinol) or pyrotechnic mixtures (e.g., $FeSiCr/Pb_3O_4$) to black powder. The output charges are secondary explosives, pyrotechnic mixtures, or propellants depending on the type of application.

In the following text, we have decided to adopt an approach in which we divide the vast group of sensitive condensed energetic materials according to various criteria (Fig. 1.2). The first criterion we used is their usefulness in real applications. We further divide those that have found a use depending upon the type of the desired function into two groups: (a) detonating substances (primary explosives) and deflagrating substances or mixtures (priming mixtures, primes). The term primary explosive is generally used for individual substances (not mixtures) which are further divided based on their response to flame into those which detonate practically immediately after ignition and those that require some distance/time for developing stable detonation. The former are sometimes referred to as detonants in Anglo-American literature, whereas in Czech literature these are called primary explosives belonging to the group of lead azide, while the latter belong to the group of mercury fulminate. In Russian literature, the latter are denominated as pseudo primary explosives because they must undergo so-called deflagration to detonation transition, which is a process of accelerating the burning reaction zone to a point where the propagation mechanism changes from being heat transfer driven to being shock wave driven.

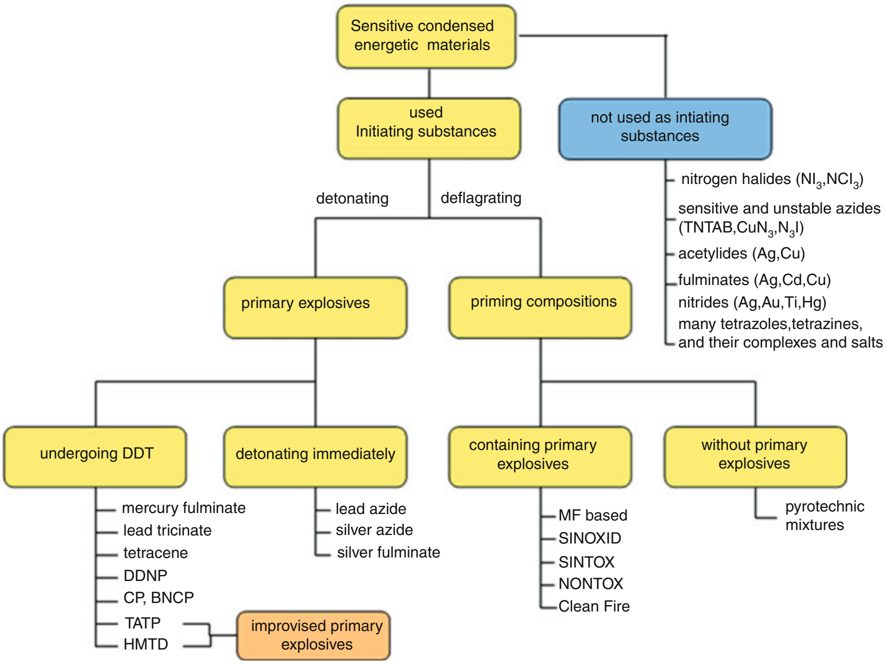

Fig. 1.2 Subdivisions of sensitive energetic materials with some common examples

It is difficult, if not impossible, to draw a clear line between substances used for igniters and those used for detonators. These two groups overlap in many compositions. Mercury fulminate, for example, is a well-known primary explosive used in the past, capable of detonation, but which found a use in priming compositions much earlier than it did in detonators. It should therefore be understood that any type of partitioning of initiating substances is rather artificial and cannot be considered rigorous or definitive. Whether a substance finds a use as a primary explosive in a detonator, as part of a priming mixture or does not find any use at all depends on a large number of criteria which we have tried to introduce in Chap. 2. Many substances are disqualified from practical application due to their inability to meet these stringent criteria. Some examples include substances that are too sensitive for practical application (e.g. fulminating silver, silver acetylide, nitrogen triiodide), substances with low initiating efficiency (e.g. nitrogen triiodide, tetrazene), chemically unstable substances (e.g. 1,6-diaza-3,4,8,9,12,13-hexaoxabicyclo[4,4,4]tetradecane—HMTD), etc. Further, there are substances that are sensitive but are not expected to explode in their typical application (diazonium intermediate products in the dye industry, dibenzoyl and other peroxides used as catalysts of radical reactions, etc.), substances used in the entertainment world for creating sound or light effects, etc.

Further we have included some of those that we believe may attract attention in the future although they are not used at the moment (tetrazole salts and complexes).

The main focus of this monograph is on the individual primary explosives that have been used or reported as promising candidates for potential use. The only exception we included is nitrogen triiodide, which we believe will never find any use. The priming compositions are covered only briefly in this chapter to give more space to discussing the use of primary explosives in a broader perspective.

1.1 Primary Explosives

Primary explosives are sensitive mixtures/compounds that can be easily detonated by an SII—nonexplosive means such as flame, heat, impact, friction, electric spark, etc. They are mainly used in applications where it is desired to produce shock for initiation of a less sensitive explosive (secondary explosive). The ability to initiate detonation of secondary explosives is the characteristic that makes primary explosives useful in detonators and blasting cups or caps (detonators used for mining). In order for this to work, primary explosives must detonate shortly after the nonexplosive initiation. The fast transition from SII to detonation (sometimes referred to as acceleration) is the most important distinction between primary and secondary explosives.

Another important use of primary explosives lies in their application as sensitizers in priming compositions. The purpose of such mixtures is to provide reliable ignition and the role of the primary explosives in such mixtures is to make them sensitive enough to be easily ignited. The detonation of such a mixture is undesirable and must be prevented by careful selection of the ingredients and their quantities for a particular application.

The first substance ever used as a primary explosive was mercury fulminate (MF). It was patented for use in priming mixtures in 1807 and it took another 60 years before Nobel realized that it was possible to use MF in "Fulminate Blasting Caps"—practically the first detonators—for initiation of detonation of nitroglycerine. The price of mercury and the toxicity of decomposition products led to the search for suitable replacements. Even though lead azide (LA) was tested before 1900 as a replacement for MF in detonators, production of MF continued to grow and peaked during World War I. The toxicity of MF, which was even at that time considered a problem in priming mixtures, was not seen as a big issue in the case of detonators. The real replacement of MF in detonators was a lengthy process closely related to improvements in manufacturing of a suitable form of LA.

Apart from the already mentioned lead azide and mercury fulmiate, the classic examples of primary explosives include lead styphnate (LS), silver azide (SA), dinol (DDNP), and tetrazene (GNGT). Primary explosives (individual components) are often mixed and used in the form of compositions rather than as single component energetic materials. Mixtures may consist of either individual primary explosives (astryl-MF/SA [2]) or primary explosives plus some nonexplosive additive (LA/LS/dextrine or ASA composition—LA/LS/Al).

Table 1.1 Example of typical historical priming composition [1]

Substance	Amount (wt%)
Mercury fulminate	13.7
Potassium chlorate	41.5
Antimony sulfide	33.4
Powdered glass	10.7
Gelatin glue	0.7

Table 1.2 Example of typical historical priming compositions without potassium chlorates [3]

Substance	Amount (wt%)		
MF	40	50	36
Barium nitrate	40	–	–
Lead chromate	–	24	–
Lead dioxide	–	20	–
Mercury chromate	–	–	40
Antimony sulfide	14	–	20
Glass powder	6	6	4

1.2 Priming Compositions

Priming compositions or priming mixtures are sensitive explosive mixtures that are designed to produce a flame in a particular application. They are most often mixtures containing a primary explosive as one of the components in such a form and amount that ensures the inability to initiate detonation of the mixture. The role of the primary explosive is to sensitize the mixture to external stimuli, not to make it detonatable. Priming mixtures are used in percussion caps for ignition of gun powder, on electric fuseheads, delay elements, etc.

The typical examples of priming mixtures used almost exclusively in the nineteenth century include mercury fulminate, potassium chlorate, antimony sulfide, glass powder, and gum Arabic. The priming mixtures widely used for small arms in the USA in the early 1900s were based on MF. The composition of the most typical one is summarized in Table 1.1.

At the time of black powder, weapons had to be carefully cleaned after use. The combustion products of priming mixtures therefore did not present such a crucial problem since they were in any case removed together with the black powder residues during cleaning. The problem of corrosive products became apparent when black powder was replaced by smokeless powder which meant much less careful cleaning of weapons. Potassium chlorates as a part of the priming composition have therefore been abandoned and replaced by other oxidizers. Some of the compositions from that time can be seen in Table 1.2 [3].

The use of alternative oxidizers led to mixtures that were not corrosive but contained MF, which liberated toxic mercury vapors during firing. To overcome the problem of toxicity, Edmund von Herz proposed replacing MF in priming compositions with lead hypophosphite nitrate (1913) and later by the lead salt of trinitroresorcine (1914). The more important of these two MF substitutes was the

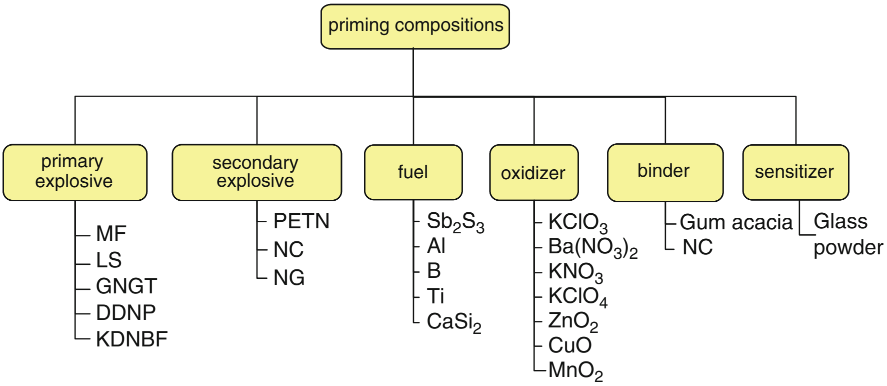

Fig. 1.3 Typical examples of components found in priming compositions

latter—the lead salt of trinitroresorcine; so-called lead styphnate, lead tricinate, or simply just tricinate. This substance, however, does not possess sufficient percussion sensitivity and therefore did not find wider use until the introduction of tetrazene by Rathsburg in 1921 [3]. Some patented compositions contained both MF and tricinate [4].

Typical primary mixtures contain some of the following: lead styphnate, tetrazene, aluminum, antimony sulfide, calcium silicate, lead peroxide, boron, metals, barium nitrate, secondary explosive, binder, sensitizer, etc. (Fig. 1.3). Variations in the ingredients and their relative amounts result in compositions which possess sensitivity and ignition properties tailored to specific requirements.

The replacement of mercury was a significant improvement with respect to the toxicity of the combustion products. It led, however, to the introduction of tricinate which also presents health problems due to its lead content. Concerns over environmental hazards resulted in the search for lead-free or, more generally, heavy metal-free compositions which would eliminate the health threat while maintaining performance and other important properties at least to the level of lead-containing predecessors [5].

1.3 Environmental Hazards: Emergence of Green Initiating Substances

The problem of toxicity, as it is seen today, is caused mainly by lead which is present in primary explosives in form of lead azide and in priming mixtures mostly as lead styphnate. The evolution in the initiating materials is therefore heading toward lead-free, environmentally friendly, "green" initiating substances or more specifically "green primary explosives" and "green priming compositions."

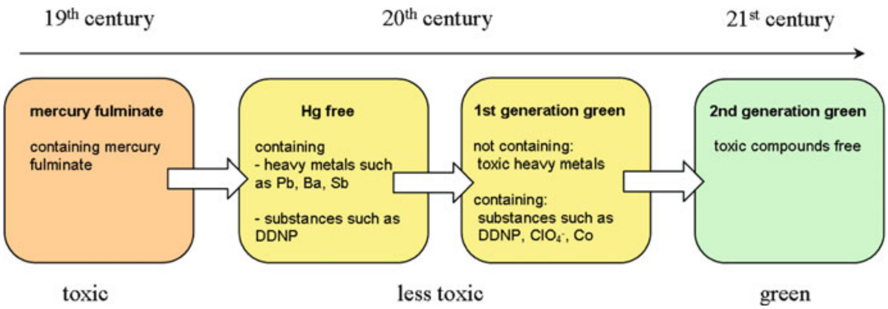

Fig. 1.4 Evolution of primary explosives and priming mixtures from the perspective of toxicity

The term “green” is “science marketing” more than anything else and is quite confusing as it describes compositions not containing lead, as well as compositions without heavy metals such as Hg, Pb, Ba, and Sb or more recently also compositions that do not contain any toxicologically potentially hazardous substances such as DDNP (often found in green compositions today). Further, the term “green initiating substances” or sometimes “green primaries” usually covers substances used as primary explosives as well as substances used in priming mixtures. This may be even more confusing and we will therefore try to distinguish only between “green primary explosives” and “green priming mixtures” with the first ones being the replacement for LA in blasting caps and detonators while the second is a replacement for LS in priming compositions.

Historically the oldest toxic initiating substance is MF. It has to all intents and purposes been replaced in both igniting and detonating initiating devices by lead alternatives. Today these lead-based alternatives coexist with the more modern lead-less compounds or compositions containing other, less toxic, heavy metals. The efforts in finding suitable priming compositions were more successful and led to mixtures not containing lead such as SINTOX, NONTOX, WINCLEAN [5], CCI Clean Fire [6], etc. [7–9]. Future research is therefore aimed toward completely nontoxic alternatives. Results from the search for lead-free primary explosives were not particularly good, and a suitable replacement of lead azide practically does not exist today. The emergence in recent years of a new class of transition metal complexes is a direct response to the toxicity of heavy metals and environmental concerns. From recently published works, one of the more promising possibilities is found in complexes with high nitrogen content such as tetrazoles with nontoxic cations such as sodium, ammonium, and iron [10]. The evolution of the initiating substances and compositions with respect to toxicity is schematically summarized in Fig. 1.4.

In Fig. 1.4 “toxic” refers to the classical compositions with toxic heavy metals, “less toxic” substances relate to those not containing toxic heavy metals but still containing some problematic ingredients, and “green” to nontoxic substances.

The search for suitable replacements of LA and LS should not be seen as a search for one universal substance. It would obviously be nice to have one substance

Table 1.3 Target properties of green explosives and priming mixtures

Criteria	Green primary explosive (blasting caps, detonators)	Green priming mixture (electric pills, percussion caps)
Chemically stable under light, moisture, and in presence of carbon dioxide	X	X
Sufficient thermal stability	X	X
Low toxicity (no heavy metals, DDNP, ClO_4^-)	X	X
Sensitivity within useful limits	X	X
High initiation efficiency	X	
Resistant to dead-pressing good compatibility with construction materials	X	
Fast DDT	X	Unwanted
High flame temperature		X
Low barrel erosion/corrosion		X
Low antilubricating effect		X
Low cost	X	X

replacing both lead salts in both applications but with respect to their different function it should not be the ultimate goal due to different requirements for suitable replacements. High initiation efficiency, very important in primary explosives, is not at all important in primers and suitable properties with respect to barrel corrosion, very important in primers, are practically meaningless in detonators.

Six criteria for "green primaries" have been proposed including [10]:

1. Lack of sensitivity to light and moisture.
2. Sensitivity to initiation in suitable limits (sensitive enough to be initiated by nonexplosive stimulus but not too sensitive to make handling and transport unnecessarily risky).
3. Thermally stable to at least 200 °C.
4. Chemically stable for an extended period.
5. Devoid of toxic metals such as lead, mercury, silver, barium, or antimony.
6. Free of perchlorate which may be a possible teratogen and have an adverse effect on thyroid function.

These criteria are in our opinion relatively broad and cover both primary explosives as well as priming mixtures but do not include some important properties specific to each group. We are therefore proposing criteria summarized in Table 1.3.

It should be also pointed out that the toxicity of combustion products of classical priming mixtures today is mainly concerned with air born lead. It must therefore be stressed that using a lead-free priming mixture would have a somewhat questionable effect if a lead bullet without at least an enclosed bottom were to be used. More

Table 1.4 Some compositions of priming compositions without heavy metals

	Composition (%)					
Substance	Reported by Kusak			FA956	SINTOX	NONTOX
DDNP	35.0	29.8	40.0	37.0 ± 5	Unreported amount	–
Tetrazene	8.0	19.8	20.0	4.0 ± 1	Unreported amount	Unreported amount
PETN	–	–	–	5.0 ± 1	–	Unreported amount
CuO	–	29.8	–	–	–	–
MnO_2	–	–	10.0	–	–	–
$Ba(NO_3)_2$	38.0	–	–	32.0 ± 5	–	–
KNO_3	–	–	–	–	–	Unreported amount
ZnO_2	–	–	–	–	Unreported amount	–
Sb_2S_3	12.0	–	–	15.0 ± 2	–	–
B	–	–	–	–	–	Unreported amount
Al	7.0	9.8	–	7.0 ± 1	–	–
Ti	–	–	–	–	Unreported amount	–
Glass	–	9.8	28.0	–	–	Unreported amount
Binder	–	1.0	2.0	0.2	Unreported amount	Unreported amount
References	[11]	[11]	[11]	[1]	[3]	[8]

suitable in this case are either fully encapsulated bullets or bullets made from metals other than lead.

Various new energetic materials have been designed and tested as potential candidates for replacement of the lead substances. The green priming mixtures for percussion caps of small arms ammunition for indoor shooting usually use DDNP or tetrazene (or both) as a replacement for tricinate. DDNP, although better than lead salts, is reported to cause some allergic reactions [10]. Example compositions without heavy metals are summarized in Table 1.4.

A suitable replacement for lead azide in detonators still does not exist even though new candidates, mostly based on tetrazole complexes, have been proposed and to a certain limited extent even employed. There are also some alternative approaches which eliminate toxic metals from the detonator by eliminating the primary explosive but they have not yet succeeded in replacing lead azide detonators.

Environmental friendliness is of course only one important aspect to be considered. Explosives that show extraordinary properties such as stability, sensitivity, initiation efficiency, compatibility, or other properties can find their application in some special cases even though they will not meet the green criteria. Typical examples of such explosives may be the mercury salt of tetrazole or cirkon (cadmium(II)tris-carbonohydrazide) perchlorate used in Russia [12, 13].

An enormous amount of work has been done in Russia on perchlorate coordination complexes. A very interesting initiative to find “green” primary explosives among the cobalt perchlorate complexes has been reported by Ilyushin et al. [14]. The differences in perception of toxicity in various parts of the world make direct comparison misleading. Perchlorates, which are not seen as a problem in many countries, are considered unsuitable from the long-term perspective in the USA [10].

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