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Research paper

Some Remarks on the Safety of Methane Penthrite Detonating Cords against the Inflammability of a Methane-Air Mixture

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Abstract: After analysing literature data some topics related to the properties and testing methods of detonating cords (DCs) are presented. The main attention is paid to the 2,2-bis[(nitrooxy)methyl]propane-1,3-diyl dinitrate (penthrite, PETN)-based DCs. In a case study of methane PETN DC, it is shown that the problem of DCs being able to fulfil safety precautions as permitted explosives is very complex, i.e. to determine their ability to ignite a methane-air atmosphere in coal mines.
The tests have shown that the relationships between safety and the performance properties of methane PETN DC are not obvious. For example, an increase in the outer thickness coating of this methane PETN DC, causes the inflammability of a methane-air mixture to be decreased. Moreover, an increase in the amount of crystalline PETN in the cord's core caused an increase in its velocity of detonation, but had no impact on its ability to ignite a methane-air mixture in the experimental gallery.

Keywords: detonating cord, 2,2-bis[(nitrooxy)methyl]propane-1,3-diyl dinitrate, penthrite, PETN, safety, methane-air mixture, inflammability, blasting work

1 Introduction

The importance of detonating cords (DCs) was much more significant in the past, when there was no other technique for remotely initiating an explosive charge. Even today DCs cannot be excluded totally, because in some applications neither electric nor other non-electric initiation means can fulfil the requirements of some types of blasting work. The most important advantages of using high energy DCs in a blasthole are to ensure complete detonation along the whole explosive column (a blasthole charge composed of several small explosive charges) and to avoid deflagration of the blasting charges, *e.g.* [1, 2]. The result of ensuring complete detonation is that there are no misfires. Another advantage of high energy DCs is that several cords can be very readily tied together to form a branched cord (a bundle) or they can be attached one to another and to easily create any blasting line structure. This enables many high explosive charges to be initiated simultaneously [3].

The dissemination of knowledge on the scientific development of DCs, known earlier as detonating fuses, has three main limitations. The first limitation comes from the commercial importance of the results, *i.e.* valuable data are not being published to prevent it being used by competitors. The second reason is that all studies on the adaptation of a given type of DC has to be restricted to given technological processes used solely by its manufacturer. Finally, there is a limited number of reviews dedicated to DC-development history and the basic sources of scientific data are mainly those published by manufacturers in the form of data sheets and patents. The US market seems to be one of the most important and such data are the most readily available. Because of these reasons, data presented here is based mostly on US patents. The production of PETN DCs, with a waterproof coating and with a velocity of detonation *ca.* 6400 m/s, commenced in 1936. Despite this, taking into consideration the further history of US patents that referred to DCs, one can say that the period from the 1960s to the 1980s is the most important because during this period the general rules and techniques of up-to-date manufacturing technologies of DCs were established. Among these are those which refer to the main topic of this paper, *i.e.* elimination of firedamp by modification of DC coatings [3-5]. On the other hand, the 40-year period, 1980s to 2020s, can be the reason why problems associated with DCs have been little explored in recent times.

However, despite these years of experience, new problems relating to DCs still appear, not only in underground blasting work but also *e.g.* in the oil and gas industry, in military applications and in space technologies. One such problem is safety in those coal-mines with a methane threat. There are many methane-air mixture ignition sources such as [6]:
– flame,
– electric spark,
– friction spark, and
– detonation of explosives.

Furthermore, some features of DCs can also influence the final level of safety against a methane-air atmosphere. According to Sobala and Sobala [7] and Zawadzka-Malota [8], the safety of methane and coal dust (PETN, 2,2-bis[(nitrooxy)methyl]propane-1,3-diyl dinitrate) DCs, is influenced by:
– mass of PETN found per unit length in a DC,
– properties of PETN,
– additives to PETN,
– detonation process of PETN,
– construction of the DC,
– outer coating thickness of the DC.

None of these factors could be excluded from the list of causes that could lead to initiation of an explosive atmosphere during the carrying out of blasting work in methane-hazard mines. On the other hand, these features can be varied during the manufacturing process.

Some remarks on the problem of methane-air mixture inflammability are shown in the present case study, prepared on the basis of results of some basic tests carried out when a DC has been submitted for official approval for use in blasting work in underground coal mines. The ability of tested DCs, filled with PETN, to ignite a methane-air atmosphere was tested in an experimental gallery. PETN was chosen because it is the most frequently utilised explosive in DCs in everyday coal mining blasting work. The tested DCs were also examined with respect to the determination of their basic properties, *i.e.* detonation velocity (VOD) and capability of detonation transmission between DCs.

The aim of this work was to focus on the problem which is still not fully solved, *i.e.* the safety of DCs applied in blasting work executed in an explosive atmosphere in underground mines.

2 Firedamp Hazard vs. Permissible Explosives

In working coal mines, the possibility of explosion of both methane- and coal dust-air mixtures, is still a serious hazard. For example, in Russian coal mines, within the period 2000-2011, most accidents were caused by explosions of these mixtures [9]. It is not stated in [9], how many of these accidents were due to the initiation of DCs, but just to show the scale of the problem it is worth noting that during this period, accidents in Russian coal mines annually took the lives of ca. 100 miners (with an extraordinary increase in 2007, of up to 216 miners). Smaller, but also significant numbers, are also reported for the US (Zipf *et al.* [10]), where, since 1976 and up to ca. 2010, a total of 185 coal miners were killed and many seriously injured as a result of underground coal mine explosions. At least 106 coal dust explosion accidents occurred in China between the years of 1949 and 2007 [11]. Taking into consideration the above mentioned examples, as well as the information that the total number of fatalities in coal mine explosions in the US is nearly 8000 [12], one can see that the problem of safety of initiation systems against firedamp is crucial all over the world.

First of all, the significance of the methane hazard comes from its low threshold of hazardous concentration. The value of the lower explosion limit (LEL), *i.e.* the minimum concentration of methane that allows its mixture with air to be ignited, is in the range of 4-5%. Experimentally estimated LEL values vary depending on the test procedure applied. For example, in Annex G of [13], one can find an LEL value equal to 4.2 mole%. Under real conditions, a lower methane concentration allows the atmosphere to be ignited, *e.g.* because of the presence of coal dust, which decreases the flammability threshold of the methane-air atmosphere. The upper explosion limit (UEL) for a methane-air mixture is about 15%. Another major reason for the importance of this hazard is the presence of ignitable methane-air mixtures not being eliminated or fully controlled in the mining environment. The reasons for this are the continuous changes in conditions of the methane released into the working environment and the continuous formation of coal dust clouds during normal coal mine exploitation.

The main reaction which allows an explosive ignition of a methane-air atmosphere (usually called firedamp) to propagate, is methane oxidation [14], *i.e.* reaction R1.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \text{(R1)}$$

Reaction R1 needs an "induction period" before it proceeds, so it will not occur if the time of duration of flames caused by the detonation of an explosive charge is shorter than this induction period. This concerns not only the flames in the detonation front but also of further deflagration reactions.

The evaluation of the ability of a methane-air mixture to ignite, as well as other critical properties connected with safety in underground coal mines, is based on complex tests, designed for interaction modelling of the explosive-gas relation under controlled laboratory conditions, carried out worldwide, *e.g.* [15-19]. The special facilities for such tests are called firing chambers or cells, or mostly experimental galleries. As mentioned earlier, the thresholds LEL and UEL for methane-air mixtures are about 4 and 15%, respectively. The firedamp tests are usually carried out in test chambers for medium methane concentrations. In [8], , 20 trials during firedamp tests of each of four tested DC samples, are reported, within the ranges of temperature and methane concentration of 28.0-30.0 °C and 9.0-9.5%, respectively.

For over 100 years, so-called permitted (permissible) commercial explosives were used in underground mines with the aim of avoiding firedamp explosions [20]. The testing of the safety of blasting explosives against a methane-air atmosphere is broadly described elsewhere [14, 21-25]. In these methods, the use of mortars is justified by the commonly applied arrangement in blastholes, *i.e.* the charge of a blasting explosive is protected from direct action on the potentially explosive atmosphere by the walls and the closures (stemming) of the blasthole. A quite different situation prevails when non-electrical initiation systems, like DCs, are taken into consideration. Naked DC lines (trunk-lines) can pass through a potentially explosive atmosphere of mining sidewalks, and detonate in the presence of such atmospheres at distances over 50 m, *e.g.* recently (in 2019), according to [26], a continuous length of a brand new DC piece made 120 m and more. In respect of an application, the length of a reel of an original piece of DC usually varies in the range of 70-200 m [27, 28]. One has to take into consideration that a DC line could be doubled in some kinds of blasting operations, *i.e.* two separate DC lines are used simultaneously in a single initiation system [29, 30]. The certainty of initiation of DCs is assured by the doubling of a line and this is also applied in military applications [31].

Finally, mortars are not used in DC tests. A straightened 2 m length of DC is placed upon the ground in the potentially explosive atmosphere. Another difference between testing permissible blasting charges and DCs can be shown in the experimental gallery located in the "*Barbara*" Experimental Mine of the Central Mining Institute (in Poland) [8, 24], and comprises a steel pipe of 18 m diameter and a length of 44 m. This pipe is open at one end (gallery outlet), and is closed at the other by a massive concrete block (gallery face). Tests are carried out in this gallery for all potentially permissible explosive items. For tests of potentially permissible explosives (also DCs), only a part of this gallery (from the closed face side) is separated from the rest of the gallery by a gas-proof membrane and contains a methane chamber of 10 m^3 capacity. In general, experimental galleries for testing industrial coal dust explosions can be much longer, e.g. such a gallery in Tremonia Experimental Mine (Germany) is 700 m long [32].

Permissible explosives ensure a lower probability of ignition of the methane- and/or coal dust-air mixtures than other explosives. This occurs due to both a lower flame temperature during detonation and a shorter duration of the combustion process. Nowadays, as far as secondary explosives are concerned, the commonly used method to reach these permissible properties is to add some inert salts into the blasting composition − mostly sodium and ammonium chlorides (NaCl and NH_4Cl, respectively). Application of inert or flame extinguishing salts decreases the detonation parameters of the cord, so their admixture into the permissible DCs is not favoured presently. It is worth noting that such systems were employed in the USSR, *i.e.* flexible permissible DCs with a sheath of inorganic salts, or with a mixture of such salts with PETN, were in service in blasting work in coal mines with a methane hazard, in the 1960s [33] and the 1970s [34]. A mixture of explosive and inert or flame extinguishing salt was applied in the Russian permissible DC type DSZP-1 (in Russian: ДШП-1). A core composed of pure explosive surrounded by a sheath of inert or flame extinguishing salt was applied in the second type, *i.e.* DSZP-2 (in Russian ДШП-2). The outer diameter was 6 mm for the DSZP-1 and 8.6-9.0 mm for DSZP-2. The VOD of both Russian DCs was 6500 m/s.

3 Detonating Cords

3.1 Milestones in the development of DCs

Because of the variable conditions in their application, as well as a near 100-year history of development, a very large number of possible shapes and structures of DCs is available. Each of these were developed independently of each of other, so presently, even those developed first historically and mentioned below, cannot be regarded as obsolete. Even DCs with an explosive gas (mixtures of oxygen with hydrogen or acetylene) were considered in the 1970s [35].

The exact date of the beginnings of DCs development is not certain, *i.e.* 1907 could be stated (according to [36]), but other sources, like [37, 38], point to 1902 as the first trials with DCs in Europe, which concluded with the introduction of commercially available DCs into the market, about 1907 in France and 1912-1913 in the US. The state-of-the-art at these times is presented in patents published in 1910 in France [39] and in 1912 in the US [40]. These first DCs were manufactured as a lead tube filled mostly with 2,4,6-trinitrotoluene (TNT), but methyl(2,4,6-trinitrophenyl)nitramide (tetryl) was also in use at the beginning of DC history [37]. Metal sheathed DCs are still in service in the aerospace industry (in aircraft canopy severance systems, [41]), as well as in space and military applications, *e.g.* [42, 43] but, in blasting work in blastholes, in both underground as well as in open cast mines, flexible DCs are preferred. Another important area of DC applications is in the initiation of shaped charges in perforating guns in the oil and gas industry, *e.g*. most recently [44-50]. However, other applications of DCs are also possible in the oil and gas industry *e.g.* for forming the wall of an oil and/or gas well [51]. DCs can be also used for seismic prospecting [52]. DCs were used in determining the VOD according to the well known Dautriche method.

A special kind of DC is the mild DC [42, 53-58], with a load density of a very few g/m. The output energy of a mild DC is so low that they are in service as initiators for blasting caps. However, they are not employed for the direct side detonation of explosive charges.

Other special requirements which have to be faced by DCs are thermal and pressure resistivities. The replacement of PETN by 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (octogen, HMX) or cyclo-1,3,5-trimethylene-2,4,6-trinitramine (hexogen, RDX) assures thermal resistivity, and the use of a metal casing assures pressure resisitvity. For example, in the 1990s in Poland, a DC manufactured from both RDX and a metal tube could be approved for blasting work, as being safe up to 160 °C and 90 MPa [59].

Recently, the most advanced and safe form of DC seems to be so-called shock or detonating tube. However, under some blasting shot conditions in Russia [60] low-energy DCs with 1-2 g/m of explosive gave a more reliable initiation system than the most commonly known commercial example of the shock tube-based system, *i.e.* NONEL®. This does not mean that systems similar to NONEL® were not developed in Russia. Russian non-electric initiation systems used in the 2000s in open-cast mines were [60]: Edilin, Snezhinka and SINV. The beginnings of shock tubes were the 1960s [36, 61]. Shock tubes enable the detonating signal to appear at the end of the tube, but side initiation is excluded. PETN can also be applied in shock tubes [62, 63] although this kind of initiating system will be not described here. This is mostly because of the quite different ways of transferrence of the explosive signal than occurs in the PETN DCs, which are useful for initiation of an explosive charge along its whole length.

Other differences between DCs and shock tubes are the sigificantly different amounts of explosive components and the use of pyrotechnic mixtures. For example, according to [62], components of the reactive material (an organic explosive not less than 70 wt.% and metallic material not more than 30 wt.%) can be nominally loaded in this kind of shock tube in the amounts of 21.6 ±2 and 2.2 ±2 mg/m, respectively. At the end of the 1980s, [63], material adhered to the inner wall of a shock tube could be aluminized HMX. Other explosives considered were PETN, RDX and 3,5-dinitro-N,N'-bis(2,4,6-trinitrophenyl)-2,6-pyridinediamine (PYX), as well as deflagrating inorganic mixtures composed of, *e.g.*:

- $BaSO_4$ with B, Ti or Zr,
- $KClO_4$ with Al, Mo, Ti, TiH_2, Zr or ZrH_2,
- $PbCrO_4$ with B, TiH_2, W or ZrNi, or
- Pb_3O_4 with B, Si, TiH_2, W or ZrNi.

The above mentioned deflagrating mixtures were used [63] in the range of 2-500 mg per 1 m of tube. The tube could be prepared from fluorinated hydrocarbons Viton® A, KEL-F® and VAAR®, a vinyl resin, and the like. Distinctive differences between DCs and shock tubes are visible also in the length a single piece. As mentioned above, usually the available length of a DC (up to approximately 200 m) can be far shorter than that of a piece of a shock tube, *i.e.* 400, 600, 800 and 3000 m long pieces are in use in blasting operations [64].

3.2 Detonating signal transmitting materials

Except for TNT, and pure PETN, other explosives could also be used in DCs for military and/or civil applications, *e.g.*:

- CL-20 [62],
- 3,3'-diamino-2,2',4,4',6,6'-hexanitrobiphenyl (DIPAM) [56],
- dibenzo-1,2,5,6-tetraazacyclooctatetraene (TACOT-TN) [65],
- bis(2,4,6-trinitrophenyl) sulphone [66],
- RDX, *e.g.* [62, 65, 67], as well as, in military applications, RDX crystals dyed with 1% of water soluble pink dye [29],
- RDX with tetryl [37],
- 1,1′-[(*E*)-ethene-1,2-diyl]bis(2,4,6-trinitrobenzene)) (hexanitrostilbene, HNS) [56, 62, 68, 69], as well as mixture of boron potassium nitrate with HNS [70],
- mercury fulminate was applied in Russian DCs in different compositions, *e.g.* with paraffin or with gelatin and tetryl [37],
- HMX, e.g. [62, 65], also with black powder [69] or with other pyrotechnic compositions [26],

– 90-97% PETN with 10-3% lead nitrate ($Pb(NO_3)_2$) and 0.1-0.2% red lead oxide (Pb_3O_4) [37],
– pentolite (PETN/TNT) [26],
– 2,2′,2′′′,4,4′,4′′′,6,6′,6′′′-nonanitroterphenyl (NONA) [48, 56],
– plastic bonded explosive PBXN-8 [71],
– PYX [72, 73],
– tetranitrocarbazol (TNC) [73].

It is worth noting that the incompatibility creates additional limitations in the use of explosives in DCs [74-76].

In some applications, the flow properties of the explosive material could be improved by rinsing with an aqueous solution of an anti-static or wetting agents, *e.g.* saturated, long chain or fatty alcohol sulphates [77] or 0.05-0.5 wt.% fumed silica (SiO_2, CAOB-O-SIL) [78]. It should be noted that DCs composed of a plurality of carbon nanotube structures coated on the outer surface with an oxidizing inorganic material, were also investigated [79]. In this case:

– nanotubes were in the shape of wires with diameters of 10-100 μm, straigtht or twisted in a helical manner, aligned along the axis of the fuse,
– the oxidizing coating could be made up of *e.g.* metal, metal oxide, metal or ammonium nitrates, and its thickness could be in the range 10-30 nm.

Metal powders can also be applied in the cord's core together with an organic explosive [62]. Despite the detonating properties not being presented in [79], they seem to be worth showing as an example of an application of nanotechnology in the transmission of an initiating impulse.

3.3 PETN DCs

As far as the characterization of explosive material in a DC is concerned, it has to be kept in mind that commonly used expressions like loading density and specific gravity are not useful in the case of DCs. All over the world, the quantity of explosive material introduced into the cord is given by its mass present in a unit length of 1.00 m. The general relationship between the VOD of PETN and its density is shown in Table 1. More precise data on DC geometry was presented by Srirajaraghavaraju [80], however these data (Table 1) refer only to a specific type of PETN DC.

Moreover, it is worth noting that there are known techniques which allow the VOD values to be to increased or decreased. Changes of VOD values are possible by, e.g.:

− subjecting the DC to elevated temperatures and pressure [81],
− inserting at selected locations within the hollow core, elongated, flexible blockage elements [82],

– adding *e.g.* phenolic microballoons (Barkley *et al.* [73]).

In general, the scatter of VOD values in the range of ±5% seems to be acceptable for manufacturers and users of industrial DCs [83]. This means that for VOD = 8000 m/s, acceptable scatter of results ought to be at the level of approximately 400 m/s. However, it is possible to reduce the scatter of VOD results. For example, Abrahamson and Huber [81] increased the average VOD and decreased the spread range of a PETN DC from 6275 ±175 to 8140 ±25 m/s. They subjected the DCs to a momentary hydrostatic pressure of 55,000 psi (379.2 MPa). This caused both an increase in the PETN density and a decrease in its density variations along the core.

Table 1. Relationships between PETN density and some features of PETN DCs

PETN	Loading density [g/m]	Diameter of PETN core [mm]	Outer DC diameter [mm]	PETN density [g/cm^3]	VOD [km/s]	Ref.
Crystalline	–	–	–	0.8-1.1	5-6	[84]
				1.1-1.4	6-7	
				1.4-1.7	7-8	
				1.76	8.650	[85]
in a DC with a polyethylene coating	3	1.8	3.7	1.32	–	[80]
	5.3	2.2	3.1	1.35	6.5	
	10	3.1	5.7	1.35	–	
In a metallic tube	–	–	–	~1.2	~6.3	[86]
				~1.45	~7.0	
				~1.65	~7.8	

From Table 1, one can see that the relationship between the loading density and the outer diameter is not obvious, *i.e.* a PETN DC with medium loading density (5.3 g/m) has the lowest outer diameter (3.1 mm). From the data presented by Pingua *et al.* [86], PETN DCs with the features presented in Table 1 are very close to those of practical importance in India, i.e. in earth excavation DCs where loading densities of 3.5, 5.5 and 10 g/m are used. Moreover, DCs with 3.5 and 5.5 g PETN/m loadings are in service in underground coal-mines as permitted explosives.

PETN DCs with loading densities of 20-49 g/m and a specific gravity of ca. 1.8. g/cm^3, composed of PETN with crystals in the range of 0.08-0.16 mm, were also taken into consideration in Poland in the 1990s [87].

Contemporarily, PETN DCs have many applications and to this end the content of PETN varies significantly, *i.e.* from 1 g/m in transfer fuses (without priming effect) to 100 g/m for cords designated for the initiation of ammonium nitrate – fuel oil (ANFO) charges (see Meyer *et al.* [14]). DCs with an explosive content of 170 g/m are also known [26]. Some examples of commercial PETN DCs are shown in Figure 1. Here the following labelling is used:

- in red – used in mines, in potentially explosive atmospheres of coal dust and/or methane,
- in black or white – used in non-coal mines and quarrying operations, for demolition and engineering work, as well as in surface and downhole applications,
- the figures depict a named series of DCs, *i.e.* ●/○/X –Daveycord [88], ■ – Nitrocord [83], ▲ – Primacord and Primaline [89], ♦ – Titacord [90].

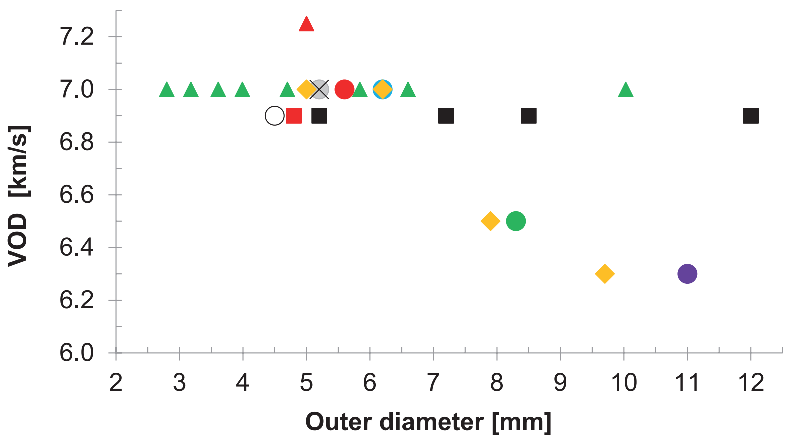

Figure 1. Trends in relationships between outer diameter and VOD of commercially available DCs

From Figure 1, one can see that commercially available methane PETN DCs usually have an outer diameter of ca. 5 mm and a VOD in the range 6.8-7.3 km/s, and that other types of DCs have a much larger diversity.

3.4 Plastic and thread sheaths

From a technological point of view, the easiest way to assure permissible properties of a DC is to modify its construction, *i.e.* especially the coating jacket, as this is limited only to changes in the non-explosive scope of a given technology. In general, a jacket composed of one layer of a coating material is possible, but multilayer construction of the cord ensures a high resistance to tension and abrasion whilst in use. Another reason for employing a number of different coverings for some kinds of DC could be, according to [91], the reduction of both the diameter and mass of the cord, while totally confining its explosive outcome. In general, it is worth stressing that a layout with a single solid explosive core through the center of a DC is not the only possible solution. For example, in military applications, DCs with a hollow core through the center of the explosive cord are not excluded [62, 69, 70, 92]. In the 1970s, for metal expansion applications, a DC encasing two explosive cores in a protective sheath [93] was patented. On the other hand, Garrison and Southern [91, 94], patented the layouts of a mild DC in which both a metallic sheath and an extruded plastic jacket are put together. Moreover, Preiss *et al.* [48, 95] recently patented DCs for perforating guns, in which there is an electrically conductive layer within a polymeric jacket. In perforating gun technology, there is also a known solution, patented by Bradley *et al.* [96], based on the coaxial incorporation of a fibrer optic cable into the sheath of a DC used for detonating such systems. The fibre optic cable may include one or more optical fibres encased in a shield. The main aim of applying both electrically and optically conductive structures is to enable an operator to communicate from the ground with at least one perforating gun located in a downhole.

Except for the most commonly known, circular cross-sectional shape, some kinds of DCs may have other forms, *e.g.* square, rectangular, triangular or N-polygonal enumeration [62, 97]. On the other hand, not only metal tubes but also spirally-wound thread-like metallic elements, could be employed as DC sheaths [1].

According to Świetlik and Duda [2] the first researches in Poland into the safety of PETN DCs against methane and coal dust mixtures with air, began in the 1960s. Świetlik and Duda [2] presented results of the VOD determination for the methane PETN DCs produced in Poland in the 1990s. The VOD for a brand new sample of this cord was 7250 m/s. The VOD results were different after thermal ageing, i.e. after 14 days at 50 °C the VOD decreased to 7116 m/s, however after 4 h in 75 °C the change was neglegible (result was 7248 m/s). The VOD of this cord, tested for sensitivity to underwater storage (6 h in room temperature at a depth of 2 m) also decreased – to 7126 m/s.

PETN methane DC is usually composed of, *e.g.* [2, 83, 87, 98]:

– an explosive core (usually crystalline PETN, however additives cannot be excluded, e.g. in the 1970s linear polysiloxanes could be applied according to [98]),
– 1 or 2 red thread(s) (core wire(s)) usually in the form of red band(s), placed inside along the DC's core or in the coatings,

– an inner coating (a textile layer(s) or a plastic tube), surrounding the core,
– a middle coating, composed of 2 other coatings, including 2-3 wound braids of cotton or viscose threads, sometimes separated by an asphalt and paper layers,
– outer textile or plastic (a polyvinyl chloride shielding with a flame retardant additive) coating.

In most references, the red threads inside the explosive core are used for identification purposes, however another explanation is that these threads ensure a more identical packing of the PETN crystals in the explosive core [34, 99]. Coatings can be prepared from a polyethylene band or polypropylene tape. The outer plastic coating can be made of a coloured polyvinyl chloride (PVC) shield. Other polymers are also possible, *e.g.* substantially amorphous chlorinated polyethylene having about 25-50 wt.% chlorine [3]. The applied colour is the identification mark of the type of a given cord. Also luminescent coated cords were patented in the 1960s [100]. An additive present in the outer coating, which could have an influence on the ability to ignite a mine's atmosphere, is a flame retardant, *e.g.* [3]. An additional layer, composed of a flame retardant, was patented in the 1970s [52]. According to [52], no flash can be observed during the detonation of a PETN DC if the layer of a flame quenching material contained inorganic salts, like:
− diammonium phosphate ($(NH_4)_2HPO_4$),
− sodium bicarbonate (Na_2CO_3),
− potassium chloride (KCl) or NaCl.

According to [3], antimony trioxide (Sb_2O_3) can also be used as a flame retardant in DCs. The most recently retrieved enumeration [62] of polymeric materials, suitable for DCs, includes among others:
– polytetrafluoroethylene (PTFE),
– copolymer of ethylene and trifluoroethylene, *e.g.* available commercially as HALAR® from Solvay,
– polypropylene,
– polyethylene,
– polyolefin,
– polyurethane.

Taking into consideration the complexity of the layout of PETN DCs, one should be aware that the thickness of some layers of a coating can be as small as 0.5 mm [8, 101]. On the other hand, thicknesses can also be in the range of over 1 mm, *e.g.* as for an outer sheath with the thickness of 1.2-1.4 mm obtained from polyvinyl chloride of a PETN DC [87]. In the case of methane PETN DC type 7, produced in Poland at the end of the 1990s, the whole thickness of the coating was 0.7 mm [2]. On the other hand, such a thin coating allows a significant reduction in impact sensitivity to be obtained, *i.e.* for the DC type 7 [2], impact sensitivity (minimum level of energy when detonation occurs) obtained in the BAM Fallhammer test (Kast apparatus) of the PETN core was 14.7 Nm, but that of a 5 cm long piece of this type of DC was 49 Nm. However, these values are not constant for all DCs and PETN used. This same manufacturer was producing another kind of DC from PETN with sensitivity to impact of 3 Nm [102].

4 Case Study

4.1 Materials

The same kind of crystalline commercial PETN was applied in all tested detonating cord samples. An outer thickness of the coating of the tested samples, as well as the presence of a flame retardant additive, are listed in Table 2. Samples T-4, T5-1, T5-N and T6 were of the same basis weight, i.e. of the same PETN mass per 1.000 m. Samples T5-2, T5-3 and T5-4 were of the same basis weight and outer thickness coating of 0.52 mm, with a flame retardant additive but different amounts of crystalline PETN were applied.

Table 2. Tested DC samples

<table>
<tr><th>Sample No.</th><th>Outer coating thickness [mm]</th><th>Flame retardant in PVC shielding</th></tr>
<tr><td>T4</td><td>0.40-0.45</td><td rowspan="5">YES</td></tr>
<tr><td>T5-1</td><td rowspan="5">0.52</td></tr>
<tr><td>T5-2</td></tr>
<tr><td>T5-3</td></tr>
<tr><td>T5-4</td></tr>
<tr><td>T5-N</td><td>NO</td></tr>
<tr><td>T6</td><td>0.60</td><td>YES</td></tr>
</table>

4.2 Test methods

4.2.1 Examination of safety against a methane-air atmosphere

Examination of safety against methane of a detonating cord was measured according to [21]. Control of the methane concentration (9.0 ±0.5% during the tests) in a face was conducted using the MSMR-4 Microprocessor Recording Monitoring System used for a continuous measurement. The test consisted in firing a single upright section of detonating cord of length 2 m suspended on hooks on the gallery's axis and observing if ignition of a previously produced methane-air mixture in the chamber (with a volume of 10 m^3) has occurred. A detonating cord is considered safe against a methane-air mixture, *i.e.* it could be further regarded as a candidate for a permissible item, if within 20 consecutive sample firings there was no ignition of the methane-air mixture.

4.2.2 Velocity of detonation

The VOD of a DC was measured according to [22]. A multichannel electric time counter was used with an accuracy of time measurement of 0.1 s. Dilation sensors (copper wire) were applied, in which cut-off of the electric circuit was caused by pressure of the front detonation wave propagating through the explosive. The determination of the VOD is based on the measurement of the propagation time of the face of the detonation wave placed between sensors in the explosive. Three sets of length 1.5 m were prepared. Each of the type of cord samples was tested 3 times. The first sensor was placed within a distance of 0.225 m from the end of the detonating cord, to which the detonator was attached. The second sensor was placing at a distance of 0.1 m from the first sensor.

4.2.3 Determination of the capability of detonation transmission between two DCs

In order to test the capability of transmission of detonation from one DC to another section DC, the standard [23] was used. Sections of DC of length 0.5 m were taken. Each of the type of cord samples was tested 5 times. In each test, to one end along the length of 0.01 m, there was fixed in parallel the end section of the second piece of this type of cord. To the end of the first DC, an electric detonator (initiating agent) was taped and to the end of the second DC, a cartridge of rock explosive was taped in order to obtain proof for the presence or lack of detonation of the tested set. The test of a DC is positive if in all five tests there was a detonation of the sample of explosive.

4.3 Results and discussion

For samples T-4, T5-1, T5-N and T6 an examination of safety against a methane-air mixture in the experimental gallery has been conducted. The results, presenting the percentage of ignitions of a methane-air mixture by the DC, is shown in Figure 2. An increase in the outer thickness coating of DC samples T-4, T5-1, T5-N and T6 lowers the inflammability of a methane-air mixture in the experimental gallery. Only sample T-6, with a thickened outer coating, fulfilled the safety requirements against a methane with air atmosphere during the tests. The lack of a flame retardant additive in sample T5-N caused an increase of 70%

in the percentage of ignitions of the methane-air mixture compared to sample T5-1 of the same thickness of outer coating wall and containing a flame retardant additive. The test results for the VOD for samples T-4, T5-1, T5-N and T6 are presented in Figure 3.

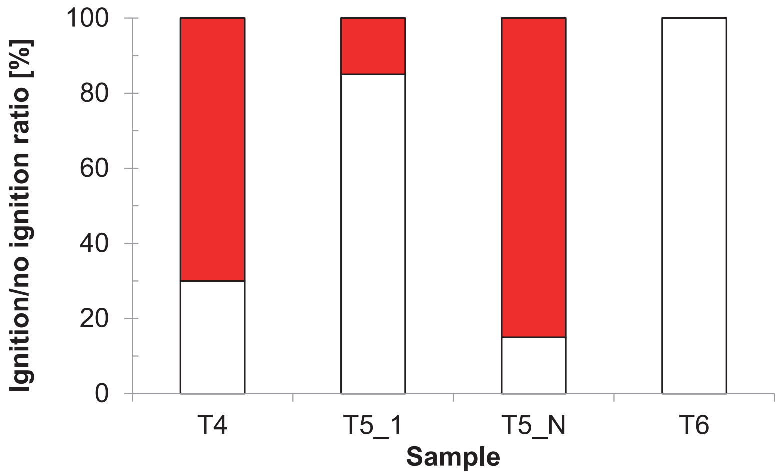

Figure 2. Test results of safety of DC samples T-4, T5-1, T5-N and T6 against a methane-air mixture (□ – no ignition, ■ – ignition)

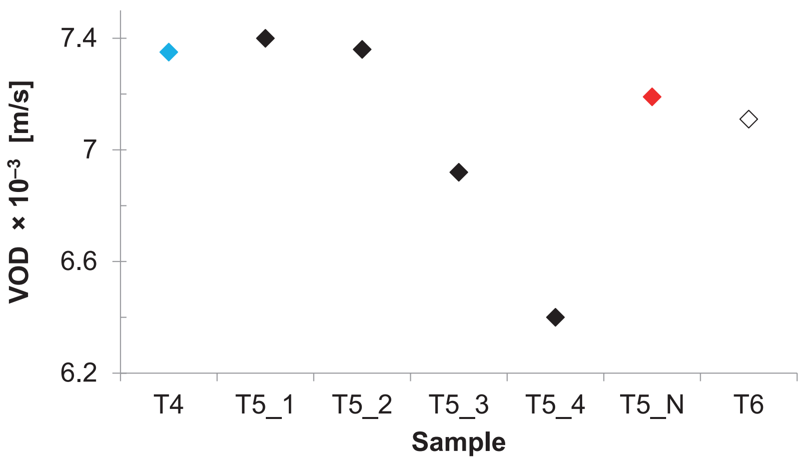

Figure 3. VOD results for the tested samples of the methane PETN DC

For each of the samples T-4, T5-1, T5-N and T6, a determination of the capability of transmission of detonation from one detonating cord to another DC was conducted. There were five tests in each case, during which there was transmission of detonation from one section of DC to another. The results are listed in Table 3.

Table 3. Results of capability of detonation transmission from one DC to another DC

Sample No.	Electric detonator	1st Section of DC	2nd Section of DC
T4	5/5*	5/5	5/5
T5-1	5/5	5/5	5/5
T5-N	5/5	5/5	5/5
T6	5/5	5/5	5/5

* Number before slash means quantity of detonations, number after slash means quantity of trials

The tests on samples T-4, T5-1, T5-N and T6 have shown their efficiency, within the scope of the determined blasting parameters, of VOD and a capability of transmission of detonation from one DC to another DC.

For each of the samples T5-2, T5-3 and T5-4, which are characterised by different pressing of the crystalline PETN in the DC’s core, an examination of safety against a methane-air mixture in the experimental gallery was conducted. Regardless of the changeable density of pressing of crystalline PETN in a DC’s core, none of above-mentioned samples of DC ignited the methane with air during a test in the experimental gallery.

The test results for the VOD of samples T5-2, T5-3 and T5-4 are presented in Figure 3. Samples T5-2, T5-3 and T5-4 were prepared with different pressing of crystalline PETN in the DC’s core, and exhibited different results of VOD. Sample T5_2 was characterised by a VOD between 6800-6950 m/s. The results for VOD tests of sample T5_1 were included in the range of 7100-7500 m/s.

For each of three samples T5-2, T5-3 and T5-4, a determination of the capability of transmission of detonation from one DC to another DC was conducted. The test results are listed in Table 4. Samples T5-2, T5-3 and T5-4 all transmitted detonation from DC to DC.

Table 4. Results of capability of detonation transmission between two DCs [24]

Sample No.	Electric detonator	1st Section of DC	2nd Section of DC
T5-2	5/5*	5/5	5/5
T5-3	5/5	5/5	5/5
T5-4	5/5	5/5	5/5

* Number before slash means quantity of detonations, number after slash means quantity of trials

5 Conclusions

- Because of its special commercial importance, the results of testing of DCs are not often published and the scope of tests is usually limited to those of commercial importance. Even if such results are published, they are strictly focused on individual parameters which are important for a given manufacturer. Finally, preparation of an exhausting comparison of properties of DCs provided to the market by different manufacturers is almost impossible. Finally, literature data are scattered among many sources, especially in patent publications.
- Thanks to their special features, DCs could be irreplaceable blasting items in some applications. Moreover, use in some applications in some outstanding branches of industry (especially oil and gas industry, military and space applications) makes them an important means of initiation. Finally, further development of DCs is necessary, however very complex problems to be solved will be encountered. This situation has been presented on the basis of the situation with methane PETN DCs, in a range of tests which have been carried out in order to improve their safety against firedamp in coal-mines.
- Presented in the Case study, tested samples have shown that methane PETN DCs, however different from the point of the outer diameter of the coating, the presence of a flame retardant in the coating, as well as the amount of crystalline PETN in the DC's core and VOD, can give similar results on inflammability of a methane-air mixture (9.0-9.5% methane) in an experimental gallery.

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