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ADVANCES IN THE DESIGN OF EXPLOSIVES DETONATORS

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Abstract

The common use of explosives to break rock for excavation leads to the constant detonators development, that over past two decades significantly increased their precision in order to improve effectiveness of the blasting works. The following article presents key achievements and milestones of detonators development as well as the directions of research aimed at improving their accuracy. The construction of detonators that are currently used for civilian purposes is shown. The requirement that should be followed during the development of time delay compositions are presented, as well as the current trends in the research of gasless compositions, the burn rate of which is independent of the pressure inside the detonator.

Introduction

A number of ground breaking solutions, which had a significant effect on the development of blasting agents and technology, can be identified [1,2], i.e.: the evolution of the architecture and elements of the detonator, the development of electric detonator, the introduction of methane- and carbon-safe detonators in mines at risk of methane or coal dust explosions, the development of the NONEL® shock tube and non-electric detonators for initiating hole and surface charges with a broad range of applications and, recently, the development of programmable electronic detonators (such as i-kon® by Orica Mining Ltd, Daveytronic® by Davey Bickford Ltd or the latest product of NITROERG S.A. which is ERGONIC-II). Despite these accomplishments, in the span of those past decades, the greatest focus and, consequently, effort was dedicated to the development of a variety of delay compositions to be used in detonators for mining and in delay elements for military applications. Due to the persistent and significant price advantage over modern electronic delay elements, initiating agents based on chemical delay systems currently constitute a large majority of the global market (approximately 95% of global consumption).

Design of time-delay detonators

Modern detonators, both electric and non-electric, widely used in engineering and mining industry are composed of a primer and an initiating element. A general scheme of a detonator is presented in Fig. 1. Each detonator is encased in a metal shell that is sealed on one end. In the case of rock detonators, the shell is made from aluminium (Al), whereas in methane-/coal-safe (for use in areas at risk of methane/coal dust explosions) detonators the shell is made of either copper or special brass alloys. Within the shell, a number of layers are found; starting from the sealed end, they are:

• The main secondary explosive charge (typically 700÷800 mg of pressed pentaerythritol tetranitrate (PETN), followed by 120÷200 mg bulk dose of PETN),

• The primary explosive charge (typically 100 mg of lead azide or of a mixture of lead azide and lead styphnate) sensitive to thermal and mechanical stimuli and capable of initiating the secondary charge,

• A bulk dose of a delay composition, ensuring the continuity of the charge in the shell,

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• Cylindrical delay element pressed into the shell. This component consists of a zinc-aluminium (Zn-Al) alloy (other alloys are also used, depending on the required heat and electrical conductivities), encasing a set amount of a pressed delay composition, which determines the length of the time delay,

• Initiating relay element capable of initiating the delay composition: – in a non-electric detonator - NONEL® shock tube, – in an electric detonator - initiating head of an initiating system, composed of resistance wire with a resistivity in the range of $0.1 \div 0.7$ $\Omega \cdot mm^2 \cdot m^{-1}$, onto which a special initiating composition is deposited. This composition includes both a thermally-sensitive initiating material (such as lead styphnate, lead dinitro-ortho-cresolate or barium dinitroditetrazenephenolate) and oxidising supplements,

• Rubber or synthetic plug, sealing the entire device and providing conditions for initiating the delay composition.
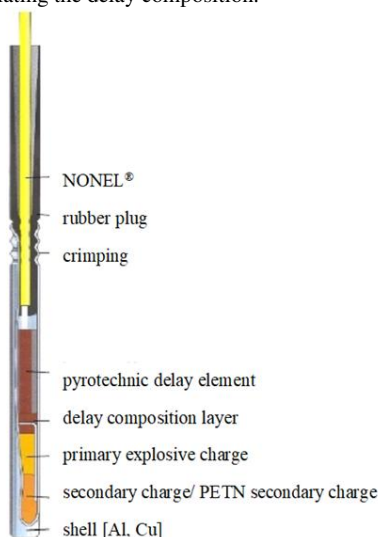

Figure 1 Scheme of a non-electric detonator for mining, equipped with a NONEL® shock tube

In terms of the parameters of the delay composition, the existence of a variety of delay element designs should be noted. It provides space for the burning of the pyrotechnic composition and protects the components of the detonator from the effects of the heat and chemicals produced during the burning of the composition. It also significantly reduces the amount of delay composition in the detonator, which improves the cost-efficiency of the detonators. The material of the delay element shell should exhibit appropriately low heat conductivity, in order to limit the amount of heat transferred from the burning delay composition to the bulk of the delay element and the shell of the detonator. Early delay elements were made of lead, which has a heat conductivity of 35.9 $W \cdot m^{-1} \cdot K^{-1}$, relatively low specific heat capacity of 129 $J \cdot kg \cdot K^{-1}$,

a high density, beyond comparison with commonly used metals, therefore providing very beneficial conditions for the burning of delay compositions. The above was particularly important for delay compositions with low rates of burning, because such a feature promotes transfer of the heat, generated during burning of the delay composition, to the surrounding environment. This in turn may result in stopping the burning reaction prematurely - before the entirety of the delay composition encased within a delay element is consumed. The recent decades, due to increasingly restrictive environmental law and the gradual retirement of lead from industrial application, have brought about a need to find alternatives, such as metal alloys, for producing delay elements. Currently, Zn-Al alloys, containing $3 \div 7\%$ Al, are the most commercially prominent group of those alternative materials. The Zn-Al alloys are used in the

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production of delay elements and feature less beneficial properties than those of lead: their heat conductivities are in the range of $116 \div 130$ W·m^{-1}·K^{-1} and specific heat capacities in the range of $390 \div 430$ J·kg^{-1}·K^{-1}. The presence of aluminium in the Zn-Al alloy is used to improve the mechanical properties and resilience of the delay elements. It is recommended, however, that alloys used for the production of delay elements contain a limited amount of aluminium, below 5%, due to its undesirably high heat conductivity and adverse effect on the burning rate of delay compositions. Due to the possibility of inter-grain corrosion of Zn-Al alloys and in order to improve its mechanical properties, the composition of the alloy is often supplemented with $0.1 \div 0.3\%$ magnesium (Mg) or silicon (Si). Often, the design of the delay element also includes a space for a primary explosive, which is in contact with the delay composition. Consequently, delay elements made from alloys containing copper are prohibited from use, because copper can react with primary explosives, i.e. lead azide and produce the extremely hazardous copper azide.

Requirements for time delay compositions

In regards to the cost-efficiency of the production of compositions, the choice of fuels, oxidising agents and auxiliary substances is primarily a question of availability and price. The choice of a component for producing a pyrotechnic composition and, delay composition in particular, is based on its quality and availability. The availability and purity of a component are two primary factors in terms of its price, therefore, directly affecting the production profitability. The quality of a component is determined by its purity, grain size and its distribution. The fineness and grain size distribution have an indirect impact on the price of a given component, as the desired grain size distribution can be achieved for many substances through simple unit operations (crushing, milling). Whereas the use of a particular component, but of lesser purity (or contaminated with another component), may appear beneficial due to reduced cost, it often results in a final pyrotechnic compositions whose operating parameters are significantly deteriorated (such as accelerated deactivation of the system) or, even worse, reducing the chemical stability of the system, which results in increased sensitivity to stimuli such as sparks, friction or impacts.

The existence of a relatively wide array of substances and compounds useable as components is a characteristic feature of all pyrotechnic compositions, including pyrotechnic delay compositions. This variety of substances, which fulfil or can fulfil the role of fuels and oxidising agents in a pyrotechnic composition means that during burning, some reagents will remain in the solid phase, others may melt or thermally decompose, producing a liquid phase, and some can evaporate, forming gaseous products. The kinetic mechanisms of the burning of pyrotechnic compositions, that determine the stages of the reaction, i.e. mass diffusion and energy transfer within the burning front, often involve reactions between the components of a pyrotechnic composition that exist in various phases [3]. Initial assumptions, about the occurrence of exothermic reactions, in pyrotechnic systems, only between reagents existing in the solid state, have turned out to be imprecise. Typically, it is the stability of an oxidising agent in the composition which determines the decomposition conditions and the reactivity of the entire composition. Energy supplied to the system causes a strong increase in the temperature of the reagents, resulting in: rapid melting, evaporation and thermal decomposition of oxidising agents, leading to further reaction of the solid phase (fuels) with the liquid and gaseous reagents (including oxygen released into the reaction environment). The following schemes of reaction between the components of the

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composition are possible: solid phase/solid phase; solid phase/liquid phase; solid phase/gas phase. These are accompanied by the likely consecutive reactions, occurring in liquid phase/liquid phase and liquid phase/gas phase systems. The final products of the reaction, dependent on the initial contents of the composition and conditions of the reaction (temperature and pressure of the reaction environment, contact of the reagents) are no less of an important issue. It should be noted that the formation of products at temperatures of about 1000°C to 3000°C (in the case of thermite compositions) usually are multi-stage and take place in multiple phases, rarely yielding the simple and most stable forms of the expected products. Reactions taking place in ternary and multicomponent systems usually yield various amounts of between several and several dozen individual products of the reactions [4].

Among substances and inorganic compounds acting as fuels in delay compositions, the following have found the widest use:

a) Metals and metal alloys: zinc, aluminium, magnesium, nickel, molybdenum, manganese, strontium, iron, chromium, as well as expensive metals, such as titanium, zirconium, beryllium and tungsten,

b) Metalloids and non-metals: antimony, boron, germanium, silicon and phosphorus,

c) Compounds:
- Simple, e.g. metal sulphides, such as Sb_2S_3, FeS_2,
- Complex: Ti-C, Cu-C.

Among organic compounds, the following are particularly noteworthy:

a) Aliphatic (alkanes) and aromatic hydrocarbons,

b) Carbohydrates, such as cellulose, starch, lactose, sucrose and their derivatives,

c) Functional compounds, such as amines and carboxylic acids,

d) Metallorganic complexes, such as vanadium, iron or lead tannates.

Currently, metal alloys (such as Zr-Ni, Fe-Ni) and composite systems (Ti-C, Zr-C) find wide use as fuels for delay compositions, due to providing the ability to control the burning process through changing the composition of the alloy. Through changing the ratios of the components of the alloy, sharply varying rates of alloy oxidation can be achieved, without the need to alter its grain size distribution. The use of the Zr-Ni alloys allows, provided an adequate grain size distribution, parameters, similar to those obtained for compositions based on pure and expensive zirconium, to be achieved. This feature of such alloys is invaluable, particularly when expensive fuel components (zirconium, titanium) would otherwise need to be used. Table 1 presents the key properties of fuels used in pyrotechnic compositions.

Table 1 Physicochemical properties of the most common fuels used in the production of pyrotechnic delay compositions [5]

Fuel	Molar mass [g/mole]	Density [g/cm³]	Melting point [°C]	Boiling point [°C]
Zr	91.22	6.52	1530	2900
Ni	58.22	8.90	1455	3177
Mg	24.32	1.74	650	1102
Ti	47.90	4.50	1727	3000
W	183.90	19.32	3380	6000

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Fuel	Molar mass [g/mole]	Density [g/cm³]	Melting point [°C]	Boiling point [°C]
B	10.82	1.73	2050	2550
Si	28.09	2.33	1440	2630
C	12.01	2.25	4350	-
S	32.06	2.07	112.8	444.6
P	30.97	2.2	590 (4.3MPa)	-

Due to the need to fulfil the requirement for producing low volumes of gaseous products during burning, mainly inorganic substances are used for the production of delay compositions. The use of nitrates (V) and salts, containing the ammonium ion, in delay compositions is not recommended because such oxidants produce increased amounts of gases. The above is also the reason why organic substances find application, but mostly as combustible supplements to compositions, typically present in small amounts (up to 5% of the composition), most often acting as auxiliary fuels in the composition. Among the substances and inorganic compounds acting as oxidising agents in delay compositions, the following have found the widest application:

a) Salts:
- Nitrates (V): $NaNO_3$, KNO_3, $Ba(NO_3)_2$, *Pb(NO₃)₂*,
- Chlorates (V): *KClO₃*, *NaClO₃*,
- Chlorates (VII): $KClO_4$, $NaClO_4$,
- Manganates (VII): $Ca(MnO_4)_2$, $KMnO_4$,
- Chromates (VI): *K₂CrO₄*, *K₂Cr₂O₇*, *BaCrO₄*, *PbCrO₄*,
- Sulphates (VI) $BaSO_4$, $SrSO_4$,

b) Metal and non-metal oxides: Fe_2O_3, *Pb₃O₄*, *PbO₂*, CuO, Cu_2O, MnO_2,

c) Inorganic peroxides, such as SrO_2, BaO_2, CaO_2.

The decomposition temperature is a particularly important physicochemical property of the oxidising agent. Temperature near or slightly above the decomposition temperature induces their rapid decomposition. The decomposition temperature provides some information about the oxidising agent as a chemical species, however, its thermal decomposition in the presence of a reducing agent, constituting a pyrotechnic composition typically occurs in significantly lower temperatures. Numerous works have investigated the above and proven that the activity of oxidising agents increases upon mixing them with combustible substances. In order to utilise the full heat yield of a unitary mass of a pyrotechnic composition, oxidising agents featuring high oxygen contents and relatively low decomposition temperatures should be used. Table 2 presents the key properties of oxidising agents used in the production of pyrotechnic compositions.

Table 2 Physicochemical properties of oxidising agents most often used in the production of pyrotechnic delay compositions [5]

Oxidising agent	Molar mass [g/mole]	Density [g/cm³]	Melting point [°C]	Boiling point [°C]
KNO_3	101.11	2.11	339	400 (decomposition)
$Ba(NO_3)_2$	261.38	3.24	592	-

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NaNO$_3$	85.00	2.25	312	-
KClO$_4$	138.65	2.52	610 (decomposition)	-
BaO$_2$	169.36	4.96	450	795
PbO$_2$	239.21	9.37	290 (decomposition)	-
Pb$_3$O$_4$	685.63	9.10	500 (decomposition)	-
K$_2$Cr$_2$O$_7$	294.18	2.68	398	500 (decomposition)
PbCrO$_4$	323.22	6.12	844	-

An important aspect of selecting the oxidising agent for a delay composition is to match the oxidising agent and fuel in such a way that avoids producing significant volumes of final gaseous products. This is important both in terms of the exothermicity of the reaction and in terms of the burning parameters of the composition. A good example of a composition featuring low gas emission is a composition devised by Boberg and composed of boron and bismuth (III) oxide, which yields less than 8 ml of gaseous products per 1g of the pyrotechnic composition [6]. An increased amount of released gases, apart from oxygen, significantly limits the amount of released heat, due to its consumption in the expansion and heating of the gaseous phase. Furthermore, the gaseous phase forming during the decomposition of the oxidising agent hinders contact between the oxygen and fuel components in the condensed state. This is important in the case of oxidising agents which do not release a large amount of oxygen from a unitary mass. In the case of most oxidising agents, this parameter is in the range of 10÷50%. In the case of Pb$_3$O$_4$ and BaO$_2$, the maximum amount of oxygen released during decomposition is respectively 10% and 18%.

Development of time delay compositions

The development of pyrotechnic compositions, with the desired combustion profile, should begin with the selection of components, based on their physicochemical and thermochemical properties, followed by estimating their optimal shares, which will allow the desired parameters to be achieved. The requirements for obtaining accurate and reproducible delay times, high chemical stability of the pyrotechnic system, whose performance after a given time is reliable, make designing an ideal delay composition difficult. Boberg postulates that a defined, stable and accurately reproducible combustion rate is a basic requirement for delay compositions, alongside with its resistance to the influence of various external factors, which can deactivate the chemical system [6]. Nakahara, based on his numerous studies of delay composition systems, notes that the combustion time of a composition is dependent on many external factors, whose sources are found not only in the chemical properties of the system. The factors, which influence the stability of the parameters of the system, are usually a complex function of the constancy of the contents of the composition, which is dependent on the purity, hygroscopicity and humidity of components, temperature, external pressure, loading conditions and others. The types of components used in the composition and their gradations have the largest influence on the nature and rate of combustion. The type of fuels and oxidising agents directly decides the energetics of the combustion reactions. The heat of the reaction, defined by the contents of the composition, largely

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influences the ability of this system to develop a reaction and has an indirect effect on its rate [7]. The heat of the combustion reaction, depending on the requirements posed to the system, should provide, in the given conditions, an appropriate surplus of energy, allowing the combustion reaction to be self-sustaining and to maintain a stable combustion rate, within the defined boundaries [8].

Patent descriptions, pertaining to the production of delay compositions, present several ideas of compositions, for which the components are mixed in an aqueous medium [6,9]. These systems often contain silicon, as a fuel, and oxidising agents that are insoluble in water, such as: Bi_2O_3, MnO, SnO_2 or $BaSO_4$. The systems proposed by Boberg and Davitt do not contain any carcinogenic or toxic substances and, therefore, fulfilling the basic work health and safety requirements. This is in line with the legal regulations in this area, which tend to eliminate carcinogens and toxic substances, i.e. lead and potassium chromates (VI) and lead oxides: PbO, PbO_2 and Pb_3O_4, from delay compositions.

In the case of delay compositions, which are used in delay elements of detonators, the type of products obtained after their combustion should be taken into consideration. Due to the large influence of pressure and temperature on the combustion propagation rate and profile of the composition along the length of a delay element, the addition of modifying substances, which decompose into high-melting or high-boiling products and do not release large amounts of gaseous products, should be considered [10,11]. Objectively, substances, whose melting point in the reaction phase is relatively low, but whose boiling point is sufficiently high, are desired in the system. Some oxides are readily fusible (Bi_2O_3, Pb_3O_4) and even at mildly high temperatures, depending on the fuel content in the composition, form complex alloys or slags with other products that comprise the incipient solid phase. Moreover, it is favourable to include components, which produce high-boiling metal oxides and more complex intermetallic compounds with oxygen, in the system.

Low-melting oxides, which exhibit relatively low heats of formation (i.e. Bi_2O_3, Sb_2O_3, Pb_3O_4, SnO_2), are often included in compositions, because upon decomposition they produce alloys and slags, which substantially increase contact between the components of the composition in the reaction phase [8]. Their presence, even in small amounts, intensifies mass exchange in the reaction zone, which may contribute to accelerating the diffusion-limited reaction. Furthermore, a high content of slag-forming compounds increases the viscosity of incipient alloys and helps "freeze" the gases, which are released from the reaction medium, in the bulk of the products. Oxidation products, which melt in temperatures that are not achieved by the chemical system during the course of the reaction, play an important role in the increase of the viscosity of the melt. These products (i.e. BaO, SrO, ZnO, ZrO_2, TiO_2, Cr_2O_3) remain stable at high temperatures. The mentioned oxides may be introduced as additives to compositions or be formed during the oxidation of corresponding metallic fuels (Ti, Zr, Cr), present in the delay composition. The course of the combustion reaction can be controlled, through careful selection of high-energy fuels and oxidising agents, to yield oxidation products not only in the form of oxides, but also other, high-melting compounds, such as silicides, borides and nitrides [8].

Research continues on the use of alternative fuels, which provide a stable combustion rate, when combined with various low-hazard oxidising agents. Earlier patents have used an array of fuels, exhibiting various heats of combustion and having a wide range of melting and oxidation temperatures, to control the combustion rates of

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compositions. In the U.S. Patent No. 3,111,438, Ball uses an addition of silicon or Ti-Ni alloy fuel, containing 50% titanium, in his $Zn/KMnO_4$ delay composition [12]. The composition is highly stable; it is, however, highly prone to changes in rate, along the length of the delay element. The varying combustion rate of the $Zn/Ti-Ni/KMnO_4$ composition stems from the fact that the composition releases a large amount of gaseous products during its combustion. Recently, the use of metallic iron and zinc in pyrotechnic compositions, which exhibit a low combustion rate, was studied [13,14]. The use of zinc in delay compositions is of lesser importance, because of the specific nature of this metal. Its melting point at 419°C is very low, effectively contributing to increasing the degree of contact between the reagents in the liquid phase. On the other hand, molten zinc exhibits relatively high viscosity, and due to significant tension occurring at the zinc/oxidising agent interface, the contact between the two phases is hindered [13]. Molten metallic zinc rather easily undergoes oxidation, only on its surface, forming the stable zinc oxide, which effectively suppresses the chemical reaction. Iron, in comparison with zinc, has a much higher melting point, but its rapid oxidation occurs even at about 250°C. Conversely, the oxidation of zinc takes place rapidly only above its melting point.

Compositions that contain iron can also be used as igniting or signalling compositions. Compositions based on Teflon®, as an oxidising agent, and iron, silicon or ferrosilicon, as a fuel, can be an example of the above [15]. The use of metallic iron in the production of delay compositions appears to be more interesting in terms of physicochemical properties.

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