CHAF Workpackage 4 Report

(Workpackage leader: A. von Oertzen, BAM)

Title Literature review of fireworks compositions, propagation mechanisms, storage legislation and environmental effects

Containing Deliverable D4-1, *Types and Compositions of Fireworks Articles*
Deliverable D4-2, *Functioning Mechanisms of and between Fireworks Articles*
Deliverable D4-3, *Storage and Transport Regulations in EU Countries*
Deliverable D4-4, *The Effect of Fireworks on Health and the Environment*

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Authors A. von Oertzen (BAM), S. Myatt (HSL), D. Chapman (HSL),
R. Webb (TNO), M. P. van Rooijen (TNO), W. Colpa (TNO),
E. G. de Jong (TNO), J. de Ruiter (TNO)

Institutions BAM, Bundesanstalt für Materialforschung und -prüfung
Unter den Eichen 87
12205 Berlin, Germany

HSL, Health and Safety Laboratory
Harpur Hill
Buxton, Derbyshire, SK17 9JN
United Kingdom

TNO Prins Maurits Laboratory
Lange Kleiweg 137
PO Box 45
2280 AA Rijswijk, The Netherlands

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Executive Summary

This report is a literature review of the current state of knowledge of fireworks and fireworks hazards. It presents work to meet Deliverables D4-1 (types and compositions of fireworks Articles), D4-2 (Functioning mechanism of and between fireworks articles), D4-3 (Storage and transport regulations in EU countries) and D4-4 (The effect of fireworks on health and the environment) of the CHAF work program.

Firework compositions are discussed in the first section. This leads to an understanding of the variability in performance of various types of fireworks. Compositions used in report effects are highlighted as being the most energetic while other compositions are seen as providing a much lesser hazard in mass storage of fireworks. Individual types of firework are examined. Large devices such as report shells are identified as posing the largest hazard in bulk storage. Lesser, but still significant, hazards are predicted for similar compositions in Roman candles and rockets. Gradations in hazard are identified corresponding to UN hazard divisions 1.1, 1.3 and 1.4.

The second section reports the literature relating to the functioning mechanism of and between fireworks articles. In this the major propagation mechanisms for fireworks compositions are examined. The main stimuli identified are: fragment impact, heat and shock wave, each of which can lead to the functioning of pyrotechnic composition in the article or in an adjacent article leading to large-scale initiation. Consideration of the pyrotechnic compositions leads to a different ranking for the three mechanisms with different fireworks types. Thus with a report composition containing a metal/perchlorate mixture shock initiation is seen to be the main propagation mechanism. Such a mechanism is likely to afford a mass explosion. At a lesser hazard, blackpowder-based compositions are reported to be more likely to propagate via a flame mechanism. This is less likely to produce a mass explosion.

National legislation concerning the storage of fireworks for many European countries is considered in the third section. Many of the national regulations are based on a cube root of explosives content to determine “safety distances”, often written as $Q^{1/3}$. Different multiplying factors are then applied depending on the type of adjacent site (production buildings, residential housing, roads etc.). Commonly $22Q^{1/3}$ is used for residential dwellings. Special provisions are enacted in many countries either to allow lesser distances or in some cases to increase the safety distances depending on the perceived hazard or extenuating circumstances.

The final section deals with the environmental hazards posed by the use of fireworks. Toxic effects of the materials used in the manufacture and the likely reaction products from functioning fireworks are highlighted. These range from heavy metal poisoning from metals present for their colour effect to respiratory problems due to pyrotechnic fume (both particulate and gaseous). Finally, noise pollution is considered. While there is a short term problem from pyrotechnic fume at times of high usage (national celebrations) there is no literature evidence, as yet, of long term detriment to the environment.

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CHAF WP4 Literature review

Deliverable 4-1 Overview and interpretation of literature on types and compositions of fireworks articles

Date June 2003

Authors A. von Oertzen (BAM), S. Myatt (HSL), D. Chapman (HSL)

Summary

This is the first section (deliverable 4-1) of a literature study in the framework of a research project funded by the European Community on the "Quantification and control of the hazards associated with the transport and bulk storage of fireworks" which was given the acronym CHAF.

This paper focusses on the range of fireworks available in the EU and the compositions they contain. The types of firework are described, the primary effect explained, and data on their compositions and how these vary is presented. The depth of description varies according to the needs of the project. Novelty articles for indoor use are included in the review for completeness. They are, however, not described in such detail as for example the display shells and Roman candles which significantly contribute to hazards with regard to accidential ignition.

European standards for fireworks are in the process of being produced under CEN (Comité Européen de Normalisation) Technical Committee 212. Where these where available and suitable for the aims of the project, they have been analysed. Further information was gained from literature sources and company data.

Types and Compositions of Fireworks Articles

1 Introduction

One of the main goals of Work Package 4 (WP4) within the CHAF research project will be to identify and select fireworks for testing. The selected fireworks will be subject to various kinds of test including those using only a few articles on a small scale, or with the same articles on a larger scale. This also includes testing within the framework of the well established UN testing scheme (UN test series 6). Obviously these tests cannot cover all possible fireworks types and variants, but aim to provide a representative sample. Testing of a limited number of types of fireworks should reflect, as far as possible, the properties of many of the other sorts of fireworks which are available within the EU. Therefore it is essential to have an overview on the types of fireworks available and the variants that are possible within one type.

Quite clearly, not all types of fireworks have the same importance in the context of the research project. Some may not pose a high hazard when accidentially ignited, while others are only used and stored in very limited numbers.

The following sections are meant to be an extensive review of firework types and compositions. It is, however, not meant to be exhaustive on every aspect and variant of every type listed. The depth of coverage varies depending on the severity of the perceived hazard and thus the relevance to the research project.

Translations and synonyms are summarised in the Annex to this section. The firework terms in languages other than English are not of immediate importance to the research project. However, they represent a useful spin-off of the literature work done in this context and may even be helpful when interpreting labels from articles arriving from different countries. The three languages of the project partners have been selected in the first instance. In addition to English, German, and Dutch, another two languages are included. French has been included because of the frequent occurance of French in the context of the standardisation process at CEN, and Spanish has been included for Latin-America and Spain being major fireworks producing regions.

2 Compositions used in fireworks

The list of compositions reproduced here is meant to be an explanation and glossary to the following section where frequent references are made to generic composition types. Consequently, this list does not cover all variants of pyrotechnic composition but shows the compositions often used.

In the descriptions some constituents are often omitted when they are added in small amounts. Such constituents are not usually responsible for the primary effect or colour, but have to be added for technical reasons. Nonetheless, these components may be essential for the proper functioning of the composition or to improve the handling properties of it. Such chemicals are typically starch, resins, and paraffin. The compositions are listed in alphabetic order.

2.1 Bengal light compositions

The composition for a bengal flame has metal nitrate and potassium chlorate or perchlorate as the main components. The colour of the bengal flame depends on the metal nitrate used, and is green for barium nitrate and red for strontium nitrate. When a large fraction of sodium oxalate is used instead of potassium chlorate the flame colour can be made yellow. A blue colour can be obtained by using copper compounds such as copper carbonate together with potassium chlorate. Table 1 shows examples of compositions listed by Lancaster[1].

Table 1: Various bengal light compostions

Material	Red 1, content (%)	Red 2, content (%)	Green 1, content (%)	Green 2, content (%)
Potassium chlorate	20	-	16	-
Potassium perchlorate	-	16	-	15
Strontium nitrate	65	63.5	-	-
Barium nitrate	-	-	70	68.5
Shellac/ accaroid resin/ sawdust/ lampblack	15	20.5	13	15
Antimony metal powder	-	-	-	1.5
Parrafin oil	-	-	1	-

2.2 Blackpowder

Blackpowder is a mixture of potassium nitrate (75%), charcoal (15%) and sulfur (10%), however, the exact figures may vary in order to obtain slower or faster burning rates. Depending on the intended use blackpowder is available as a fine powder (also called meal powder) or as grains of up to millimeter size.

By adding small amounts of other chemicals to the primary blackpowder mixture modified compositions can be produced which either react more violently (by adding powders of metals, such as aluminum). Strictly speaking, these variants cannot anymore be called blackpowder.

2.3 Flame producing composition

For flame production various different mixtures exist and it is not possible to give a general formula. There are mixtures based on potassium perchlorate and another component which gives the colour (see a list of colour agents in section 2.8). This can be barium chlorate, strontium carbonate, or copper compounds for the colours green, red, or blue, respectively. A silver or white flame can be obtained from barium nitrate and aluminium mixtures. Lancaster[1] lists several examples as reproduced Tables 2-7, however many more variations exist and can be found in other texts[2-4].

Table 2: Blue flame composition

Material	Typical range of content (%)
Ammonium perchlorate	30-46
Potassium perchlorate	26-40
Copper carbonate	10-15
Accaroid resin and stearine	15-18

Table 3: Green flame composition

Material	Typical range of content (%)
Ammonium perchlorate or potassium chlorate	26-50
Barium nitrate or chlorate	35-55
Accaroid resin and stearine	12-20

Table 4: Red flame compositions		
Material	**Typical range of content (%)**	**variant, content (%)**
Potassium perchlorate	66-68	-
Potassium chlorate	-	13
Strontium carbonate	11-22	-
Strontium nitrate	-	66
Accaroid resin, shellac, or woodmeal	14-21	17
Charcoal	-	4

Table 5: Yellow flame composition	
Material	**Content (%)**
Potassium perchlorate	75
Accaroid resin or shellac	15
Cryolite or sodium oxalate	10

Table 6: White flame composition		
Material	**Variant 1, content (%)**	**Variant 2, content (%)**
Potassium nitrate	74	13
Potassium perchlorate	-	64
Sulfur	8	-
Orpiment	18	-
Antimony powder	-	64
Copal gum	-	10

Table 7: Silver flame composition	
Material	**Content (%)**
Potassium nitrate	15
Barium nitrate	45
Aluminium	35
Accaroid resin	5

Even though Lancaster lists the composition in Table 7 under flame compositions it is likely to show a sparkling effect and could also be mentioned under the sparks producing mixtures.

Blackpowder and additional potassium nitrate can be the basis for flame mixtures which are frequently used in fountains and gerbs. The blackpowder based flame compositions have similarities with some of the compositions above, however the colour range being limited from white to yellow. The following is an example from Lancaster[1]:

Table 8: Blackpowder based flame composition	
Material	**Content (%)**
Meal blackpowder	56
Potassium nitrate	22
Charcoal	11
Aluminium	11

2.4 Flashing (or strobe) compositions

Flashing or strobe compositions exhibit intermittent burning and consequently produce a flashing or twinkling effect. Many variants of twinkle-composition are possible based on ammonium perchlorate. Shimizu[4] suggests the following composition ranges (Table 9). Different colours can be obtained by substituting another metal sulfate for barium sulfate in these compositions.

Table 9: Flashing composition	
Material	**Typical range of content (%)**
Ammonium perchlorate	50-60
Magnesium/Magnalium	30-40
Barium sulfate	15
Potassium bichromate	5

2.5 Noise producing compositions

The general term noise in the context of fireworks includes both whistles and reports which are discussed in subsections 2.5.1 and 2.5.2.

2.5.1 Whistles

A whistling sound in fireworks is normally produced by an intermittently reacting composition pressed in a tube with one open end. This effect is only achieved with a select few pyrotechnic compositions. The reaction speed at the composition surface periodically increases and decreases in very short succession producing the whistle effect. It appears that all the fuels producing this effect contain a benzene ring.

Some examples of these compositions are mixtures of 70% potassium perchlorate and 30% potassium benzoate, Conkling[2] and with similar proportions in Lancaster[1]. A variant with potassium salicylate instead of the potassium benzoate is said to be hygroscopic making articles with this composition hard to store for extended periods of time. Other mixtures which appear to be less frequently used are based on 75% potassium chlorate and 25% gallic acid. The first whistles were based on picric acid and salts made from this acid. Futher details about the physical and chemical phenomena responsible for whistle effect are described in for example Podlesackand Wilson[5].

2.5.2 Report compositions

The report composition most widely used is a mixture of potassium perchlorate and aluminium powder. Variants exists which have barium nitrate, sulfur, and aluminium powder as constituents. Both compositions have an ignition temperature above 360°C and are only moderately sensitive to friction[6]. They are, however, fairly sensitve to shock ignition and show explosive behaviour even under weak confinement. Furthermore, these compositions propagate detonation[6]. Three compositions from the literature[1,3] are shown in Table 10.

Table 10: Report compositions

Material	Variant 1 content (%)	Variant 2 content (%)	Variant 3 content (%)
Potassium perchlorate	50	66	-
Aluminium powder	23	34	23
Barium nitrate	-	-	68
Sulfur	-	-	9
Antimony trisulfide	27	-	-

Often mixtures with potassium chlorate instead of perchlorate are included in the listings. However, because of their very low ignition temperatures, which increase the explosive hazards it is suggested that such compositions should not be used. Perchlorate compositions produce similar effect without the enhanced risk. Similar compositions are also found in the book by Shimizu[4].

Report compositions are also referred to as flash-report composition due to the fact that a bright flash of light is produced. The effect can be modified to give more light at the expense of noise by using the report compositions described in Table 10 but increasing the fraction of aluminium considerably.

2.6 Rocket propellants

The composition of rocket propellants is very similar to blackpowder, i. e. potassium nitrate, sulfur and charcoal but with a higher proportion of charcoal. A range of compositions proposed by Shimizu [4] is shown in Table 11.

Table 11: Rocket propellants	
Material	**Typical range of content (%)**
Potassium nitrate	59-64
Charcoal	20-31
Sulfur	8-13
Blackpowder	0-12

2.7 Spark producing compositions

Sparks are produced when particles are ejected from the primary source of effect and these particles continue to react, often involving atmospheric oxygen, as the particle flies through the air. The duration of the spark effect depends very much on the size of the particle, but also on the kind of particle. Grains of charcoal produce orange coloured sparks, iron particles produce yellow to white sparks and aluminum, titanium, and aluminum-magnesium-alloy particles produce white sparks.

The spark producing particles have to be embedded in some other pyrotechnic composition which provides burning and ejection of the particles. This is often achieved by using blackpowder. Table 12 lists a composition based on a blackpowder-like mixture presented by Lancaster [1].

Table 12: Spark composition	
Material	**Typical range of content (%)**
Potassium nitrate	55
Sulfur	9
Hemp coal	13
Coated iron powder	23

Sparks can also be produced by using specialised types of charcoal which will form glowing particles as they are ejected from the article. Table 13 lists the composition ranges taken from examples by Shimizu[4] and Lancaster[1]:

Table 13: Sparks composition	
Material	**Typical range of content (%)**
Potassium nitrate	36-61
Sulfur	22-34
Different types of charcoal	16-42

2.8 Star compositions

Formulation of star compositions is a complex subject. The typical fireworks star is based on a fuel oxidiser mixture with additional binder, colour agent (if not a white star) and in the more modern formulations an organic chlorine source.

Typical fuels could be carbon or in the more modern compositions metal (aluminium, magnesium or magnalium alloy). Oxidisers are nitrate, chlorate or perchlorate (the latter two additionally being chlorine donors). Nitrate oxidisers are often used where a particular colorant is required e.g. strontium nitrate in a red star or barium nitrate for a green star.

Colour agents generate unstable high energy species which have appropriate electron energy changes to give emission at desired wavelengths for the required colour. Typical materials are listed in Table 14.

Table 14: Commonly used colour agents[7]		
Colour	**Colour Agent**	**Formula**
Red	Strontium carbonate	$SrCO_3$
	Strontium nitrate	$Sr(NO_3)_2$
	Strontium sulfate	$SrSO_4$
Green	Barium chlorate	$Ba(ClO_3)_2$
	Barium nitrate	$Ba(NO_3)_2$
	Barium sulfate	$BaSO_4$
Blue	Copper(II) carbonate	$CuCO_3$
	Copper(II) oxychloride	$CuO.CuCl_3$
	Copper (II) oxide	CuO
Orange	Calcium carbonate	$CaCO_3$
	Calcium sulfate	$CaSO_4$
Yellow	Cryolite	Na_3AlF_6
	Sodium nitrate	$NaNO_3$
	Sodium oxalate	$Na_2C_2O_4$

Lancaster[1] reports typical Chinese red stars as having the following compositions, shown in Table 15.

Table 15:Red star compositions	
Material	**Typical range of content (%)**
Potassium perchlorate	30-60
Magnalium	15-30
Strontium carbonate	10-15
Parlon $(C_2H_3Cl)_n$	6-14
Accariod resin	5-8
Dextrin/rice starch	4-5

Similar formulations replacing strontium carbonate with a barium compound would produce corresponding green stars, or replacing strontium carbonate with a sodium compound would produce yellow stars. Stars can produce a flitter or glitter effect when the contained aluminium burns as flake or droplet, the latter produced during an intermediate melting stage of the composition. Such stars can be obtained by the using the compositions in Table 16.

Table 16: Glitter star compositions[2]		
Material	**Gold glitter** **Typical content (%)**	**White glitter** **Typical content (%)**
Potassium nitrate	55	55
Aluminium powder	5	-
Atomized aluminium	-	10
Sulfur	8	10
Charcoal	8	10
Dextrine	4	-
Antimony sulfide	14	-
Iron oxide	-	5
Barium carbonate	-	5
Barium nitrate	-	5

Long traces of light behind the stars can be obtained by a larger fraction of charcoal by which so called willow stars are obtained. The compositions proposed by Shimizu[4] are shown in Table 17.

Table 17: Star compositions	
Material	**Typical range of content (%)**
Potassium nitrate	35-55
Sulfur	6-12
Pine charcoal	33-50
Rice starch	5-8

3 Listing of individual types of fireworks articles

This section describes types of fireworks with the following information: the name, its main components and design, and the kind of effect under conditions of normal operation. The more important types of fireworks are described with additional information concerning the range of sizes or amount of charge typically found and variations in the type of pyrotechnic composition included. Details of pyrotechnic compositions are given in the previous section and can also be found in the paper on reaction mechanisms (deliverable 4-2). Wherever it seemed relevant a remark on the density of the explosive is added. The less hazardous fireworks articles as they are mentioned in the CEN Standards[8] are included for completeness. Their descriptions can be found in the Standards. The information is complemented by many details from literature on fireworks[1-10].

Within the following listing fuses, time fuses, ignitor cords, and quick matches do not appear. They are not fireworks in a strict sense, however, they may be part of a fireworks storage and they are frequently used in the set-up of a fireworks display. The composition used is essentially blackpowder with less potassium nitrate for a slower burning. Fuses would normally not burn violently but rather show a slow and delayed reaction which partly stays enclosed in the yarn wrapping of the fuse. The quick match, in contrast, should be considered hazardous in case a larger amount is packaged densely. Through confinement in a dense package the gun powder from the quick match may react instantaneously leading to effects similar to having a package of blackpowder with the same mass as the explosive content of the quick match.

3.1 Aerial wheel

An aerial wheel consists of tubes containing propellant charges and sparks-, flame-, and/or noise-producing pyrotechnic compositions. The tubes are fixed to a supporting ring. The aerial wheel performs concurrently rotation and ascent with emission of sparks and flames, and produces a visual and/or aural effect in the air. Due to the design characteristic the density of explosive is relatively low. Flash and report compositions are normally not used in aerial wheels.

3.2 Banger

A banger is a non-metallic containing blackpowder which produces a report. The amount of explosive is typically up to 10 g which may be ignited by a fuse or friction head. Bangers with other compositions than blackpowder are considered flash bangers. The regular banger, discussed here, produces its report by bursting the case.

3.3 Battery

A battery is an assembly including several elements, each of the same type, with one point of ignition. Construction and effects are according to the individual elements of the battery.

3.4 Bengal flame

A tube containing slow-burning pyrotechnic composition with the purpose of emitting a coloured flame is called a bengal flame. The density of explosive is relatively high. On the other hand, the typical pyrotechnic composition for bengal flames is not very sensitive. Its burning properties are moderate even under conditions of confinement. Bengal flames can include up to several kilograms of pyrotechnic mixture.

3.5 Bengal match or stick

A short wooden stick partially coated (along one end) with slow-burning pyrotechnic composition for producing a coloured flame and sparks. The bengal match has a dot of friction-sensitive pyrotechnic composition at the tip. Bengal matches or sticks are designed to be held in the hand. The properties of the pyrotechnic composition are as described for the bengal flame.

3.6 Crackling granules

These consist of a bag or other container made out of paper or plastics enclosing small granules of pyrotechnic composition to produce a crackling sound. The crackling granules are ignited via a fuse. Usually crackling granules are a small article with only a few grams of pyrotechnic composition.

3.7 Double banger

Two portions of blackpowder are contained in a non-metallic tube and are connected by a delay fuse. The double banger produces two reports one after the other. See also section 3.2 banger.

3.8 Flash banger

A non-metallic case containing metal-based pyrotechnic composition, with a friction head or a fuse at one end, separated from the flash charge by a delay fuse. A flash banger produces a report and a flash of light. Flash bangers may contain two types of flash composition, either a nitrate/metal- or a perchlorate/metal-composition. Typical amounts of pyrotechnic composition are in the range of 0.1 g to 5 g of perchlorate/metal-composition or in the range of 0.2 g to 10 g of nitrate/metal-composition.

3.9 Flash pellets

These are pellets of intermittently-burning pyrotechnic composition producing multiple flashes of light. The explosive content of a single flash pellet usually lies below 20 g. The composition consists of strontium or barium nitrate, aluminium-magnesium alloy, and potassium perchlorate. Data on sensitiveness were not available, however the last two components form a typical flash composition, thus the properties of the flash pellet composition could also be fairly friction and impact sensitive.

3.10 Flying squib

A flying squib is a tube made out of paper or plastics, with a choke, containing gas- and sparks-producing pyrotechnic composition of several grams. The flying squib performs a motion on the ground and emits sparks, with or without a report.

3.11 Fountain

Fountains contain sparks- and flame-producing pyrotechnic composition in a non-metallic case. A fountain is designed to be placed on the ground, or to be fixed in the ground, or to be fixed to a support. While fountains for placement on the ground can have as much as 1 kg of pyrotechnic composition, there also exists a hand-held type with typically not more than 15 g. The same article which is mounted on some kind of support rather than on the ground or held in the hand is called a gerb.

3.12 Ground spinner

A ground spinner is a non-metallic tube or consists of several such tubes containing gas- and sparks-producing pyrotechnic composition which are fixed on a ring. The pyrotechnic may include a noise-producing composition. The ground spinner performs a rotation which can also be interrupted by a jumping motion while emitting sparks and flames. Ground spinners typically contain up to 25 g of pyrotechnic composition.

3.13 Jumping cracker

A jumping cracker consists of a paper tube containing blackpowder, folded back on itself several times and bound together. It produces reports in succession, with jumping motions. A jumping cracker contains several grams of explosive.

3.14 Lancework

These consist of a large number of lances mounted on a frame in a pattern (shapes, letters) and fused together for instantaneous ignition. Due to its construction lancework has a very low density of explosive matter. The pyrotechnic composition of lancework is the same as for fountains, i.e. flame and sparks producing compositions.

The individual items of lancework, the lances, are often also called flares.

3.15 Mine

A mine is a mortar (tube closed at one end) containing propellant charge and pyrotechnic units, and designed to be placed on the ground or to be fixed in the ground. It ejects all the pyrotechnic units in a single burst producing a widely dispersed visual and/or aural effect in the air. Mines may contain report and star effects as well as flame and spark producing compositions.

The size of mines can reach up to 400 mm and they can contain more than a kilogram of pyrotechnic composition. During storage or transport the mine, which contains the propellant charge and pyrotechnic units, may be handled separate from the mortar. If this is the case large numbers of mines can be packed closely together for storage or transport which means that ignition between articles can take place much more readily. It is evident that the density of pyrotechnic composition is relatively high, and mines exhibit similar hazard to shells and Roman candles.

3.16 Novelty matches

The novelty match looks like a normal match but has a dot of pyrotechnic composition. It is designed to be held in the hand and produces a report and/or visual effect. Because these matches contain such a small amount of pyrotechnic they are of minor importance to the research project.

3.17 Party popper

A device operated by a pull-string with an abrasive surface in sliding contact with a friction-sensitive pyrotechnic composition is called a party popper. It is designed to be held in the hand and produces a report while ejecting streamers and/or confetti. Because this article contains such a small amount of pyrotechnic it is also of minor importance to the research project.

3.18 Percussion cap

Percussion caps are used in toy weapons to produce a report. The pyrotecnic composition, usually several milligrams of a composition consisting of chlorate or perchlorate and sulfur[10], is contained in a non-metallic envelope or cup. The report is produced when the device is hit. Due to the small quantity of explosive in each unit the overall explosive density is very low.

3.19 Rocket

Rockets are constructed as a tube containing pyrotechnic composition and/or pyrotechnic units. A stick or other means for stabilisation of flight, such as fins, are attached to the tube. Rockets may also consist of a cylindrical rocket motor and an attached head to hold the effect load. Rockets are designed to be propelled into the air. After an ascent, with or without additional visual and/or aural effects, the rocket produces visual and/or aural effects in the air.

Rockets, especially for professional fireworks, can have a considerabe amount of pyrotechnic composition up to several hundreds of grams. The effect charge can include flash and report compositions, which in turn can be very sensitive to impact or friction. Frequently the rocket head contains stars which are dispersed by a small bursting charge.

The density of explosive matter depends very much on the kind of packaging. Packages of sticked rockets usually have a region where the rocket heads are close to each other. A larger part of the package where the sticks are, may be essentially an empty region. Packages of unsticked rockets have a constantly high density of explosive which corresponds approximately to the density only present in the region of rocket heads for the sticked rockets.

3.20 Roman candle

Roman candles consist of a tube containing a propellant charge and a pyrotechnic unit or containing alternating propellant charge, pyrotechnic unit and transmitting fuse. The roman candle ejects the pyrotechnic unit(s), producing a visual and/or aural effect in the air or respectively a sequence of such effects. As has already been stated for rockets, Roman candles (especially in the case of professional fireworks) can have a considerable amount of pyrotechnic composition up to a few kilograms and can include flash and/or report compositions. The typical calibres of Roman candles range from around 10 mm to 100 mm.

Since the tube has to withstand the pressure during the ejection of the effects it is usually fairly robust even when made out of paper- or fibreboard-like material. In packages a high density of articles can be achieved, possibly leading to critical conditions regarding density of explosive in combination with strong confinement.

Similar items containing only a single effect are referred to as shot-tubes. They are designed for incorporation into batteries and combinations and contain less explosive than Roman candles of similar calibre.

3.21 Shell

A shell is a device containing a propellant charge, a delay fuse, and a bursting charge with pyrotechnic unit(s) or loose pyrotechnic composition, and is designed to be projected from a mortar (tube closed at one end). The bursting of the shell case at height then leads to ejection of the pyrotechnic units, thereby producing visual and/or aural effect(s). Shells exist in a huge number of varieties including different colours, colour changes, nested effects being released with temporal delay, and with reports and/or flashes. Accordingly the variety of compositions used include almost any possible type of pyrotechnic composition.

Generally shells have diameters in the range 38-500 mm. Larger shells are rather rare. A rough estimate of the explosive content of shells depending on the calibre can be made, which is approximately 300 g of net explosive content for a 100 mm diameter shell. The cubic relation has to be taken into account and a 200 mm shell could have around 2400 g of explosive content. However, apart from the amounts, the type of composition should always be considered carefully in terms of impact and friction sensitiveness.

Report and flash shells, or both effects combined, have to be considered due to their hazard independent of size. The sensitiveness of the report composition to impact ignition makes report shells exhibit mass explosive behaviour, no matter whether there are many small calibre shells or only few large calibre shells. Shells with colour effects only and no report composition, but of large calibres can contain a bursting charge almost reaching 1 kg and are therefore already very dangerous as a single article.

As a special variant cylindrical shells exist where a succession of effect compartments are stacked one on top of another forming a cylindrical shape. Even within one of these compartments, further sub-units may be included which after being deployed function with a time delay and eject more stars. Obviously for these special shells the above formulated size-mass relation is not applicable.

3.22 Snap

Snaps are two overlapping strips of cardboard or paper, or two strings, with a friction-sensitive pyrotechnic composition in sliding contact with an abrasive surface. A report is produced when the device is pulled apart. Snaps are a type of fireworks-toy and usually have several milligrams of silver fulminate composition[10].

3.23 Sparkler

A sparkler has a wire of up to 75 cm length partially coated with slow-burning pyrotechnic composition. Sparklers may have an ignition tip and emit sparks, with or without aural effect. Usually sparklers are to be held in the hand. The typical sparkler composition being a nitrate and small iron chips is very insensitive to all kinds of igniting forces.

3.24 Spinner

A spinner is very similar to a ground spinner except that aerofoils are attached which allow the spinner to perform an ascent during rotation.

3.25 Table bomb

A table bomb can be considered a fireworks toy and has a paper, cardboard or plastics tube with firm bottom and closed top, containing a propellant charge and non-pyrotechnic objects which are ejected.

3.26 Throwdown

A throwdown functions when thrown on the ground and produces a report. It consists of an impact-sensitive pyrotechnic composition and grains of inert material wrapped in tissue paper or foil.

3.27 Waterfall

A waterfall is constructed by placing a long series of fountains suspended upside-down, usually from a bridge-like construction. When ignited the firework produces long-lasting sparks that resemble a waterfall. The pyrotechnic composition for waterfalls being a nitrate, metal-powder, and some sulfur, is not very sensitive. In a package where the elements of the waterfall are folded densely together a considerable amount (several kilograms) and density of explosive may be present.

3.28 Wheel

An assembly including a non-metallic tube or tubes containing pyrotechnic composition and provided with a means of attaching it to a support so that it can rotate is called a wheel. During operation it emits sparks and flames, with or without aural effects. The compositions used are sparks and flame producing compositions. Due to its construction the overall density of explosive is not very high.

3.29 Whistler

A whistler is constructed as a non-metallic tube containing pressed, whistling pyrotechnic composition and may have a report-producing pyrotechnic composition. It moves in the air or on the ground while producing a whistling sound with or without sparks and with or without a report.

4 Summary and discussion

In terms of importance to the research project the types of fireworks articles can be grouped into a number of distinct categories. Novelty articles, where the pyrotechnic composition is only present in very small amounts in order to produce a limited motion of elements, e.g. flitter being ejected, or in order to produce a sound, which are designed to surprise the user of such articles. These are party poppers, snaps, table bombs, and the like. They have a very low overall density of explosive and are unlikely to add to the hazard of larger amounts of fireworks. Accordingly these articles are quite often assigned a hazard division 1.4S (see UN classification scheme for explosives). Testing of such articles will not be necessary in the framework of the CHAF research project.

A number of fireworks types exist where every single article has very hazardous effects if ignited outside the area of a professional fireworks display. These are shells, Roman candles, mines, and rockets containing flash and report composition. Their hazards are beyond doubt. However, it may be of interest to investigate package designs or methods of artificially reducing the density of such articles (by using spacers), in order to limit the explosive effects to such a degree that the worst case reaction, i.e. the quasi simultaneous explosion of a whole storage compartment, can be avoided. Fireworks types that exhibit different explosive effects depending on their packaging or density would be of particular interest for studying the conditions which make the propagation possible, and for finding conditions under which the fast propagation of ignition does not proceed.

In the middle range between the two extremes outlined above are articles such as fountains, lancework, mines, bangers, starburst rockets, and wheels. Also the fuses and cords used to connect display fireworks can be taken to this group. These articles are often considered to be low hazard, at least not comparable to flash and report articles, but can under appropriate conditions considerably promote the ongoing reaction, or even participate at an equivalent level with flash and report articles in a quasi simultaneous explosion of a mixed storage depot. That is, such articles from the middle range should be characterised properly with respect to their intrinsic behaviour, but will also be subject to combined investigations where the ignition is transferred from more explosive articles to these, and where the ignition is then back-transferred to articles of the most hazardous kind.

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Annex

Translation of types of fireworks into different languages

English	Dutch	German	French	Spanish
Aerial wheel	Luchtwiel	Steigende Krone	soucoupe volante	rueda aérea
Banger	Knalvuurwerk	Knallkörper	pétard à mèche	trueno
Battery	Batterij	Batterie	batterie	bateria
Bengal flame	Bengaals vuur	Bengalfeuer	feu de bengale	bengala de tubo
Bengal match or stick	Bengaalse lucifer	Bengalholz bzw. -fackel	allumette ou baguette bengale	bengala de cerilla o de palo
Crackling granules	Knetter granules	Knatterartikel	crépitant	gránulos crepitantes
Double banger	Dubbelslag	Doppelschlag	pétard aérien	trueno doble
Flash banger	Knalvuurwerk met flits	Blitzknallkörper	pétard à composition flash	trueno
Flash pellets	Stroboscoop	Blitztablette	clignoteur pyrotechnique	tableta intermitente
Flying squib	Zwermer	Schwärmer	serpenteau	serpiente
Fountain	Fontein	Fontäne	fontaine	fuente
Ground spinner	Grondbloem	Bodenfeuerwirbel	tourbillon	torbellino
Jumping cracker	Zevenklapper	Knallfrosch	pétard sauteur	correcamas
Lancework	Lichtjes of zunders	Lichterbilder	-	figuras de lucería
Mine	Vuurwerkbom	Feuertopf	pot à feu en mortier	surtidor
Novelty matches	-	Scherzzündholz	allumette détonante	-
Party popper	Scherts-item	Party-Knaller	party popper	lanzador de confetis
Percussion cap	Klappertje	Amorce	amorce	pistón de percusión
Quick match	Gebuisde lont	gedeckte Stoppine	-	mecha de rápida
Rocket	Vuurpijl	Rakete	fusée	volador, cohete
Roman candle	Romeinse kaars	Römisches Licht	chandelle Romaine	candela romana
Shell	Granaathuls	Feuerwerksbombe	bombe d'artifices	carcasa
Snap	Trektouwtje	Knallziehband	pétard à tirette	-
Sparkler	Sterretje	Wunderkerze	cierge magique	vela milagro
Spinner	-	Wirbel, steigend	tourbillon volant	torbellino
Table bomb	Tafelvuurwerk	Tischfeuerwerk	bombe de table	sorpresa japonesa
Throwdown	Knal-erwt	Knallerbse	pois fulminant	bombeta
Waterfall	Waterval	Wasserfall	-	cascada
Wheel	Waaier	Rad	soleil	rueda
Whistler	Luchthuiler	Luftheuler	pétard siffleur	silbador

CHAF WP4 Literature review

Deliverable 4-2 Literature review of the functioning mechanisms of and between fireworks articles

Date June 2003

Authors M. P. van Rooijen (TNO), R. Webb (TNO), W. Colpa (TNO), E. G. de Jong (TNO), J. de Ruiter (TNO)

Summary

CHAF (Quantification and Control of Hazards associated with the Transport and Storage of Fireworks) is an EU 5th framework project by HSL (UK), TNO (The Netherlands) and BAM (Germany). Its aims are to obtain a better understanding of the conditions that give rise to explosions in packaged fireworks under transport and storage conditions and to improve classification methods for fireworks. Work package 4 is focussed on a review of the literature.

This report is on the second task (4-2) in that work package and focuses on the reaction mechanisms within and between fireworks articles. A review of the literature is presented as well as a general method to approach the problem of selecting fireworks for the experimental workpackages and primarily the benchmark testing.

Functioning Mechanisms of and between Fireworks Articles

1 Introduction

The objective of work package 4 is *"to define the current state of knowledge and research, and the regulations in different EU countries with regard to fireworks, reaction mechanisms, storage and impact on the environment. The WP also has a critical role in feeding into WP6 on the selection of fireworks for the initial tests"*

This review will cover task 4-2: Literature review of Fireworks – Functioning mechanisms of and between articles. The aim of this task is defined as follows: *"The literature relating to research on the reaction mechanisms taking place in fireworks after ignition as well as between adjacent fireworks articles will be reviewed."*

This task is done in preparation for the benchmark testing, and the small- and medium-scale tests. Before small-scale tests can be developed, knowledge is required about the behaviour of firework articles in the propagation of an explosive reaction. For example, the performance of packaged pyrotechnics ('non ideal' explosives) in a fire will depend on a number of parameters (type of firework, its explosive content, the loading density in storage, (self)confinement, the role of packaging, total amount of fireworks involved in the fire, etc.).

Depending on these parameters one or several reaction mechanisms could be the major driving force on the propagation of the reaction through the firework or packaged articles.

In order to discuss the reaction mechanisms which are responsible for the propagation of the explosive reaction one could use two approaches. One approach is to select groups (families) of firework articles and discuss which will be the key reaction mechanism in propagation of the reaction depending on their explosive content and construction.

The second approach is to discuss possible reaction mechanisms in the propagation of an explosive reaction. By relating pyrotechnic sensitivity parameters to the different mechanisms one could rank the probability that a certain reaction mechanism will be responsible for the propagation of the reaction. The last approach was chosen in this literature survey.

From literature it is evident which initiation mechanisms can start an explosive reaction in pyrotechnic compositions. In Figure 1 some, but not all, of the <u>accidental</u> initiation sources are listed. This review will not focus on accidental initiation but on propagation of the reaction. For the propagation of the reaction three major effects (stimuli) can be identified in literature. These effects, which are shown schematically in Figure 1 are:

1. Fragment impact
2. Heat
3. Shock waves

If a “stimulus” impacts on an article, the article will respond to this stimulus, possibly leading to the initiation of the article. For example a fragment which impacts (stimulus) a shell can cause initiation by impact, friction or heat (in case of a hot fragment). The stimuli can be attenuated or enhanced by external conditions like confinement, packaging or the orientation of the articles in the packaging.

The time effect is also an important parameter. Multiple initiations at the same time can enhance the effect, and thus the stimulus on an adjacent article. Furthermore, the sensitivity of some compositions can increase when different stimuli act on the pyrotechnic composition. This is for example the case for the impact sensitivity of burning surfaces[1]. The mechanisms and their interactions have been visualized in Figure 1.

A complicating factor is that explosive reactions may accelerate under certain circumstances leading to unexpectedly violent behaviour. In order to understand this phenomenon, an insight in the reaction mechanisms is necessary.

In the next section the different initiation mechanisms are discussed and an overview is given of the sensitivity of different pyrotechnic mixtures for these types of initiation.

Section 3 will give an overview of literature which describes the research into the propagation of an explosive reaction in pyrotechnic articles.

The authors felt that, in general, normal controlled functioning of fireworks was outside the remit of this report. Having stated that, in Annex A a brief description is given of the normal reaction mechanisms of pyrotechnic compositions.

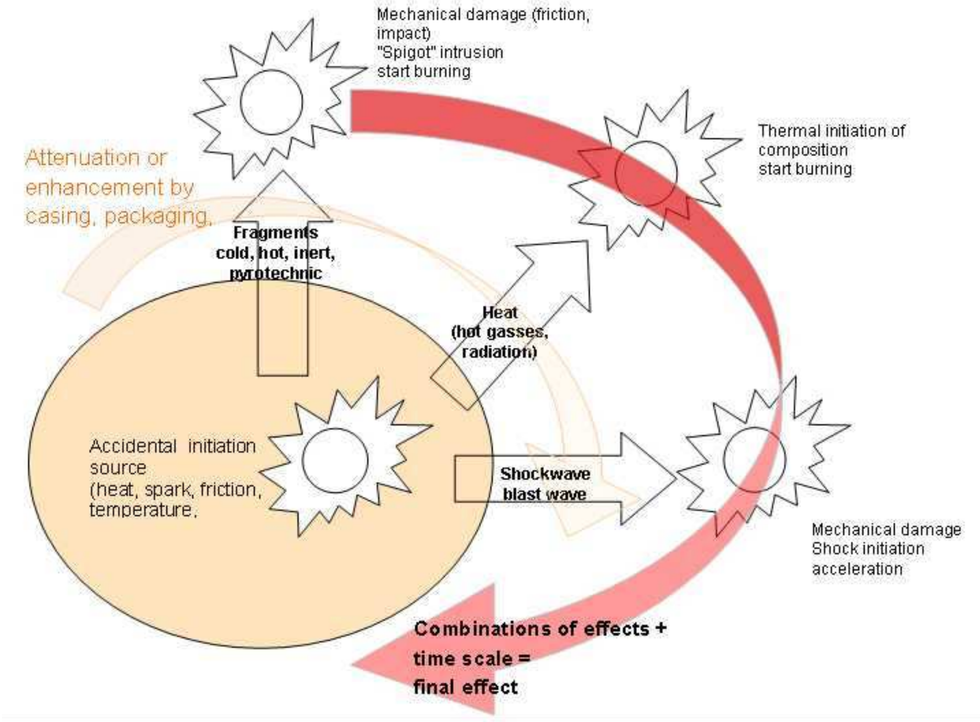


Figure 1: Schematic overview of reaction mechanisms responsible for explosive propagation in pyrotechnic articles

2 Mechanisms of propagation of initiation

This section describes the mechanisms of propagation for pyrotechnic compositions in general, as found in literature sources.

2.1 Mechanical sensitivity

In relation to pyrotechnics no fundamental research on mechanical initiation phenomena has been found in the literature studied. However, the initiation of high explosives has been investigated thoroughly. Explosives which are subjected to high pressure shock waves can initiate immediately. This kind of initiation is often referred to as SDT (Shock to Detonation Transition). Numerous conditions exist under which an energetic material is subjected to loads and load rates well below that of SDT but which still results in an energetic response. Field [2] lists initiation mechanisms most likely to manifest under mechanical deformation as:

1. Adiabatic compression of trapped gas
2. Viscous heating of material rapidly extruded between impacting surfaces or grains
3. Friction between impacting surfaces, the explosive materials and/or grit particles in the explosive layer
4. Localized adiabatic shear of the material during mechanical failure

In standardized sensitivity testing it is impossible to distinguish between the different initiation mechanisms. Although tests have been defined for, for example impact sensitivity, the mechanism involved in the initiation of the material will not be limited to the impact (adiabatic compression, viscous heating). By the movement of the particles in the composition during the test, friction will also be present. For this reason it is impossible to relate the test results obtained by different test methods directly to a mechanism as listed by Field[2]. For the same reason the test values of tests which determine the same sensitivity (for example all impact tests) can not be directly related to each other. Although the test results obtained with the BAM fallhammer test and the Bureau of explosives impact machine can both be expressed in Joules they have no direct correlation, because of the different test set-up. The ranking of pyrotechnic substances tested with the same apparatus can be compared with the ranking obtained with another apparatus. Often, reference substances are used to allow comparison between different test methods. This ranking will indicate the sensitivity of the material for the stimulus tested. In the following paragraphs the test methods in which the mechanical sensitivity of pyrotechnic substances can be tested are listed. Tables with test results obtained from such test are listed in Annex B.

2.1.1 Impact sensitivity

A composition can be initiated by a shock generated by the impact of a fragment. Not only is the impact sensitivity of the pyrotechnic composition an important parameter in this case, but also the type and thickness of the casing material. The impact can be attenuated by the casing material in such a way, that the pyrotechnic composition will not initiate. When the impact of the fragment deforms the casing of the pyrotechnic article, other (internal) forces can initiate the composition inside it.

The impact sensitivity of a substance can be determined with several test apparatus. Because of the differences in design of the test method, test results obtained with different test apparatus can not be compared directly. To obtain comparable results the ranking of the compositions in the different test methods have to be compared.

The following paragraphs describe briefly the test apparatus in which comparable results in the literature have been found.

2.1.1.1 BAM Fallhammer

The BAM Fallhammer is the best known apparatus in Europe for testing impact sensitivity of solids and liquids. The test is also used for transport classification and is described in [3]. The apparatus consists of a steel block with base, an anvil, the column, the guides for the drop weights and the impact device. A sieved sample (40 mm^3) of the substance under test is enclosed in an impact device consisting of two coaxial steel cylinders, one above the other in a hollow cylindrical steel guide ring. The impact device is placed on an intermediate anvil. The drop weight, suspended at the required height, is released. The limiting impact energy, characterizing the impact sensitivity of a substance, is defined as that lowest impact energy at which the result “explosion” is obtained from at least one out of at least six trials. The impact energy is calculated from the mass of the drop weight and the fall height (e.g. 1 kg x 0.5 m $\cong$ 5 J). The 1 kg drop weight is used at discrete fall height interval of 10 to 50 cm (impact energy 1 to 5 J). The 5 kg drop weight is used at discrete fall heights intervals of 15 to 60 cm (impact energy 7.5 to 30 J) and the 10 kg drop weight is used for fall heights of 35, 40 and 50 cm (impact energy 35 to 50 J).

2.1.1.2 Bureau of Mines Apparatus (BoM)

In the impact sensitivity test of the Bureau of Mines a 20 mg sample is placed between two parallel hardened steel surfaces. The 2 kg weight is raised to the desired height and allowed to fall upon the sample. The impact value is the minimum height at which at least one of 10 trials results in an explosion.

2.1.1.3 Bureau of Explosives Apparatus (BoE)

With the Bureau of Explosives test apparatus a series of twenty tests are performed to determine the sensitivity of the sample material to mechanical shock. A 10 mg sample is placed in the test cup. The 2 kg test weight is dropped from a predetermined height, striking the sample.

The results of the 20 test per sample, 10 at 9.5 cm (3 ¾ inch) drop height and 10 at 25.4 cm (10 inch) drop height, are reported as the number of trials exhibiting explosion, decomposition, and no reaction.

2.1.2 Friction sensitivity

In general terms friction is the resistance to motion which occurs whenever an object slides across another surface. The laws of sliding friction may be summarized as follows[4]:

1. Frictional force is directly proportional to the load of the total force acting normal to the sliding surface.

2. Frictional force for a constant load is independent of the contact area.

Friction between unlubricated surfaces is due to a combination of adhesion and plastic deformation. Adhesion occurs at the regions of contact. For friction to occur, the junctions or welds have to be sheared. Plastic deformation is caused by ploughing, grooving or cracking of the surface asperities. An important aspect of friction in explosive materials is the temperature rise of the material. This can be caused during sliding, stick-slip (friction induced oscillations), friction of rolling bodies, fretting (a severe form of wear), and internal friction. The more brittle the explosive material or explosive crystals, the more sensitive the substance will be to impact and friction. When a brittle substance is impacted, high pressures will develop and be transmitted without rapid attenuation. Because of the displacement within the material internal friction will occur. Explosive materials which have a high fluidity (elasticity or plasticity) will, in general, not be very sensitive to friction due to a low coefficient of internal friction. Because initiation by friction is partly a thermal mechanism the friction sensitivity of a substance may change with temperature. Also the humidity of the test sample can strongly effect the friction sensitivity[5]. New “fresh” surfaces appear to be more sensitive compared to surfaces exposed briefly to the normal environment[6].

2.1.2.1 BAM Friction apparatus

As with the BAM fallhammer, the BAM friction apparatus is also well known. The apparatus and the test rationale are described in detail in several publications. The apparatus consist of a base plate of cast steel on which the actual device is mounted. This comprises a fixed porcelain peg and a moving porcelain plate. The plate is fixed in a carriage running in two guides and is moved by means of a connecting rod and an eccentric disc. A weight can be attached at discrete intervals on the loading arm resulting in discrete loads at intervals in the range 5 N – 360 N. The explosive material can be, depending on the test results, classified as follows.

1. Not sensitive to friction
   Explosive substances showing no response up to a load of 360 Newton
2. Moderately sensitive to friction
   Explosive substances reacting under change of colour or decomposition, possibly connected with odour, up to a load of 360 Newton
3. Sensitive to friction
   Explosive substances reacting between a load of 10 and 360 Newton with ignition, crackling or explosion
4. Very sensitive to friction
   Explosive substances reacting with ignition, crackling or explosion below a load of 10 Newton.

Tables with test results obtained from these tests are listed in Annex B.

2.2 Thermal sensitivity

A third initiation method is thermal initiation. A heat load applied to the pyrotechnic substance will ignite the composition. If a fuse is exposed and there is sufficient exposure to heat (as the main stimulus), this will be the route to ignition.

A heat-load can be generated by radiation or hot gasses. Although the heat source can be different, the substance will in both cases ignite because locally the auto-ignition temperature of the substance has been reached. The efficiency of heating the substance is strongly dependent on the confinement and the exposure (time) to the heat source. It will be relatively difficult to ignite a substance that is confined in a casing. The thermal conductivity of the casing material will influence the temperature rise in the substance and therefore the moment that the auto-ignition temperature is reached. Hot gasses can more easily enter a casing, especially when the casing is deformed or broken due to a mechanical load.

2.2.1 Auto-ignition temperature

The auto-ignition temperature is the temperature at which a material will react when the specimen begins to liberate heat due to self-heating. This is determined by placing the sample in an automatically controlled oven with a thermocouple embedded in the sample. The oven temperature is increased at a controlled rate until the sample material begins to liberate heat. At this point, the oven temperature is maintained at a constant temperature until the specimen reacts rapidly at its own auto ignition temperature. The reported value is usually less than the value reported for decomposition temperature as determined by a DTA apparatus. The auto-ignition temperature is the more critical value when comparison of various mixtures is made. Above the reported value, spontaneous ignition may occur, below this value, spontaneous ignition is unlikely. It should be pointed out that the values reported are dependent on the heating rate used (oven type, control method, etc.).

2.2.2 Decomposition temperature

The decomposition temperature is the determination of the ignition temperature and other physical and chemical reactions which may occur in a pyrotechnic mixture when the mixture is heated. The test measures the temperature difference between the pyrotechnic mixture and a thermally inert reference material as both are heated at a constant rate of increase in temperature (DTA).

The test detects exothermic or endothermic changes that occur in the specimen while it is heated. These changes may be related to dehydration, decomposition, crystalline transition.

2.3 Shock sensitivity

The preceding mechanisms are mechanisms where the initiation is a relatively slow process. When an explosive material is subjected to a shock wave, direct initiation can occur. The initiation mechanism is not based on mechanical deformation of the explosive material, but is related to the energy that is transferred into the explosive material by the shock wave. Most pyrotechnic materials are known to be rather insensitive to shock and more sensitive to temperature effects. The ability of a pyrotechnic material to be initiated by a shock wave can be tested with several tests.

2.3.1 Card gap test

In the card gap test the donor charge generates a shock wave, which is attenuated by a number of cards, before entering the acceptor (pyrotechnic) material. By varying the number of cards between the donor charge and the acceptor, the energy in the shock wave applied to the test sample, can be varied. In the card gap test a material is said to be insensitive to shock when no initiation occurs with a minimum of 400 cards[7] between the donor and acceptor material.

Apart from the shock wave that is generated by the detonation of an explosive substance, a blast wave will be developed. The shock wave can be well characterized by its amplitude (shock pressure), whereas a blast wave is difficult to quantify. In case of a pyrotechnic which is not initiated directly by the shock wave it will be subjected to the blast wave. The blast wave will not initiate a pyrotechnic article directly. When an article is impacted by the blast wave, it can be deformed and thus be initiated by the mechanical initiation mechanisms described earlier.

2.3.2 Ability of a composition to detonate

As stated before, most pyrotechnic compositions are difficult to initiate by shock mainly because most pyrotechnic compositions are not able to detonate. Even under optimised conditions (high confinement, optimum particle size, etc.), the composition will not show a sustained supersonic reaction. The ability of pyrotechnic compositions to detonate will depend strongly on several parameters such as: composition, density, particle size and confinement. Flash powders have been subjected to several tests over the past years to investigate whether this type of substance could detonate[8].

3 Literature review

In the literature very little work has been done on the reaction mechanisms causing propagation between adjacent fireworks articles. The studies dealing with propagation mechanisms have been carried out in the framework of transport classifications or accidents. In addition there are experimental studies on ignition processes, blast pressures and ejection velocities. Data from these studies can be used in combination with information on sensitivities of compositions (friction, shock, impact) to predict propagation mechanisms.

3.1 Ignition and burst processes of aerial shells

Burst delay times of aerial shells were investigated[9] as part of a study into malfunctions that can occur during the ignition of fireworks, like for instance in-mortar ignition of aerial shells (the so called “flowerpots”) or muzzle breaking aerial shells. Experiments were done on shells sizes between 76 and 155 mm. It was found that burst delay times increase with shell diameter, while the mortar exit times decrease with shell diameter. This explains the fact that muzzle breaks occur almost exclusively with larger diameter shells (the shells exit the mortar before they have time to explode). In general however, flowerpots occur more frequently than muzzle breaks. The experiments gave no explanation why flowerpots greatly outnumber muzzle breaks. It is supposed by the authors however, that the burst delay times are a function of the level of stimulus used. An explosive charge for example, causes a more rapid flame spread through a pyrotechnic composition than contact by a hot wire. Shorter burst delay times, causing flowerpots, are therefore expected for more powerful stimuli. These powerful stimuli would include shell casing failure caused by too weakly constructed shells or by shells that jam inside the mortar, loose or even removed delay fuses by the forces inside the mortar enabling burning lift gasses to enter directly into the shell, or burning lift gasses blowing through the delay fuse when the powder in the delay fuse is not compact enough.

Burst processes were investigated [10-12] using so called “Japanese warimono” aerial shells with a bursting charge composed of potassium perchlorate-based powder. Experiments on 83 mm shells indicate maximum internal pressures between 4.4 and 11.9 MPa after ignition. The initial pressure wave propagates at the speed of sound of the burned gas (~ 600 ms^{-1}). It therefore passes before the pressure rises uniformly in the shell. Radial fragmentation and radial star ejection occur simultaneously after shell burst.

A formula for the ejection velocity of the stars was mathematically derived, which is a function of the pressure decay process that occurs at the shell burst. Experimentally the velocity was determined to be 95 ms^{-1} for 11 mm stars (weight 1 gram).

3.2 Effectiveness and propagation of aerial and report shells

3.2.1 Effectiveness

The effectiveness of fireworks shells as energetic materials with different compositions was determined[13] with 50, 76, 102 and 127 mm report shells, stars shells and blackpowder. In the paper no chemical information on the compositions of the report shells is given. From pipe burst tests the relative effectiveness was determined from the number of fragments. It was found that as expected report shells are more effective than star shells, and star shells are more effective than blackpowder shells.

3.2.2 Propagation

Peak pressures of bursting aerial shells were measured as a function of distance. In the experiments the shells, with outside wrap, fuse, and lift charge removed, were hung on a string suspended from the ground and electrically ignited. It was found that the blast pressure increases with the size of the shell, with the mass of the composition, and with the number of shells igniting. When multiple report shells were taped together side by side, initiation of one shell did not communicate to the other shells. All shells had to be ignited separately.

Experiments were also done with full cases of report shells. With the bare shells packaged in egg-crate fashion, no propagation occurred. In order for the shells to function en masse, six bare shells were taped around a central, electrically initiated shell, with the blackpowder lift charges and fuses bundled and placed in the case.

Takishita[14] conducted experiments on the propagation between two aerial shells (diameter of 147 mm containing 32 mm diameter stars) placed in a thick paper box. When the primary shell was ignited, ignition of the receptor shell took place when the shells were placed in the box with the delay fuse of the receptor shell facing away from the delay fuse of the igniting shell (Figure 2). With the fuse facing towards the ignited shell, no propagation takes place. No information is given on the chemical composition of the charges of the shells or their mass.

The secondary shell explodes with a time delay of 1.0 second due to the delay in initiating the delay fuse of the secondary shell (that is, a time delay of 1.0 second in addition to the delay of the delay fuse of the secondary shell). This time delay occurs even when considerable mechanical damage has occurred to the secondary shell.

From the extra time delay, it is concluded that ignition of the secondary shell is caused by the heat flux from the hot gasses and/or hot fragments generated by the explosion of the primary shell. Also, when a paper sheet is used to separate the shells no mechanical damage occurs to the secondary shell.

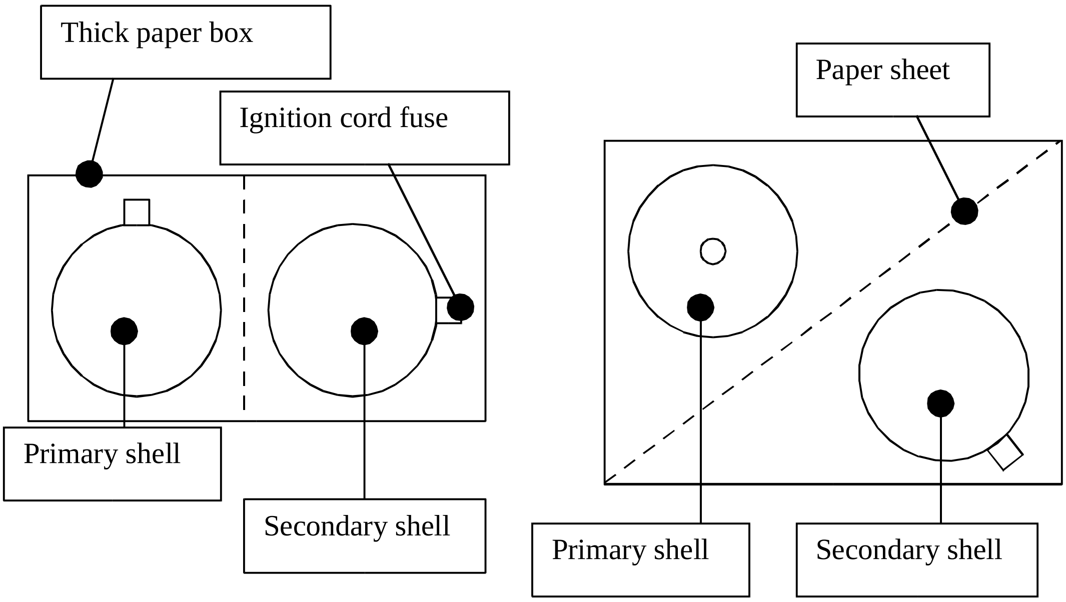


Figure 2: Shell configuration during test

No explanation is given as for why the secondary shell does not explode when the delay fuse is faced towards the primary shell.

Ettore Contestabile has also conducted tests with multiple aerial shells placed inside a steel tube, and ignited by various means. The resulting explosion and steel fragments were evaluated. At the time of writing, only limited information was available[15].

3.3 Mass explosion of 2-inch Roman candles containing flash powder: propagation

Three 50 mm Roman candles firing white and gold tail comets exploded en masse during a fireworks display in Australia in May 2000, something that was thought impossible by experts for that particular type of Roman candle[16].

The Roman candles were placed (relative close fit) in steel twin-tubes welded on a heavy steel base, the tubes being 15 mm apart (Figure 3). The explosion occurred after the first comet in the first tube (tube A) functioned normally. Research showed that the event started with the explosion of the second comet of the Roman candle in tube A while it was still in close proximity to its at-rest position.

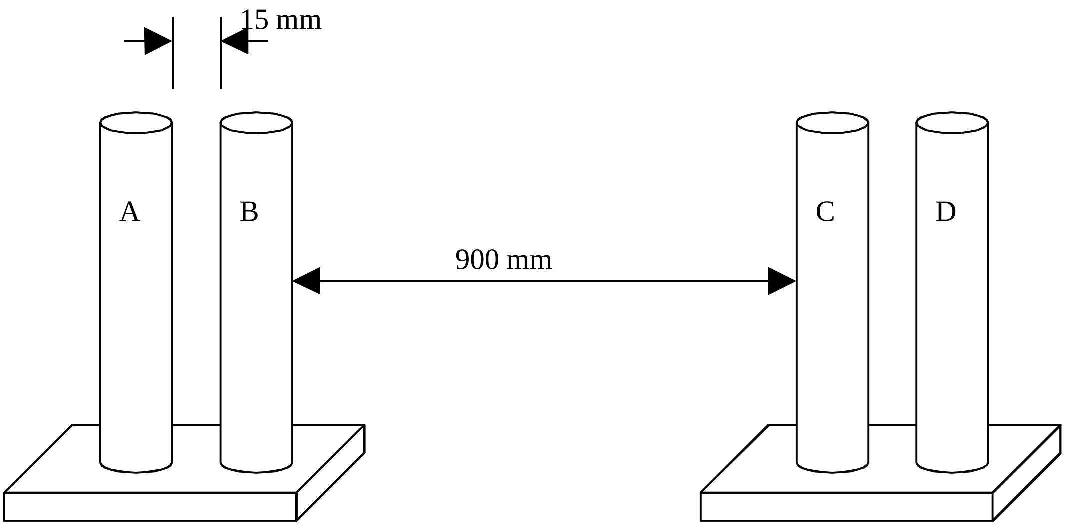


Figure 3: Arrangement of Roman candles

Its explosion caused all of the remaining comets and blackpowder in that Roman candle to explode en masse. The exploding Roman candle caused the metal tube surrounding it to expand and fragment. The tube impinged or struck tube B and caused the steel to be dented inwards, compressing the contents of the second Roman candle which caused it to explode en masse. Steel fragments similar in form and mass were produced in this explosion. Fragments from the first twin-tube stand struck tube C. The 2 inch, 5-shot gold tail Roman candle inside this tube exploded en masse, partially rupturing the steel tube and producing several fragments. Tube D was damaged, but not fragmented.

The cause of the comet exploding powerfully was a combination of three properties of the comet which, together, caused the candle to explode en masse. The first property was the use of a higher energy and more reactive composition than commonly used, namely potassium perchlorate and fine-grained magnalium. This composition is also known as “flash powder”, a composition that is known to be able to detonate under certain circumstances.

The second property was the significant permeability of the composition; the internal voids were sufficiently well connected to provide ‘fire-paths’ into and through the comets’ interior. Such ‘fire-paths’ allowed the comet to burn in a fraction of a second rather than a few seconds resulting in a rapid release of energy which manifested itself in a violent explosion. The third property was the substantial structural strength of the comets; the composition was extremely confined. The rise in pressure when confined causes the rate of combustion to accelerate (Vieille’s law), which in turn acts to build up the pressure even more. Normally, a 50 mm Roman candle comet takes several seconds to burn and release its chemical energy. In this case the energy was released on a time scale of several milliseconds. It was concluded that the hard comet itself provided its own confinement, not the steel tube in which the Roman candle was placed.

3.4 Propagation of pyrotechnic ammunition containing a flash composition

In a German investigation[17], the transport classification of 15 mm pyrotechnic ammunition containing flash powder was determined for different kinds of packings. The units, used for bird-scaring purposes, have a rolled paper casing and a cardboard or plastic end cap and an igniter and delay composition of blackpowder. In UN 6(c)-tests these articles can explode en masse, giving them a 1.1 classification by definition.

Because of the open igniting area of the articles, but in general for all pyrotechnic devices, the propagation is thought to proceed via the exposed composition in the confined primary pack causing easy ignition and quick propagation. In addition, it is thought that, for these particular units, direct propagation occurs by explosion of the flash composition through the article case. More over, the first explosion can squeeze the end caps out of the tubes of the adjacent units causing dispersion of the flash composition causing a mass explosion.

Mass explosion could be prevented by modifying the packing methods. Mass explosion occurred for example when the inner packing (ip) consisted of 100 units in 3 layers in a carton, the outer packing (op) consisted of 3 ip in a cardboard box. Different classifications, and therefore different ways of propagation, were found for different ways of packing. For example, an ip of 50 bullets in 5 layers in a carton where the op consisted of 40 ip separated by corrugated paper or cardboard rolls in 4 layers in a box of wood-wool padded cardboard resulted in a 1.4 G classification. It was concluded that lower classifications could be achieved by an efficient separation of the inner packings.

As mentioned in the above, flash powders are known to be able to detonate. In reference 10 a review is presented on work done on the explosive properties of flash powders. Factors influencing the propagation velocity of the explosion are summarized. Some of these factors are for example particle size, dimensions, loading density and initiation. Accidental ignitions during mechanical consolidation have led to a study of the mechanical sensitivity of titanium/blackpowder pyrotechnic compositions[18]. Both the friction sensitivity and the impact sensitivity were found to be dependent on the titanium content in the composition. For impact sensitivity, the rule of thumb can be used that the higher the titanium content the more sensitive the composition. The most sensitive compositions for friction stimuli are compositions containing 20%-30% titanium. As an explanation it is thought that, since the sensitivity to accidental ignition increases with the inclusion of grit and impurities in the composition, the hardness of the titanium works in a similar fashion. The maximum in the friction sensitivity indicates a change in mechanism. This change however was not investigated further in the paper.

Shimizu[19] presents results from experiments which should determine the initiation mechanism in several accidents. It is assumed that some flash powder can only develop a full detonation when a multiple initiation source is present. Three types of flash powder were used: 64% of potassium perchlorate, 23% of aluminum and sulfur (composition A), 64% potassium chlorate, 23% of aluminum and 13% sulfur (composition B) and 57% potassium chlorate and 43% of realgar (composition C). These compositions were used to fill either shells (25 gram in cardboard, different wall thickness and a density of approximately 0.65 gcm^{-3}) or cylinders (steel tube, 27 mm inner diameter, wall thickness 1-4 mm). In the first series of experiments the propagation of reaction is determined between three shells or cylinders. The first donor charge is ignited either with an electrical fuse, a detonating cord or black fuse. Variables in the experiments are the distances between the charges, the thickness of the paper, the initiation method of the donor and the composition. Table 1 shows the results of the series of experiments.

Table 1: Propagation experiments using three identical charges. First (donor) charge is initiated.

No.	Compo-sition	Form	Material	wall thickness [mm]	distance between [mm]	initiation method	A	B	C
1	A	Shell	paper	1.5	115 (2,5 D)	de + dc	⦿	●	○
2	A	Shell	paper	1.5	92 (2 D)	de + dc	⦿	●	○
3	A	Shell	paper	1.5	46 (1 D)	de + dc	⦿	●	○
4	A	Shell	paper	1.5	0	de + dc	⦿	●	○
5	A	Shell	paper	1.5	92 (2 D)	el. fuze	⦿	○	○
6	A	Shell	paper	1.5	69 (1,5 D)	el. fuze	⦿	○	○
7	A	Shell	paper	1.5	46 (1 D)	el. fuze	⦿	○	○
8	A	Shell	paper	1.5	23 (0,5 D)	el. fuze	⦿	●	○
9	A	Shell	paper	1.5	0	el. fuze	⦿	●	○
10	A	Shell	paper	1.5	0	bl fu.	⦿	●	○
11	A	Shell	paper	0.7	50 (1,1 D)	de + dc	⦿	●	○
12	B	Shell	paper	0.7	100 (2,2 D)	de + dc	⦿	●	●
13	B	Shell	paper	1.5	200 (4,4 D)	de + dc	⦿	○	○
14	C	Shell	paper	0.7	100 (2,2 D)	de + dc	⦿	●	○
15	C	Shell	paper	1.5	100 (2,2 D)	de + dc	⦿	○	○
16	A	Cylinder	paper	0.5	29 (1 D)	de + dc	⦿	●	●
17	A	Shell	paper	1.0	29	de + dc	⦿	●	●
18	A	Shell	paper	2.0	29	de + dc	⦿	●	◉
19	A	Shell	paper	4.0	29	de + dc	⦿	○	○
20	B	Shell	paper	2.0	29	de + dc	⦿	●	●
21	C	Shell	paper	2.0	29	de + dc	⦿	●	●
22	A	Shell	steel	1.0	30 (1 D)	de + dc	⦿	○	○

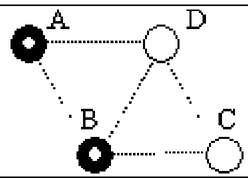
Legend:
- ⦿: donor charge with igniter
- ●: acceptor charge, fully detonated
- ◉: acceptor charge, partly detonated
- ○: acceptor charge, not detonated
- de+dc: detonator + detonating cord
- el. fuse: electrical fuse
- bl fu: black fuse

The only conclusion which is drawn from the first series of experiment is that the propagation from the donor charge to the acceptor charge is dependent of the initiation mechanism. Although an initiation source as powerful as the detonating cord will not be present under normal conditions the detonating cord will be used for the following series because of the need to initiate two acceptor charges simultaneously.

In the second series of experiments (Table 2) four charges are hung in a parallelogram arrangement. The charges A and B are initiated simultaneously by means of a detonating cord. The propagation of the detonation to the acceptor charges is determined

Table 2: Propagation experiments using four identical charges. Two donor charges (A and B) are initiated simultaneously using detonating cord.

Charge: Form: Shell; Material: paper; Thickness: 1,5 mm

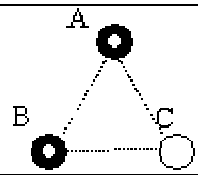


No.	Composition	Distance between charges [mm]	A	B	C	D
23	A	74 mm (1,6 D)	◉	◉	●	○
24	A	140 mm (3 D)	◉	◉	○	○
25	A	74 mm (1,6 D)	◉	◉	●	●
26	A	118 mm (2,5 D)	◉	◉	●	○
27	A	118 mm (2,5 D)	◉	◉	●	○

From this series the conclusion is drawn that the in position C the shock wave is stronger than in position D. In all experiments acceptor charge C detonated except for test 24, in which the distance between the donor and acceptor charges was much larger than in the other experiments. In only one case (experiment 25) did acceptor charge 25 detonated. Some additional tests were executed (Table 3), but no conclusions were drawn from this Table.

Table 3: Propagation experiments using three charges of different mass. Two donor charge initiated simultaneously.

Charge: Form: Shell; Material: paper; Thickness: 1,5 mm



No.	Composition	Distance between charges [mm]	initiation method	A	B	C
S1	A	300 mm (6,5 D)	de + dc	25 g ◉	25 g ◉	15 g ○
S2	A	100 mm (1,8 D)	de + dc	25 g ◉	25 g ◉	15 g ●
S3	A	100 mm (1,8 D)	de + dc	15 g ◉	15 g ◉	15 g ●
S4	A	100 mm (1,8 D)	de + dc	10 g ◉	10 g ◉	10 g ○
S5	A	100 mm (1,8 D)	el. fuze	25 g ◉	25 g ◉	15 g ○

The pressure profiles produced with a simultaneous initiation of two donor charges is measured using pressure measurements films (PRESCALE) from FUJIFILM

Co. When a force is applied on this film, the colour will permanently change, because of the breakage of micro encapsulations. Using a colour density measurement the maximum pressure at a certain position can be determined (Table 4). The measurement does not reveal information on the time scale of the pressure pulse. Three films were placed behind each other with a distance of 11 cm between each plate. The measurements show that the maximum pressure increases when the two donor charges are initiated simultaneously. It is also concluded that amplitude and direction of the pressure pulse which is generated by the donor charge is dependant on the position of the detonating cord in the donor charge. If the two donor charges are initiated with electrical fuses, and thus not simultaneously, the pressure amplitude is rapidly decaying. However, the initiation of two donors at the same time will increase the possibility of propagation of the reaction. It is also concluded that the possibility of propagation of detonation in a cylindrical form is higher, than in a shell form. This is probably due to the higher maximum pressure generated by the cylindrical donor charge. The last conclusion which is given in this paper is that an increase in wall thickness will decrease the possibility of propagation of the detonation reaction.

Table 4: Results of pressure measurements with double charges

No.	Comp.	Form	Distance between charges [mm]	paper thickness	initiation method	Pmax (kgcm^{-3})	Pmax (kgcm^{-3})
28	A	shell	66 mm (1,5 D)	0,7 mm	dif	52	30
29	A	shell	110 mm (2,5 D)	0,7 mm	sim	57	64
30	A	shell	110 mm (2,5 D)	0,7 mm	sim	60	50
31	A	shell	110 mm (2,5 D)	0,7 mm	sim	65	52
32	A	shell	110 mm (2,5 D)	0,7 mm	sim	66	44
33	A	shell	110 mm (2,5 D)	0,7 mm	sim	57	22
34	A	shell	110 mm (2,5 D)	0,7 mm	sim	33	22
35	A	cyl.	110 mm (2,5 D)	1,0 mm	sim	76	47
36	A	cyl	110 mm (2,5 D)	1,0 mm	sim	76	56
37	A	cyl	110 mm (2,5 D)	1,0 mm	sim	68	55
38	A	cyl	110 mm (2,5 D)	1,0 mm	sim	68	48
39	A	cyl	110 mm (2,5 D)	1,0 mm	sim	19	22
40	A	cyl	110 mm (2,5 D)	n.a.	sim	10	-

3.5 Impact sensitivity of burning compositions

An effect called surface explosion occurs when a burning pyrotechnic composition (for example the star of an aerial shell) hits the ground. The explosion occurs only on the surface, causing the fire to go out and leaving an unburned part. The sensitivity to shock of burning compositions is clearly higher as a result of the higher temperatures. In an experimental study[1] into this phenomenon iron balls with different weights were dropped from a series of heights onto the burning surface of several pyrotechnic compositions. It was found that the outbreak and propagation of the explosion are strongly influenced by the intensity of the shock and the width of the shock area; the fire is not extinguished when a lighter iron ball is used. Mixtures with the highest sensitivity and the highest propagation effect were mixtures containing metal powders such as magnesium or aluminium. Least sensitive was a blackpowder mixture which did not explode at all. The effect of pressure was investigated using small rocket motor engines. It was found that with pressure sensitive compositions like potassium perchlorate and potassium chlorate mixtures containing metals, the surface explosion may easily proceed to a detonation.

3.6 Deflagration of blackpowder under self confinement

In a report by Pfeil[20] an unexpected build up of pressure in blackpowder was experimentally studied. When a pile of blackpowder is ignited inside the pile, the blackpowder will deflagrate with a pressure build-up in the pile until the self-confinement fails. The deflagration under self confinement will generate a first pressure maximum, which can be observed in closed and open environments. The rest of the ejected unreacted blackpowder will react producing a second pressure maximum, the amplitude of which is dependent on the volume and possibilities for pressure relief of the space in which the reaction takes place.

4 Conclusions

1) All three mechanisms (fragment, heat and shock) occur in reaction mechanisms between fireworks articles. In practice there are often combinations of these mechanisms. Very little experimental work has been done to try to isolate one mechanism from another.

2) Often there is no scientific conclusion drawn from results or observations reported in literature. This may be because the goal of the work was not to present scientific work, but rather to report on classification, or on an incident.

3) Very little scientific research has been conducted on propagation mechanisms between fireworks articles.

4) Often the fuse, as a fireworks element, is identified as a possible source for propagation, however, this can not explain a fast propagation reaction between articles.

5) The incident with the Roman Candle, where unexpected explosive results were observed, may be related to bad production processes. There are no details to look into this aspect.

6) Very fast reactions (be it a true "detonation" or not) occur most often with flash compositions.

7) It is only possible to offer recommendations for the selection of firework articles. For example if one wishes to test an article sensitive to heat propagation, one should focus on fireworks which contain compositions that have high thermal sensitivity. Tables in Annex B rank pyrotechnic compositions for different reactivity to such stimuli. In addition, firework manufacturers' data sheets may provide details about the compositions used in a fireworks article and this data should be used for the different stimuli discussed in this paper .

8) The literature did not reveal technical information about the reasons why (and if) fireworks can behave more explosively than should have been expected, based on their classification. The mechanisms have not been studied yet.

Annex A

Although a detailed description of the normal functioning mechanisms of pyrotechnics are outside the scope of this study, this Annex contains some basic information about reaction mechanisms of pyrotechnic compositions.

The rate of normal pyrotechnic combustion appears to be influenced greatly by a number of physical and chemical factors. These factors include:

- Particle Size Distribution and Particle Shape
- Density of chemical mixture
- Surface area of a consolidated chemical mixture
- Oxidation state of fuels (metals)
- Impurities
- Catalysts

Pyrotechnic combustion rates are greatly influenced by a number of parameters. It appears that there are almost no general models available which can predict the burn rate of a pyrotechnic composition. Most models focus on thermochemical calculations, where the question only addresses IF a reaction can occur. HOW FAST a reaction occurs is a kinetic problem in chemistry. There are only a few models which focus on one particular pyrotechnic system (MTV, KNO_3/Boron). These fall inside the field of military pyrotechnics, which is outside the scope of this study.

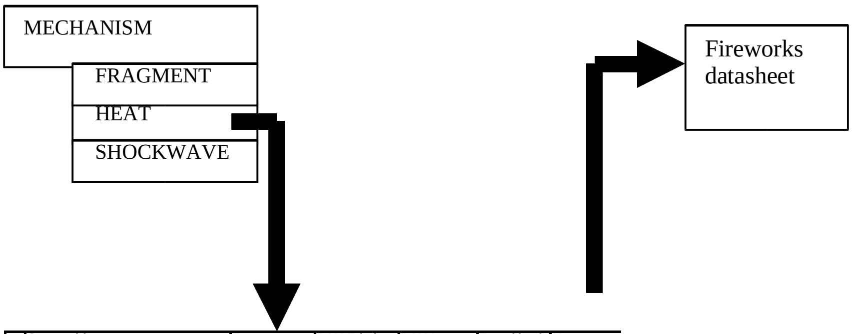
Normally ignition temperatures are influenced by intrinsic factors such as melting of one of the reactants. Fisher and Grubelich[21] state that an accurate calculation of the adiabatic reaction temperature is important to determine whether a reaction is self-propagating. A strong indication of a self-propagating reaction is if at least one reactant is brought to it's melting temperature. Another indication is if the adiabatic reaction temperature exceeds 2000 K. In practise this implies that heat losses to the surroundings are no longer significant for successful propagation.

Certain fireworks compositions are meant to exhibit sparks. This places them on a unique group, where the combustion mechanism relies heavily on atmospheric oxygen. Additionally, numerous fireworks stars fly at high speed through the air. The combustion mechanism of stars is influenced by cooling effects. For fireworks these physical influences have never been quantified by experimental study.

The focus of this report is on reaction mechanisms which are meaningful in studying propagation mechanisms during mass explosive events.

Annex B

Data concerning the sensitivity of pyrotechnic compositions have been studied in literature sources, such as Ide et al.[22] ("The BAM tables"). Other sources, such as Shimizu[23] and McIntyre[24] were also studied. An attempt has been made to compare the ranking of data from independent sources, but it was concluded that the compositions used in the different sources did not allow this. Therefore we were unable to correlate the rankings of composition types between sources. In the current report, the values from "The BAM tables" are used to illustrate the suggested approach.



	Composition	Temperature of Ignition	BAM Friction test results	BAM Impact test results	Trauzl lead block tests	Koenen test results
		[ºC]	[kp]	[kpm]	[ml/d.ag]	mm
1	whistle [KClO3/Gallic acid/additives]	236	1	0.2	190	24
2	whistle [KClO3/BaClO3/Gallic acid]	218	1	0.2	183	24
3	whistle [KClO3/Gallic acid]	216	2	0.2	193	24
4	star green	263	2	0.2	194	24
5	star green	256	6	0.4	185	24
6	xylokoll / nitrocellulose	182	24	0.5	330	12
7	star red	230	4	0.2	97	20
8	star green [BaClO3/charc/shellac]	238	8	2.0	205	24

In Table B1 pyrotechnic compositions are ranked with increasing ignition temperature. This ranking of compositions could be useful when small scale tests are conducted to test for possible propagation via heat transfer mechanisms.

In Table B2 pyrotechnic compositions are ranked with increasing sensitivity to friction. This ranking of compositions could be useful when small scale tests are conducted to test for possible propagation via friction sensitivity related mechanisms.

In Table B3 pyrotechnic compositions are ranked with increasing sensitivity to impact. This ranking of compositions could be useful when small scale tests are to be conducted to test the possible propagation via impact sensitivity related mechanisms.

Table B1: Pyrotechnic compositions ranked with increasing ignition temperature.

No.	Composition	Temperature of Ignition [°C]	BAM friction test results [N]	BAM impact test results [J]	Trauzl lead block tests [cm^3 per 10g]	Koenen test results [mm]
1	xylokoll / nitrocellulose	182	240	5	330	24
2	smoke	185	160	6	74	24
3	ref comp	199	80	15	106	24
4	ref comp	199	120	8	212	24
5	ref comp	200	40	5	192	24
6	ref comp	200	80	8	235	12
7	ref comp	200	240	8	158	20
8	ref comp	200	360	10	107	24
9	ref comp	202	360	20	42	24
10	ref comp	202	360	25	7	10
11	ref comp	206	360	25	3	24
12	whistle [$KClO_3$/Gallic acid]	216	20	2	193	24
13	whistle [$KClO_3$/$BaClO_3$/Gallic acid]	218	10	2	183	20
14	star red	230	40	2	97	24
15	"snake" comp / residue	232	360	8	36	20
16	whistle [$KClO_3$/Gallic acid/additives]	236	10	2	190	20
17	star green [$BaClO_3$/charc/shellac]	238	80	20	205	10
18	report [$Ba(NO_3)_2$/Al…]	239	160	8	89	24
19	star green	256	60	4	185	24
20	star, silver [KNO3/Ba/Al]	260	20	4	79	20
21	star green	263	20	2	194	16
22	blue color [$KClO_3$/SchweinfGr/coloph]	270	60	4	110	10
23	star, yellow	287	360	10	34	20
24	Bengal comp red	303	360	8	67	16
25	meal powder [black powder]	304	360	10	109	16
26	star red	318	80	4	56	5
27	rocket comp [KNO_3/Charc/S]	318	360	10	22	12
28	bengal green	318	360	15	27	20
29	intermediate comp Mg stars	319	360	25	116	12
30	wheel comp	320	360	20	74	20
31	star, silver [KNO_3/Ba/Al]	321	80	4	102	8
32	First Fire Comp	330	360	5	43	20
33	ignition comp / first fire comp	334	240	4	113	8
34	silver rain comp	335	360	10	28	4
35	Gold fire/rain comp	336	360	15	26	10
36	intermediate comp nitrate stars	345	240	4	87	8
37	screen smoke comp	358	360	15	51	18
38	report comp [KClO4/Pyro-Schliff Al]	360	60	15	72	12
39	report comp [KClO4/Al]	360	120	5	79	18
40	report comp	360	120	10	83	5
41	report comp	360	160	6	43	3
42	Smoke comp [KNO_3/S/Charc/Zn]	360	240	2	52	5
43	Bengal comp green	360	240	4	141	8
44	Bengal, red [$Sr(NO_3)_2$/$KClO_3$…]	360	240	5	86	10
45	star, green	360	240	8	52	14
46	waterfall comp	360	240	10	40	4
47	smoke comp	360	240	10	35	3
48	screen smoke comp	360	360	8	11	2.5
49	Goldstream comp	360	360	10	112	2
50	Illum comp yellow	360	360	10	14	1
51	waterfall comp	360	360	10	83	4
52	"Leuchtzeichensatz"	360	360	10	88	1
53	sparkler comp	360	360	15	82	1
54	star, red [$Sr(NO_3)_2$/Mg/PVC]	360	360	25	36	4
55	star, yellow [$NaNO_3$/Mg/wax]	360	360	25	111	14
56	screen smoke comp	360	360	25	73	18
57	smoke comp yellow	360	360	35	22	20
58	waterfall comp	360	360	50	32	20
59	smoke comp	360	360	50	28	20
60	Illum cart comp	377	360	15	30	3

Table B2: Pyrotechnic compositions ranked with increasing sensitivity to friction.

No.	Composition	Temper-ature of Ignition [°C]	BAM friction test results [N]	BAM impact test results [J]	Trauzl lead block tests [cm^3 per 10g]	Koenen test results [mm]
13	whistle [$KClO_3$/$BaClO_3$/Gallic acid]	218	10	2	183	20
16	whistle [$KClO_3$/Gallic acid/additives]	236	10	2	190	20
12	whistle [$KClO_3$/Gallic acid]	216	20	2	193	24
20	star, silver [KNO3/Ba/Al]	260	20	4	79	20
21	star green	263	20	2	194	16
5	ref comp	200	40	5	192	24
14	star red	230	40	2	97	24
19	star green	256	60	4	185	24
22	blue color [$KClO_3$/SchweinfGr/coloph]	270	60	4	110	10
38	report comp [KClO4/Pyro-Schliff Al]	360	60	15	72	12
3	ref comp	199	80	15	106	24
6	ref comp	200	80	8	235	12
17	star green [$BaClO_3$/charc/shellac]	238	80	20	205	10
26	star red	318	80	4	56	5
31	star, silver [KNO_3/Ba/Al]	321	80	4	102	8
4	ref comp	199	120	8	212	24
39	report comp [KClO4/Al]	360	120	5	79	18
40	report comp	360	120	10	83	5
2	smoke	185	160	6	74	24
18	report [$Ba(NO_3)_2$/Al…]	239	160	8	89	24
41	report comp	360	160	6	43	3
1	xylokoll / nitrocellulose	182	240	5	330	24
7	ref comp	200	240	8	158	20
33	ignition comp / first fire comp	334	240	4	113	8
36	intermediate comp nitrate stars	345	240	4	87	8
42	Smoke comp [KNO_3/S/Charc/Zn]	360	240	2	52	5
43	Bengal comp green	360	240	4	141	8
44	Bengal, red [$Sr(NO_3)_2$/$KClO_3$…]	360	240	5	86	10
45	star, green	360	240	8	52	14
46	waterfall comp	360	240	10	40	4
47	smoke comp	360	240	10	35	3
8	ref comp	200	360	10	107	24
9	ref comp	202	360	20	42	24
10	ref comp	202	360	25	7	10
11	ref comp	206	360	25	3	24
15	"snake" comp / residue	232	360	8	36	20
23	star, yellow	287	360	10	34	20
24	Bengal comp red	303	360	8	67	16
25	meal powder [black powder]	304	360	10	109	16
27	rocket comp [KNO_3/Charc/S]	318	360	10	22	12
28	bengal green	318	360	15	27	20
29	intermediate comp Mg stars	319	360	25	116	12
30	wheel comp	320	360	20	74	20
32	First Fire Comp	330	360	5	43	20
34	silver rain comp	335	360	10	28	4
35	Gold fire/rain comp	336	360	15	26	10
37	screen smoke comp	358	360	15	51	18
48	screen smoke comp	360	360	8	11	2.5
49	Goldstream comp	360	360	10	112	2
50	Illum comp yellow	360	360	10	14	1
51	waterfall comp	360	360	10	83	4
52	"Leuchtzeichensatz"	360	360	10	88	1
53	sparkler comp	360	360	15	82	1
54	star, red [$Sr(NO_3)_2$/Mg/PVC]	360	360	25	36	4
55	star, yellow [$NaNO_3$/Mg/wax]	360	360	25	111	14
56	screen smoke comp	360	360	25	73	18
57	smoke comp yellow	360	360	35	22	20
58	waterfall comp	360	360	50	32	20
59	smoke comp	360	360	50	28	20
60	Illum cart comp	377	360	15	30	3

Table B3. Pyrotechnic compositions ranked with increasing sensitivity to impact.

No.	Composition	Temper-ature of Ignition [°C]	BAM friction test results [N]	BAM impact test results [J]	Trauzl lead block tests [cm^3 per 10g]	Koenen test results [mm]
12	whistle [$KClO_3$/Gallic acid]	216	20	2	193	24
13	whistle [$KClO_3$/$BaClO_3$/Gallic acid]	218	10	2	183	20
14	star red	230	40	2	97	24
16	whistle [$KClO_3$/Gallic acid/additives]	236	10	2	190	20
21	star green	263	20	2	194	16
42	Smoke comp [KNO_3/S/Charc/Zn]	360	240	2	52	5
19	star green	256	60	4	185	24
20	star, silver [KNO3/Ba/Al]	260	20	4	79	20
22	blue color [$KClO_3$/SchweinfGr/coloph]	270	60	4	110	10
26	star red	318	80	4	56	5
31	star, silver [KNO_3/Ba/Al]	321	80	4	102	8
33	ignition comp / first fire comp	334	240	4	113	8
36	intermediate comp nitrate stars	345	240	4	87	8
43	Bengal comp green	360	240	4	141	8
1	xylokoll / nitrocellulose	182	240	5	330	24
5	ref comp	200	40	5	192	24
32	First Fire Comp	330	360	5	43	20
39	report comp [KClO4/Al]	360	120	5	79	18
44	Bengal, red [$Sr(NO_3)_2$/$KClO_3$...]	360	240	5	86	10
2	smoke	185	160	6	74	24
41	report comp	360	160	6	43	3
4	ref comp	199	120	8	212	24
6	ref comp	200	80	8	235	12
7	ref comp	200	240	8	158	20
15	"snake" comp / residue	232	360	8	36	20
48	screen smoke comp	360	360	8	11	2.5
18	report [$Ba(NO_3)_2$/Al...]	239	160	8	89	24
24	Bengal comp red	303	360	8	67	16
45	star, green	360	240	8	52	14
8	ref comp	200	360	10	107	24
23	star, yellow	287	360	10	34	20
25	meal powder [black powder]	304	360	10	109	16
27	rocket comp [KNO_3/Charc/S]	318	360	10	22	12
34	silver rain comp	335	360	10	28	4
40	report comp	360	120	10	83	5
46	waterfall comp	360	240	10	40	4
47	smoke comp	360	240	10	35	3
49	Goldstream comp	360	360	10	112	2
50	Illum comp yellow	360	360	10	14	1
51	waterfall comp	360	360	10	83	4
52	"Leuchtzeichensatz"	360	360	10	88	1
3	ref comp	199	80	15	106	24
28	bengal green	318	360	15	27	20
35	Gold fire/rain comp	336	360	15	26	10
37	screen smoke comp	358	360	15	51	18
38	report comp [KClO4/Pyro-Schliff Al]	360	60	15	72	12
53	sparkler comp	360	360	15	82	1
60	Illum cart comp	377	360	15	30	3
9	ref comp	202	360	20	42	24
17	star green [$BaClO_3$/charc/shellac]	238	80	20	205	10
30	wheel comp	320	360	20	74	20
10	ref comp	202	360	25	7	10
11	ref comp	206	360	25	3	24
29	intermediate comp Mg stars	319	360	25	116	12
54	star, red [$Sr(NO_3)_2$/Mg/PVC]	360	360	25	36	4
55	star, yellow [$NaNO_3$/Mg/wax]	360	360	25	111	14
56	screen smoke comp	360	360	25	73	18
57	smoke comp yellow	360	360	35	22	20
58	waterfall comp	360	360	50	32	20
59	smoke comp	360	360	50	28	20

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CHAF WP4	Literature review
Deliverable 4-3	Overview and interpretation of literature on EU storage and transport regulations with regard to fireworks
Date	June 2003
Author	A. von Oertzen (BAM)

Summary

This work belongs to a research project funded by the European Community on the "quantification and control of the hazards associated with the transport and bulk storage of fireworks" which was given the acronym CHAF.

The review on national regulations regarding storage and transport of fireworks is a subsection of work package four (WP4) concerned with a literature review on the current state of knowledge and research, the regulations in different EU countries with regard to fireworks, reaction mechanisms, storage and the impact of fireworks on the environment. Throughout this work the transport regulations play a minor role since these have been the same for all EU countries countries for many years. The "European Agreement concerning the International Carriage of Dangerous Goods by Road" (ADR) regulations are only dealt with briefly.

The review shows that the storage regulations in a number of countries are similar with regard to safety distance determination. This refers to countries applying quantity-distance tables such as Germany, Greece, Portugal or Spain and others. Other assessment systems exist which are difficult to compare with the former type. In France, for example, the probability of an accident can be taken into account, and in the United Kingdom two levels of population density enter the assessment. Due to the Enschede disaster The Netherlands has comparatively very restrictive regulations for the storage of fireworks.

As might be expected, the overview study did not reveal a major lack of regulations in any of the member countries. Detailed aspects of best practice in different countries or how the laws are enforced is obviously beyond the scope of a literature survey of this type.

Storage and Transport Regulations in EC Countries

1 Introduction

This paper describes the national regulations regarding storage and transport of fireworks and covers countries currently in the European Community. A brief review with respect to possible future members of the EU or other neighbouring countries is included at the end. The regulations for the transport of dangerous goods, which includes fireworks in class 1, follow the ADR/RID regulations ("European Agreement concerning the International Carriage of Dangerous Goods by Road“ and "Regulations concerning the International Carriage of Dangerous Goods by Rail“) do not require a discussion by country. The aspect of storage, however, is dealt with in detail through a subsection for each member country.

It should be mentioned that the sources of information on national regulations where not equally accessible. Of course, the different languages within the European Community pose a considerable difficulty on the analysis. Where government-hosted web-sites with legal material was available, this provided in most cases a detailed insight into national laws. This revealed a large variety of structures ranging from a single and concise law covering essentially all aspects of explosives and fireworks, to systems with many amendments made on the basis of old laws on explosives or workers protection.

The full official name of the respective regulations is printed in this work whenever this could be found in the national language including the document code or number. The reason for printing the full name in original language is that the sources in most cases can only be found in the internet when the exact national name and/or code is used for an internet search.

In some other cases it was necessary to rely on reviews written about the national regulation scheme in some other language. In most cases, however, the original law text could be found and analysed directly with the help of a dictionary where necessary. This procedure does not exclude the chance of overlooking important aspects of a national law text and therefore, the results published here cannot be regarded as official statements of the respective countries, but rather reflect the author's understanding of the sources found. Furthermore the collected information can only reflect a temporal snapshot, and information should be cross-checked for validity before relying on it. However the greatest care was taken to interpret the national laws accurately. If there are still mistakes present the author would like to apologise herewith.

2 Transport regulations

The transport of dangerous goods has to be performed according to the ADR/RID regulations which are available and in force for every member country of the European Community. The regulations are based on the United Nations (UN) scheme for the classification of dangerous goods. The classification of fireworks according to the UN scheme with hazard divisions 1.1 to 1.6 within class 1 for explosives plays a central role in this work. Of these divisions only the divisions 1.1 to 1.4 are applicable to fireworks.

Because of the importance for this work the definitions for the hazard divisions 1.1 to 1.4 are reproduced here in full text. Going from division 1.1 to division 1.4 behaviour with decreasingly hazardous effects is defined. The following are citations from the ADR:

> ***Division 1.1***
> *Substances and articles which have a mass explosion hazard (a mass explosion is an explosion which affects almost the entire load virtually instantaneously).*
>
> ***Division 1.2***
> *Substances and articles which have a projection hazard but not a mass explosion hazard.*
>
> ***Division 1.3***
> *Substances and articles which have a fire hazard and either a minor blast hazard or a minor projection hazard or both, but not a mass explosion hazard:*
>
> *(a) combustion of which gives rise to considerable radiant heat; or*
>
> *(b) which burn one after another, producing minor blast or projection effects or both.*
>
> ***Division 1.4***
> *Substances and articles which present only a slight risk of explosion in the event of ignition or initiation during carriage. The effects are largely confined to the package and no projection of fragments of appreciable size or range is to be expected. An external fire shall not cause virtually instantaneous explosion of almost the entire contents of the package.*

Additionally every explosive is assigned to one of the compatibility groups denoted with letters A-H, J-L, N, and S reflecting certain properties or features of the article. Joint transportation of goods with differing compatibility groups is in most cases forbidden or subject to strict limitations. In the case of fireworks only the compatibility groups G and S are applicable.

The definition of compatibility group G is:

> *Pyrotechnic substance, or article containing a pyrotechnic substance, or article containing both an explosive substance and an illuminating, incendiary, tear- or smoke-producing substance (other than a water-activated article or one which contains white phosphorus, phosphides, a pyrophoric substance, a flammable liquid or gel or hypergolic liquids).*

And the definition of compatibility group S is:

> *Substance or article so packed or designed that any hazardous effects arising from accidental functioning are confined within the package unless the package has been degraded by fire, in which case all blast or projection effects are limited to the extent that they do not significantly hinder or prevent fire-fighting or other emergency response efforts in the immediate vicinity of the package.*

In the description of compatibility group S the very important aspect of packaging is named explicitly and in many cases the type of packaging influences the behaviour under conditions of an accident and thus influences which classification is appropriate.

The ADR regulations prescribe many details concerning labelling, placarding, permitted packaging and types of vehicles. Specially designed vehicles are required for the transport of certain types of explosives or quantities above set limits. Such vehicles have normally been modified to protect the load from the risk of ignition via heat from the engine or the exhaust system. To facilitate this there is a requirement to use only vehicles with compression ignition type engines.

The ADR allows for exemptions related to small quantities carried per transport unit. With respect to fireworks these exemptions allow for transportation in normal vehicles and by people who do not have special authorisations for transport of dangerous goods. The mass limits are, however, fairly low and transportation under an exemption does not play an essential role in this research project. The mass limits are 20 kg net explosive content of 1.1G or 1.3G articles, 333 kg net explosive content of 1.4G articles, and 1.4S articles can be carried without mass limitation.

The national governments may in some cases have formulated restrictions or special permissions with regard to combined loading or concerning other aspects. These provisions have not been analysed here. Transport accidents with fireworks seem to be fairly rare and the involved amounts are limited as compared with storage facilities.

3 Storage regulations

The regulations on storage are summarised by countries in alphabetical order. Because of the similarity of legislation in Great Britain and Northern Ireland with respect to fireworks they are treated in a single section. A section on possible future member states and other neighbouring countries has been added at the end.

3.1 Austria

In Austria the storage of pyrotechnic articles is regulated in the "Pyrotechnik-Lagerverordnung" (BGBl. Nr. 512/1977). A revision is currently being evaluated and about to be published. More general issues on pyrotechnics and in particular fireworks are regulated in the "Pyrotechnikgesetz 1974" (BGBl. Nr. 282/1974).

Storage of fireworks is solely oriented on the national classification scheme for fireworks which consist of classes I, II, III, and IV. The general description of these classes are similar to the CEN categories. However, the Austrian classification scheme relies only on net explosive content thresholds without taking into account the different types of fireworks or the kind of effect. The use of fireworks of classes III and IV is restricted to events which require special permits or can be fired by professional fireworkers only.

The legal requirements on the type of storage facility, i.e. special storage buildings, containers, or storage places without special provisions depend on two parameters: the gross weight of stored fireworks and the classification according to the national system. The UN hazard divisions as defined for the transport of dangerous goods are not used. The details are:

Large scale storage of more than 500 kg gross weight of class IV articles is only allowed in special half-underground stores with a safety distance calculated by a formula with the cubic root of the net explosive content. Similar formulae are used by many other countries as well. The separation distance in meters is obtained by taking the cubic root of a mass in kilograms (mostly the net explosive content) multiplied by a given factor. The factor varies according to the desired degree of safety or hazard division of the explosive stored. These factors are often given in this work for comparison purpose. The formula will be referred to as the cubic-root-formula throughout the text.

The factor for the above mentioned situation of more than 500 kg gross weight of class IV articles is 22 for dwellings and 15 for public areas other than dwellings. For up to 500 kg gross weight of class IV articles above-ground constructions are permitted and a safety distance of 30 m to other buildings is prescribed. This restriction remains also for mixed stores as long as class IV articles are present. Up to 2000 kg gross weight of class III articles can also be stored in above-ground storage buildings with a safety distance of 20 m prescribed.

Articles of class I and II can be stored in above-ground storage buildings up to 5000 kg or in storage containers up to 800 kg and with a safety distance of 10 m. A mass limit of 100 kg applies for class I and II for other storage, as for example in special mobile shop-containers, in rooms not originally designed for explosives belonging to shops, or inside the shop itself.

3.2 Belgium

According to information obtained from the Belge Ministry of Economy no general statements on safety distances during the storage of fireworks can be made. A large scale fireworks depot is licensed by the ministry and the conditions of storage are fixed through a safety study taking into account various parameters. For the hazard assessment the previewed amounts of fireworks is analysed while applying a default list in order to obtain classifications according to the UN classification scheme. It is interesting to note that the default list does not include the 1.2 classification for any type of firework. The safety distances and standards as found in some NATO documents are used. By this mass limits for the depot are fixed.

In the case of 1.3G fireworks the storage in Mavo-boxes or steel ISO containers is possible, while certain limitations apply. Not more than 1000 kg of net explosive content will be permitted and the density of explosive must not exceed 20 kg per cubic meter. Furthermore, the doors must open readily on slight overpressure. 1.1G fireworks will only be permitted in smaller amounts with further isolation between articles.

3.3 Denmark

Issues concerning fireworks in Denmark can be found in the "Tekniske forskrifter om fyrværkeri" which have been published in relation to the regulation "bekendtgørelse nr. 778 af 14. oktober 1999 om fyrværkeri". Accordingly, Denmark has four categories for fireworks denoted with the Roman numerals I to IV, of which the categories I and II are for public use and III and IV are for professional fireworkers. Categories I and III can be used indoor, i.e. category III is theatre fireworks, and categories II and IV may only be used outside.

Fireworks shall be stored in their transport packs. Small quantities of category I and II fireworks (up to 5 kg, or 150 kg for shops) do not require special permission for storage. The safety distances applied to category I and II fireworks stored in larger amounts lie between 5 m and 10 m depending on two threshold levels being 500 kg and 2000 kg and depending on environmental conditions.

Storage of fireworks of more than 2000 kg is generally an issue for the "Danish Emergency Management Agency (DEMA)" and safety distances are evaluated individually for the present situation of storage buildings, the relation to neighbouring buildings, and the amounts to be stored. However, no general pattern exists. According to information from the DEMA agency the treatment of fireworks with 1.1 classification would be similar to the treatment of military goods of the same classification.

3.4 Finland

Legislation on fireworks and storage is found in three national regulations with the numbers 263/1953, 130/1980, and 473/1993. The decree 130/1980 "Kauppa- ja teollisuusministeriön päätös räjähdystarvikkeista", revised in 1993, includes information on the hazard divisions and on the calculation of safety distances.

The classification of fireworks for storage in Finland follows a national scheme which essentially coincides with the hazard divisions defined in the UN recommendations on the transport of dangerous goods for explosives. The assignment of articles to a hazard division is either done by the manufacturer or, in case of doubts, checked by the national Safety Technology Authority (TUKES, Turvatekniikan Keskus). This authority is also responsible for approving storage facilities.

Safety distances are determined according to the cubic-root-formula. The factors used are close to those found in the German legislation, i. e. the safety distance between a store with fireworks of hazard division 1.1G to public areas where people congregate is calculated by applying the factor of 22 to the cubic root of the net explosive content. The quantity-distance relation is not used for articles of hazard division 1.4G.

Fireworks for the public are approved by the national authority TUKES as well, and storage during selling for New Years Eve and the celebration of the end of the holiday season is limited to 50 kg net explosive content in the shop and another 100 kg net explosive content in a corresponding storage room.

3.5 France

In France fireworks are assigned to a national classification scheme with classes K1, K2, K3, and K4. The class descriptions do not include the purpose or scope of the articles, as in many other countries, but are essentially based on mass limits of net explosive content. The boundaries for these classes differ somewhat from the figures in the classification scheme used by CEN. As in the CEN draft standards and as in many other countries, articles in class K4 are meant to be only for professional fireworkers and are not available to the public.

While the above mentioned classes are defined in the "arrêté du 24 février 1994 relatif au classement des artifices de divertissement", essential regulations on workers safety in production facilities for pyrotechnics are found in the "décret 79-846 du 28 septembre 1979 portant règlement d'administration publique sur la protection des travailleurs contre les risques particuliers auxquels ils sont soumis dans les établissements pyrotechniques".

A facility in which pyrotechnics are handled requires a very detailed hazard study assessing the risk of an accident and its probability according to regulations given in the "arrêté du 26 septembre 1980 fixant les règles de détermination des distances d'isolement relatives aux installations pyrotechniques". From this study different safety distance requirements for different types of facilities arise. The details are quite interesting and outlined in the following.

The area surrounding a storage facility (the same applies to production facilities) is divided into five danger zones with the radii depending on the amounts stored and the hazard division of the stored materials. The hazard divisions are the same as for the transport of dangerous goods and are generally taken from an available classification. In case of doubt, or for yet unclassified articles, the state institute for the industrial environment and related risks (INERIS, "institut national de l'environment industriel et des risques") is responsible for performing, or supervising, a qualified assessment via testing of such articles. The radii of the five danger zones are defined in the mentioned regulations and are calculated via the cubic-root-formula using the net explosive content and a factor similar to those used in the regulations of other countries.

In the case of 1.1 articles the inner-most zone label Z_1 which equates to a lethal hazard is determined by multiplying the cubic root of the NEC by 5, while the outermost zone labelled Z_5 ranges from 22 to 44 times the cubic root of the NEC. The zone Z_5 is defined to have a hazard of light injuries in rare cases. For the other hazard divisions the radii are defined differently and extend less far in the case of 1.3 or 1.4, for example.

Every activity in a facility with pyrotechnics is assessed with regard to the probability that an accident can occur. The probability is again divided into five levels and ranges from extremely rare (labelled P_1) to frequent (P_5). The mentioned regulation then prescribes by means of a matrix with a row for each danger zone and a column for each probability level which kind of other facilities, roads, or locations with presence of people are permitted in each danger zone.

Returning to the above example with hazard division 1.1 articles, depending on the probability of an accident a factor of 8 to 22 is applied in the cubic-root-formula, while areas with public concentration such as schools or market places will always have to lie outside the danger zone Z_5 calculated with 44 as a factor in the the cubic-root-formula. With 1.2 articles and a projection hazard of heavy fragments the safety distance can range up to a maximum value of 800 m.

However, the figures may not be taken too literally since the assessment is performed individually for every facility and it is possible to modify numbers depending on natural barriers or protective installations. Moreover, a document not published in the official journal of the government, the "circulaire du 8 mai 1981 concernant l'application de l'arrêté du 26 septembre 1980", contains important details as to how the regulations are to be interpreted, and examples of activities and the corresponding probability levels are given.

Storage of fireworks on a smaller scale of up to 500 kg and with a time limitation, such as for the selling of new-years fireworks, is subject to an exemption given in the "arrêté du 10 février 1998". The local authorities issue the permission and the safety study is less elaborate than described above.

3.6 Germany

In Germany a law called "Sprengstoffgesetz" and two Ordinances ("1. Verordnung zum Sprengstoffgesetz" and "2. Verordnung zum Sprengstoffgesetz") cover all legal issues regarding explosives such as classification, use, permission, and also storage of fireworks. Testing with regard to storage classification is described in a regulation "SprengLR 010 - Richtlinie für das Zuordnen explosionsgefährlicher Stoffe zu Lagergruppen".

For any article containing explosive substances brought into the scope of the German Explosives Law, an assignment of this article to a storage and compatibility group is required. The storage and compatibility groups and the necessary testing procedures for classification are described in detail in an ordinance and directive belonging to the Explosives Law, and follow exactly the same scheme as described in the United Nations regulations for the transport of dangerous goods. I.e. for fireworks the classification codes 1.1G, 1.2G, 1.3G, 1.4G, and 1.4S apply. Just as in the UN regulations the type of packaging enters into the assessment process. In case different packaging is used for transport and for storage, the classification for storage may be different from the classification obtained for transport. By law the assessment is the responsibility of the Federal Institute for Materials Research and Testing (BAM).

Explosives may only be stored in specially designed facilities and may not be kept in open-air depots. Facilities for the storage of fireworks have to meet a number of requirements. Their construction has to satisfy certain conditions regarding safety against fire, electromagnetic effects, theft, intrusion and water. In addition, a detailed scheme of quantity-distance relations limits the storage in buildings satisfying the aforementioned conditions.

The quantity-distance scheme makes a distinction between distances to buildings within the grounds of a company and belonging to a company, and distances to the public, again differentiating between public roads or other areas and private housing. Other parameters which enter into the quantity-distance assessment are below- or above-ground depots or environmental conditions such as hills or trees on the grounds of the company storing the explosives. As an example, the prescribed safety distance for a depot with 1.1 articles is calculated with the factor 22 in the cubic-root-formula.

Some further details in relation to storage of fireworks are summarised here: in a depot with mixed hazard groups 1.1 to 1.4 the amount of 1.4 articles does not always have to be calculated for the quantity-distance procedure. The calculation is then based on the net explosive content of 1.1 to 1.3 articles. The assessment is based on the total net explosive content qualified by the most dangerous hazard group. Depots for the hazard group 1.4 do not require any safety distance for up to 100 kg gross weight of articles. The safety distance for more than 100 kg gross weight of 1.4 articles is 25 m independent of the amount. This safety distance may be zero if special provisions are taken. Outlining all the details, however, would go far beyond the scope of this work.

Regular storage facilities have to be approved by responsible authorities of the regional governments being in charge of merchandise and workers health protection. Exemptions from the requirement to have an approved storage facility are being made for small scale storage as it occurs in the course of selling new-years fireworks in small shops and for short term storage by private people, or professionals using pyrotechnic articles for technical purposes. These quantities range from 5 to 25 kg net explosive content for 1.1 articles depending on usage and location of the storage rooms, and are between 10 and 200 kg gross weight for pyrotechnic articles of storage group 1.4. It should be mentioned that the latter applies only to fireworks articles of class I and class II which are meant for private use. The national classification scheme with classes I, II, III, and IV defines mainly who may use which types of fireworks. The classes roughly coincide with the CEN categories for fireworks CAT1 and CAT2. The German law allows that articles in a special display packaging (selection pack) are available to the general public and allows storage of up to 800 kg of such selection packs in a safe container outside the shop.

3.7 Greece

The explosives law of Greece is called "Κανονισμοί για την παραγωγή, αποθήκευση και διάθεση σε κατανάλωση εκρηκτικών υλών" with the number 3329/15.2.1989. The English transcription is approximately "*Kanonismoi gia ten paragogi apothikefsi kai diathesi se katanalosi ekriktikon ylon*" which means "regulations for the production, storage and disposal when using explosive materials". Despite the difficulty of finding the way through the Greek explosives law, it was possible to identify the Tables which concern safety distances for the different hazard divisions 1.1 to 1.4. The numbers found there confirm the information obtained by personal communication with experts that the Greek explosives law is very close to the German explosives law. As a matter of fact, the Tables are structured in exactly the same way and contain the same numbers meaning that for the quantity-distance information one may also refer to the German explosives law. I.e. in Greece safety distances are also calculated applying a third-root quantity distance relation where the factor for the distance of 1.1 stores to dwellings is 22 and to roads 15.

3.8 Ireland

The regulations concerning fireworks in Ireland seem to be quite similar to those in the United Kingdom, according to information provided during expert communication. The "Dangerous Substances Act of 1972" contains some general provisions as to licensing of fireworks depots. Concerning fireworks, referrals are made to the 1875 Explosives Act of the United Kingdom. Since authorisation for depots are issued by local authorities presumably similar guidelines as reported in the section for the United Kingdom are applied.

3.9 Italy

The Italian regulations are based on a legal document from 1931, the "Testo unico leggi di publica sicurezza (T.U.L.P.S.)" which has been amended by many later ministerial decrees. The legal requirements for factories and storage facilities for explosives are outlined in the "Regolamento di esecuzione del T.U.L.P.S", which has the more detailed regulations on how to guarantee the public safety. The annex of this regulation contains information on safety distances.

With regard to production and storage, explosives are sub-divided into five categories of which the first three are powders and blasting explosives, category IV refers to pyrotechnics, and category V covers ammunition. The safety distance scheme for the first three categories resembles the regulations in other European countries. The third-root-formula is applied and factors in the range of 0.8 to 22 are used for different types of adjacent site (i.e. process buildings, residential roads etc.). Additionally, minimum distances to the public of 270 m and 400 m apply in several cases. Fireworks do not seem to be subject to such a differentiated safety distance scheme. A large part of the regulation is dedicated to the keeping of powder and ammunition, perhaps reflecting a tradition of hunting, and the situation concerning fireworks could not be clarified from a study of the legal texts only.

3.10 Luxembourg

Regulations concerning pyrotechnics in Luxembourg are summarised in the document "Prescriptions de sécurité pour les dépôts d'articles pyrotechniques, ITM-CL 41.4, du 15 octobre 1999". The national classification scheme seems to be very similar to the German classification scheme. I.e. fireworks are divided in classes I to IV (pyrotechnic articles for entertainment purpose), and pyrotechnics with a technical purpose are denoted with T_1 and T_2. The mass threshold levels are exactly the same as in the German law. The fireworks categories III and IV and technical pyrotechnics T_2 are limited to professional use, only.

The storage of class I, II, and T_1 articles has less restrictions than for the more dangerous articles. According to the regulation, up to 100 kg can be stored in retail shops and up to 300 kg in adjoining storage rooms. Such places may have windows while these are forbidden for the storage of class III and IV articles. Larger depots of class I and II articles with up to 1000 kg gross weight are possible but have to maintain a safety distance of 25 m to dwellings.

For the storage of more than 1000 kg class I and II, or for the storage of class III and IV the regulations for special storage apply ("dépôts spéciaux"). For more than 5000 kg of such articles a special permission and case study by the mining and workers authority is required. In the range up to 5000 kg the safety distance values are split for articles up to a diameter of 60 mm or above this value. For articles up to a calibre of 60 mm the safety distance is 90 m to housings for on-ground storage and 60 m for underground storage. The distances to public roads are 60 m and 40 m respectively. Fireworks with a calibre above 60 mm require safety distances of 135 m (on-ground) or 75 m (underground) to dwellings and 90 m (on-ground) or 60 m (underground) to public roads.

3.11 The Netherlands

In consequence of the Enschede disaster The Netherlands has adopted a new law dealing with consumer and professional fireworks, the "Vuurwerksbesluit" of January 22, 2002. This law distinguishes the two categories of fireworks, i. e. consumer and professional fireworks, which are defined by their purpose of use and by threshold values. Any fireworks article which is not clearly indicated as consumer fireworks automatically belongs to the category of professional fireworks. Fireworks which have been assigned to hazard division 1.3G are also automatically regarded to be professional fireworks.

The law requires a proper classification to a hazard division according to the ADR regulations before fireworks articles can be brought to Netherlands and before they can be stored. The hazard division from the transport classification is the basis for the storage.

The rules for the storage of professional fireworks are very strict. Storage of professional fireworks is only allowed with up to 6000 kg gross weight per storage facility, and a safety distance of 800 m to sensitive objects has to be maintained regardless of the amount stored up to the 6000 kg limit.

The storage of consumer fireworks distinguishes between smaller installations, i.e. storage facilities with up to 10 000 kg gross weight of consumer fireworks or more than 10 000 kg. The smaller kind of storage facilities has to have a minimum safety distance of 8 m and a fire resistant wall must be placed in the direction of the door opening. In case of larger storage plants for consumer fireworks a list of safety distances exists each depending on the direction with respect to the door opening and the amount stored in each subsection (individual storage buildings or containers).

3.12 Portugal

Portugal has a law especially dedicated to the safety of facilities for the production and storage of explosives which is called: "Aprova o Regulamento de Segurança dos Estabelecimentos de Fabrico e de Armazenagem de Produtos Explosivos", (decreto-lei No. 139/2002 de 17-05-2002). The central aspect of this law is the classification of explosives, which includes any kind of pyrotechnic article, according to the scheme known from the transport of dangerous goods, i.e. classes 1.1 to 1.6 and the compatibility groups A to S are used. Depots for pyrotechnics have to be approved by the local authorities on the basis of an application with very detailed information on all installations, actions, and quantities involving explosive substances. Every installation for explosives is thus surrounded by a safety zone equivalent to the safety distance and within which the erection of houses and roads are essentially forbidden.

Many parameters contribute to the calculation of safety distances such as: the hazard division of the explosive to be stored, 8 different levels of safety for objects to be protected (on-site or off-site objects, working, living areas, power lines, etc.), and the amount of explosive to be stored. The calculation is based on the net explosive content in kilograms, in most cases calculated with the cubic root, but also with fourth and sixth root for the hazard division 1.2. The result of the n-th root is multiplied by a factor given in eight Tables for the different levels of safety.

The safety distance between a licensed storage for fireworks of hazard division 1.1 and public roads is calculated with the factor of 12 and for dwellings or other places with concentration of the public with the factor of 20.

The small scale storage of fireworks for the purpose of selling is generally limited to 50 kg net explosive content and only permitted for such fireworks articles that are legally available to the public.

3.13 Sweden

In Sweden a law, the "Lag (1988:868) om brandfarliga och explosiva varor", covers more general issues and an ordinance called "Förordning (1988:1145) om brandfarliga och explosiva varor" deals, among other aspects, with permissions and fees. The details of the storage of explosives can be found in the regulations "Sprängämnesinspektionens föreskrifter om hantering och import av explosiva varor (1989:8)" which cover handling and import of explosives. According to this regulation the same classification scheme as outlined in the ADR regulations with hazard divisions 1.1 to 1.5 and compatibility groups A to S are used.

The regulation focusses mainly on handling and storage of blasting explosives, however it also includes sections on pyrotechnics and fireworks. Overground storage is therefore limited to a maximum net explosive content of 200 000 kg. The safety distance Table for different storage amounts from 100 kg to 200 000 kg given in appendix B of the regulation is meant only for explosives with a mass explosion hazard, i.e. for hazard division 1.1. Distances are different depending on the need for protection of built-up areas with large concentrations of people and/or groups of dwellings, areas with only few dwellings, or other areas. Within this scheme two levels of protection are distinguished.

The Tables are based on the frequently used cubic-root-formula of the net explosive content with varying factors. The factor is 30 for the highest level of protection. For less frequented areas a factor of 3 can be used for up to 15 000 kg and for a depot with good protection against the effects of an explosion. For higher amounts a factor of 15 applies. If goods with no mass explosion hazard are stored, as will be the case for many types of fireworks, the distances can be reduced to 25% of the distance for 1.1 type explosives.

3.14 Spain

The Spanish legislation on explosives can all be found in one law, the "Reglamento de Explosivos" (Real Decreto 230/1998) and the technical instructions belonging to that law.

As in all other European countries, Spanish storage facilities for explosives have to be approved by governmental authorities. The Spanish Explosives regulation distinguishes above-ground, half-underground, and underground stores. Storage facilities up to 10 000 kg of net explosive mass are approved by a local body and larger depots have to be authorised by the Ministry of Industry and Energy. Licensed stores for explosives have to satisfy requirements of safety against intrusion of unauthorised persons either by an alarm system or by a security service. Requirements concerning safety distances apply which are different for on-site installations and for the distance to public spaces or dwellings. In all cases the safety distance is calculated by the cubic-root-formula on the basis of the net explosive content to be stored.

The Spanish regulation comprises a number of technical instructions sheets where the factors for the safety distance calculation are given depending on the hazard divisions following the UN-system for the transport of dangerous goods. The figures obtained are to be taken as minimum distances. As an example, the required minimum safety distance from a licensed store with 1.1 material to dispersed individual houses uses the factor of 20 and for highly frequented public areas a factor of 35. In the presence of favourable conditions of the terrain these distance can be reduced to one half.

The storage of pyrotechnic articles outside the above mentioned licensed stores is possible in a number of special cases where exemptions apply. These exemptions are, however, based on the classification of fireworks to national classes where class I, class II, and class III articles are meant to be used by the public. These classes coincide, at least by their general description, with the categories found in the CEN standards. The technical instruction sheet number 23 has a detailed table with mass thresholds for the different types of fireworks and the assignment to different classes I, II, and III.

Exemptions apply to the storage of fireworks in relation to sales. While class I articles can be stored in an adjoining storage room without limit, the storage of class II and III articles will be allowed up to a limit of 50 kg. Pyrotechnic articles may not be placed in a display (except if these are specimens without composition) and the fireworks need to be securely stored to prevent access by the public. Limitations as to who may sell and who may buy such pyrotechnic articles are not covered by these exemptions.

3.15 United Kingdom

Handling of explosives is regulated in the "1875 Explosives Act", the "1883 Explosive Substances Act", the "1923 Amendment to the Explosives Act", and a number of later regulations such as the "Control of Explosives Regulations 1991 (COER)" and the "Manufacture and Storage of Explosives Regulations (MSER)", the latter is a new legislation which will be introduced shortly. Currently authorisations for fireworks storage are issued either by local authorities if the amount stored does not exceed 1800 kg NEC (2000 kg in future) or by the Health and Safety Executive for larger depots. Part of the revision work concerning regulations will also be directed towards achieving consistency with respect to criteria and the quantity-distance scheme applied.

Over the years the Explosives Act has been overlaid with a considerable amount of secondary legislation with the result that it has become very difficult to work out which legal requirements apply in particular situations. For this reason the following statements mainly refer to the newly proposed MSER regulations which, however, are not yet in force. While in the past and in the present situation the population density is not explicitly taken into account when determining separation distances, the new regulations will distinguish two levels of population density. Articles that are to be stored are sub-divided according to four hazard types (HT) defined essentially in the same way as the United Nations classification system for explosives. In this HT1 corresponds to division 1.1 and HT4 corresponds to division 1.4. The idea of using a different terminology is to allow for a differing assignment as compared with the classification for the transport of dangerous goods. In a small number of cases the responsible authority may regard the bulk storage of certain pyrotechnic articles to represent a greater hazard than given by the transport classification.

The safety distances set out in the draft MSER regulations are in the same range as found for other countries (Germany or Spain). A 1000 kg NEC depot of division 1.1 articles requires a safety distance of 204 m to a low density area and 250 m to a high density area. The corresponding figures would be 150 m and 220 m for Germany or

200 m and 270 m for Spain. However, the sensitive area descriptions between countries differ slightly and comparison should take this into account.

Distances for a division 1.4 depot range from 5 m for 200 kg up to 30 m for 2000 kg being about the range used in Germany or Spain which is 25 m for more than 100 kg.

Regarding the currently active regulations in Great Britain as set out in the Control of Explosives Regulations of 1991 the public may store up to 5 kg of fireworks permanently in a safe place and may even store an unlimited amount of fireworks as long as the storage place is safe and the time period does not exceed two weeks.

3.16 Other European countries

From other European countries the legal texts of Swizzerland and Malta are available on the internet. In Switzerland a single ordinance the "Verordnung über explosionsgefährliche Stoffe, 941.411" covers all issues related to explosives. It should be mentioned that, although Switzerland is not a member of the EC, it puts blasting explosives under the directive 93/15/EWG and has the same conformity assessment procedure. Storage of fireworks is generally limited to 2000 kg gross weight in non heavy-duty buildings and may not exceed 5000 kg gross weight in heavy-duty buildings with earth cover and exhaust openings. In that situation the safety distance between storage buildings has to be 7.5 m and the distance to neighbouring property has to be a 20 m minimum. The door openings may not point to other windows or doors.

Storage of up to 300 kg gross weight of fireworks are regarded as small quantity storage and do not require special buildings and may also be within residential areas. Another threshold level is set at 30 kg for the keeping of fireworks in shops for retail sale. Switzerland also applies a quantity-mass relation but this is only to blasting explosives.

Malta has an English version of its explosives and fireworks ordinances. Concerning storage a number of restrictions are made concerning the construction of the facility, for the safety distance, however, it seems that the figure valid for gunpowder factories and similar installations applies here which is 183 m to any inhabited area or streets.

4 Summary

The analysis of national regulations on the storage of fireworks has revealed that essentially two differing approaches exist to the issue of safeguarding the public in relation to stored fireworks. These are:

- Quantity-distance relations, where quantity in most cases refers to the net explosives content of the fireworks, and a
- Probability-risk assessments.

A larger number of countries have regulations relying on quantity-distance schemes and the critical numbers have become more and more similar in recent times. It could even be said that during the past decades a tendency to installing a quantity-distance scheme, if this had not been present in a country beforehand, or towards harmonising the numbers used in the quantity-distance scheme, is observable. It seems likely that new versions of regulations in one country have been inspired by the regulations present in others.

In this sense the regulations of Finland, Germany, and Greece are very similar and Portugal and Spain have regulations which also follow a similar pattern. Direct comparison is, however, difficult since the categories of areas or objects to be protected differ, for example either 8 categories for Portugal or 2 categories for Germany or the United Kingdom. Furthermore, the regulations quite often include some vague instructions that distances may be reduced under special conditions, or have to be increased under others. Therefore the actual distance which is applied can vary according to the judgement of the competent authority issuing a permission for a depot.

An exhaustive database from testing of safety distances of stored fireworks would definitely be helpful for the countries of the European Community, since the span of safety distances found in the regulations is unlikely to indicate a differing desire for safety, but rather indicates the lack of accurate information concerning the hazards posed by fireworks depots.

Another aspect regarding storage safety which seems quite critical is the accurate assignment of fireworks articles to a system of hazard groups. Apart from perhaps differing numbers in the quantity-distance schemes and the different levels of strict enforcement of laws in different countries (the latter an aspect clearly beyond the reach of a quantitative assessment) any deviation in assigning a particular fireworks type to one hazard division or another could lead to completely different situations with regard to public hazard.

Only Germany and United Kingdom have a formally independent system of storage groups to be applied to fireworks. Most countries with quantity-distance schemes use the hazard divisions given by the transport regulations. Looking closely, Germany also belongs to this category since the storage group system relies on exactly the same tests as given in the test handbook of the UN recommendations for the transport of dangerous goods. While the question has been raised a number of times, whether the UN hazard division are suitable for fireworks at all, the UN hazard divisions are quite clearly only meant for the limited quantities that can be transported in a single load and not for the large amounts stored in a fireworks depot. Such stores can contain hundreds of tonnes of fireworks.

In contrast, some countries have formulated their storage regulations on the basis of their national classification scheme for fireworks which is usually a system with increasing grades of hazard with respect to usage. As a matter of fact, no country has a system which incorporates explicitly the testing of fireworks under mass storage conditions and the extrapolation from the UN tests is the current way of dealing with this issue.

France appears to be the only country using a probability-risk assessment. Consequently, a comparison of the corresponding regulations with the other countries can prove difficult. However, the different zones of danger mainly apply to on-site installations and working, and the public will have to be kept outside the largest zone, anyway. For a detailed comparison a number of sample safety-studies would be necessary in order to compare the French safety distances with regulations of other countries. This information was not available, at the time of publication.

In this work safety distances have been compared since this was the only information which could be subjected to a *quantitative* comparison. The laws and regulations usually contain many more details than can be included. Such details concern types of doors, windows, dimensioning of pathways and, for example, the ban of smoking in and around explosives depots. The differences in these points do not seem to be very large among the EC member countries.

Some countries prescribe a maximum explosive limit for individual depots on larger storage sites which may result in division into smaller units necessary. The aspect of storage density, however, does not play a major role in regulations although this could be a significant parameter for avoiding the virtually instantaneous explosion of a fireworks depot. The CHAF project may perhaps give some helpful indications on this particular aspect.

As a major goal the research undertaken for CHAF will produce as output a more refined testing methodology. Three major points of interest can be summed up here where explosive regulations differ between EU member countries and where the results of the CHAF project can be expected to provide clarifying information:

(1) which classification scheme for fireworks is the most suitable to meet the needs of classification under bulk storage conditions,

(2) a clear indication of how packaging density influences classification, and

(3) the appropriate safety distances to be applied to fireworks depots.

Consulted documents

In this section all the legal texts which have been consulted during this work are listed in alphabetical order.

Austria	Pyrotechnik-Lagerverordnung, BGBl. Nr. 512/1977
Denmark	Tekniske forskrifter, fastsat i medfør af § 3, nr. 3, i lov nr. 193 af 24. maj 1972 om fyrværkeri, ... i § 2 i Indenrigsministeriets bekendtgørelse nr. 778 af 14. oktober 1999 om fyrværkeri
Finnland	130/1980, Kauppa- ja teollisuusministeriön päätös räjähdystarvikkeista
France	Arrêté du 24 février 1994 relatif au classement des artifices de divertissement Décret 79-846 du 28 septembre 1979 portant règlement d'administration publique sur la protection des travailleurs contre les risques particuliers auxquels ils sont soumis dans les établissements pyrotechniques Arrêté du 26 septembre 1980 fixant les règles de détermination des distances d'isolement relatives aux installations pyro-techniques
Germany	Sprengstoffgesetz vom 10. September 2002 (BGBl. I Nr. 65 vom 13.9.2002 S. 3518; 11.10. 2002 S. 3970) 1. Verordnung zum Sprengstoffgesetz vom 31. Januar 1991 (BGBl. I S. 169) zuletzt geändert am 11. Oktober 2002 (BGBl. I S. 4013) 2. Verordnung zum Sprengstoffgesetz vom 10. September 2002 (BGBl. I S. 3543) SprengLR 010 - Richtlinie für das Zuordnen explosionsgefähr-licher Stoffe zu Lagergruppen, Ausgabe April 1978 (BArbBl. 6/78 S. 231)

Greece	Κανονισμοί για την παραγωγή, αποθήκευση και διάθεση σε κατανάλωση εκρηκτικών υλών, 3329/15.2.1989
Italy	Testo unico leggi di publica sicurezza (T.U.L.P.S.) and Regolamento di esecuzione del T.U.L.P.S
Luxembourg	Prescriptions de sécurité pour les dépôts d'articles pyrotechniques, ITM-CL 41.4, du 15 octobre 1999
Malta	Ordnianza dwar L-Esplożivi Regolamenti dwar il-Manifattura u l- ażna ta`Esplo żivi Regolamenti dwar Kontroll ta`Xog lijiet tan-nar u Esplożivi o ra
The Netherlands	Vuurwerksbesluit of January 22, 2002
Portugal	Aprova o Regulamento de Segurança dos Estabelecimentos de Fabrico e de Armazenagem de Produtos Explosivos, decreto-lei No. 139/2002 de 17-05-2002
Spain	Reglamento de Explosivos, Real Decreto 230/1998
Sweden	Lag (1988:868) om brandfarliga och explosiva varor, Förordning (1988:1145) om brandfarliga och explosiva varor Sprängämnesinspektionens föreskrifter om hantering och import av explosiva varor (1989:8)
Swizzerland	Verordnung über explosionsgefährliche Stoffe (Sprengstoffverordnung, SprstV)
United Kingdom	Control of Explosives Regulations 1991 (COER), Proposal for Manufacture and Storage of Explosives Regulations 2002 (MSER)

CHAF WP4	Literature review
Deliverable 4-4	The effect of fireworks on health and the environment
Date	June 2003
Author	S. Myatt (HSL)

Summary

This section will cover task D4-4 of the literature review described at the beginning of the report. The aim of D4-4 is to provide an overview of the types of chemicals used or generated during fireworks manufacture and use, to indicate their toxicological and physiological hazards, and to assess the likely impact of such chemicals on health and the environment. In addition, other pollutants such as particulates and noise are considered. Examples of firework accidents are given towards the end of the section to illustrate the types of damage and pollution that can occur.

The Effect of Fireworks on Health and the Environment

1 Introduction

The Chinese have been credited with the discovery of gunpowder, or blackpowder as it is often called, in about the eighth century[1]. However, some reports suggest that its development may have occurred independently in Europe and in the Far East[2]. Various proportions of the three ingredients used to make blackpowder (charcoal, potassium nitrate (saltpetre), and sulfur), have been used throughout its development until the modern mix of 75% potassium nitrate, 15% charcoal and 10% sulfur was recorded in 1781[1]. While Europe developed blackpowder for military purposes such as the propulsion of cannonballs and 'bombs', the Chinese used it for religious ritual, to develop fireworks for recreational entertainment, and for crude incendiary weapons[2].

There is little doubt that the development of fireworks occurred in far-eastern countries such as India or China and that the techniques needed to make them were probably transferred to Europe during trade with Arab nations[1]. Many texts suggest that firework development in Europe started in the early 16th century in Italy [1,3,4] and spread rapidly to the rest of Europe. Firework displays had reached the far west of Europe by 1572 when it is reported that Queen Elizabeth I of England witnessed a display[1]. Over the coming centuries the popularity of firework displays grew and many books were written on the subject, Philip[5] produced a bibliography such books in 1985.

Blackpowder was virtually the only explosive used in fireworks[6,7] until the late 18th century[3] when the addition of metal salts, such as those of strontium and barium, enhanced the range of colours that could be generated. It was not until after Berthollet made potassium chlorate in 1786 that pyrotechnists had the oxidiser/metal fuel compositions to produce vivid saturated colour. By 1880 the use of finely divided metals, such as magnesium[3], to increase the brilliance of fireworks effects and the noise they could produce, was well established.

The increase in the popularity of fireworks in modern times is illustrated by the sales of fireworks in the United States. Their retail value has risen from $16 million in 1960 to $625 million in 1999[8]. The latter value equating to approximately 71,300 tonnes of fireworks (approximately 21,400 tonnes of explosive assuming a loading of 30%). Alenfelt[9] estimates that in Sweden in 1998 $30 million of fireworks were used and Fleischer et al.[10] state that 30,000 tonnes ($80 million) of fireworks are fired in

Germany annually which equates to approximately 10,000 tonnes of explosive based on the 30% loading described previously. These figures demonstrate the huge popularity of fireworks throughout the world and indicate that large quantities of fireworks are being imported, transported, stored and fired within the European Union.

Firing such large quantities of fireworks raises many environmental issues, some of which are listed below:

- Can the firing of a display cause damage to health from smoke fume or noise?
- Does the fallout from the display cause an accumulation of chemicals in the surrounding area ie. as soil contamination?
- Can soil or air borne contamination enter water courses?
- What social effect does the increased use of fireworks have?

In the following sections the types of chemicals used in fireworks are reviewed and suggested combustion products summarised. The toxicological and environmental impact of such chemicals are also discussed.

2 Firework compositions

2.1 Blackpowder

As has already been stated the constituents of modern blackpowder are potassium nitrate (75%), charcoal (15%) and sulfur (10%). Minor variations on this mixture by adding metals to produce sparks etc are the basis of almost all fireworks.

2.2 Chemicals to generate coloured light

A wide range of chemicals are used to produce coloured light for use in fireworks and are discussed in detail in many texts on the subject[11-16]. As a guide, coloured light generation requires a fuel and an oxidiser. Additional chemicals are often added to act as colour enhancers and binders. The situation is further complicated due to the dual use of some chemicals i.e. to perform more than one of the functions listed, or the inclusion of scavenger compounds to remove chemical species that may interfere with the desired colour generation. Some colour reactions can produce competing colour species and the use of metal fuels can produce incandescent particles which also interfere. Conkling[17] and Lancaster[18] list a wide range of compounds used in pyrotechnic articles, some of those listed by the former are probably only used for military purposes due to their toxic or energetic properties which could make them difficult or expensive to handle in normal fireworks manufacture. A range of compounds used for firework articles are given in Tables 1 to 4. The lists are not intended to be exhaustive but demonstrate the types of compounds commonly used.

The majority of colour enhancing compounds tend to generate chlorine from organic compounds (Table 4) particularly when barium, strontium, calcium or copper are used as the colour agent, although Kosanke[11] also mentions the use of hydroxide species. Where a purple flame is required, often using a combination of SrCl and CuCl, the presence of hydroxide degrades the colour and therefore needs to be absent from the flame. To achieve this hydrocarbon based fuels/binders are not used.

Table 1: Fuels

Name	Formula	Comments
Aluminium	Al	Stable & readily available
Carbon (as charcoal etc.)	C	
Magnesium	Mg	More reactive than Al. Care needed
Magnalium	Mg/Al	Combine reactivity of Mg with stability of Al
Sulfur	S	Often used
PVC	$(\text{-}CH_2CHCl\text{-})_n$	Man made polymer
Lactose	$C_{12}H_{22}O_{11}.H_2O$	Natural disaccharide
Dextrin	$(\text{-}C_6H_{10}O_5\text{-})_n.H_2O$	Natural polymer
Red Gum	-	Complex natural substance
Shellac	-	Complex natural substance

Table 2: Oxidisers

Name	Formula	Comments
Ammonium perchlorate	NH_4ClO_4	A more recent compound for use in fireworks
Barium chlorate	$Ba(ClO_3)_2$	Sensitises compounds to shock & friction. Little used.
Barium nitrate	$Ba(NO_3)_2$	Generally requires metal fuel to obtain required burning temperature (poisonous)
Potassium chlorate	$KClO_3$	Historically widely used. Being phased out due to hazards from increased senstiveness of some mixtures
Potassium nitrate	KNO_3	Often needs a high energy fuel (C, Mg, AL etc.)
Potassium perchlorate	$KClO_4$	Has generally replaced $KClO_3$
Strontium nitrate	$Sr(NO_3)_2$	Rarely used as the only oxidiser

Table 3: Compounds that can form coloured flames			
Colour	**Compound**	**Formula**	**Comments**
Green	Barium sulfate	$BaSO_4$	
	Barium oxide	BaO	A weak green light emitter
	Barium chlorate	$Ba(ClO_3)_2$	Sensitises compositions to shock & friction. Being phased out
	Barium nitrate	$Ba(NO_3)_2$	Requires a chlorine source
	Barium carbonate	$BaCO_3$	Use in low percentage because inert carbonate anion can reduce flame temperature
Red	Strontium nitrate	$Sr(NO_3)_2$	Requires a chlorine source
	Strontium carbonate	$SrCO_3$	Use in low percentage because inert carbonate or sulfate anions can reduce flame temperature
	Strontium sulfate	$SrSO_4$	
Blue	Copper acetoarsenite (Paris Green)	$3CuO.As_2O_3$	Toxic. Now obsolete
	Copper(II) oxychloride	$3CuO.CuCl_2$	
	Copper(II) oxide	CuO	
	Copper(II) carbonate (basic)	$CuCO_3.Cu(OH)_2$	
Orange	Calcium carbonate	$CaCO_3$	
	Calcium sulfate	$CaSO_4$	
Yellow	Cryolite	Na_3AlF_6	
	Sodium nitrate	$NaNO_3$	Hygroscopic
	Sodium oxalate	$Na_2C_2O_4$	
Purple	Generally mixtures of red & blue emitters		

Table 4: Typical chlorine donors		
Compound	**Formula**	**Percent chlorine (w/w)**
Hexachloroethane	C_2Cl_6	90
Dichlorane	$C_{10}Cl_{12}$	78
Saran Resin	$(C_3H_2Cl_2)_n$	73
Parlon	$(C_5H_6Cl_4)_n$	67
Polyvinylchloride (PVC)	$(C_2H_3Cl)_n$	56

2.3 Noise compositions

The three main types of firework noise effect are whistles, crackling stars, and reports (sometimes referred to as salutes). Details of the different firework compositions used for these effects are given in many texts[19-25].

Whistle compositions tend to use a very limited range of compounds. The general requirement is for an oxidising agent combined with an aromatic compound, or its salt, which is pressed into a tube allowing a portion of the tube to remain empty. On ignition the empty length of tube acts as a resonator resulting in the whistling sound. Reported mixtures are listed in Table 5.

Table 5: Compounds used in whistle compositions

Oxidisers		**Fuels**	
Compound	**Formula**	**Compound**	**Formula**
Potassium perchlorate	$KClO_4$	Potassium benzoate	$KC_7H_5O_2$
Potassium nitrate	KNO_3	Sodium benzoate	$NaC_7H_5O_2$
		Sodium salicylate	$NaC_7H_5O_3$

Crackling stars have become popular in recent years[12]. The main constituents tend to be metal fuels such as magnalium, and metal oxides such as lead, copper or bismuth. While bismuth produces good stars they are not often used due to the high price of the metal.

Historically, report/salute compositions tended to be based on blackpowder charges which were heavily confined. However, blackpowder has almost universally been replaced with a small range of flash compositions which are based on finely divided metal powders such as aluminium or magnesium and powerful oxidisers such as potassium perchlorate, potassium chlorate or barium nitrate. Chlorate oxidisers are not recommended due to the tendency to increase the sensitiveness of compositions to shock and friction. In some instances antimony trisulfide (Sb_2S_3) or sulfur (S) may be added. Most references only mention aluminium as the metal fuel though Lancaster[21] also mentions a magnesium containing composition. Use of magnesium requires even more care than aluminium due to its higher reactivity.

Many other materials can be used in fireworks but those mentioned are probably used most frequently.

3 Combustion products

The wide range of chemicals available and the almost infinite way in which they can be combined in firework compositions makes a detailed breakdown of combustion products difficult. This is further complicated by the high temperatures encountered in pyrotechnic flames. Shidlovskiy[26] states that high temperature products of potassium chlorate combustion are potassium chloride and oxygen rather than the expected potassium perchlorate and potassium chloride encountered in low temperature decomposition. This indicates that care needs to be taken when trying to predict combustion products from firework compositions.

Blackpowder reactions have been studied extensively due to its historical links to military applications. Consequently its combustion products are well known. Russell[1] suggests that combustion of blackpowder follows the following reaction:

$$KNO_3 + C + S + H_20 \rightarrow N_2 + CO_2 + CO + CH_4 + H_2S + H_2 + K_2CO_3 + K_2SO_4 + K_2S_20_3 + K_2S + KSCN + (NH_4)_2CO_3 + C + S$$

This is supported by work by Hussain and Rees[27] who experimentally determined that combustion products of blackpowder contained 31% (by weight) of gaseous products, consisting of CO_2 (50%), CO (4-5%), N_2 (40%) and small quantities of water and hydrogen sulfide. The solid products (55-60% by weight) consisted of K_2CO_3 (34%), K_2SO_4 (8.5%) and small amounts of potassium thiocyanate, potassium nitrate, carbon and sulfur. It is clear that the reaction of only 4 compounds during combustion can produce a wide variety of products.

Where additional compounds such as metals, metal salts, chlorine donors hydrocarbon fuels and binders are incorporated into compositions, for colour or sound effects etc., there is little data in the literature to indicating what products are generated. Shidlovsky suggests theoretical equations for the reaction of barium chlorate with long chain alcohols, and for potassium chlorate with basic copper carbonate and sulfur. Common products to both reactions are CO_2 and water. In addition, the first reaction produces barium chloride while the second produces copper chloride, potassium chloride, potassium sulfate and sulfur dioxide. A similar report by Kosanke[11] suggests that a glitter composition produces K_3SbS_3, K_2S_2, CO_2 and nitrogen from a mixture of potassium nitrate, carbon fuel, sulfur and antimony sulfide

Environmental papers[28-30] tend to report combustion products in general terms, stating that fireworks generate solid metal oxides, nitrates, chlorides, sulfates and carbonates and gaseous products such as hydrocarbons, polycyclic aromatic hydrocarbons, chlorinated hydrocarbons, hydrochloric acid and oxides of carbon, and sulfur.

Experimentally determined data seems relatively rare. Rossol[30] demonstrated that a fine solid deposit collected after ignition of fireworks consisted of aluminium oxides, titanium oxides, strontium carbonate, carbon, strontium chloride, potassium chloride, potassium sulfate, strontium hydroxide and potassium carbonate. A report by Chung[31] identified barium sulfate and barium nitrate from mini gerbs and pyroflash fireworks. He also found long chain hydrocarbons and substituted aromatic compounds.

Hatanaka and Miyahara[32] showed that the products from combustion of aluminium with potassium perchlorate or potassium chlorate theoretically generates a range of species:

$$Al_2O_3 + KCl + Al + Al_2O + AlO + AlCl + K + Cl$$

However, experimental measurements indicated that only Al_2O_3 and KCl were produced. The experimental data cited tends to confirm the generalised view of environmental papers and reports i.e. that the majority of combustion products from fireworks are solid metal oxides, nitrates, chlorides, sulfates and carbonates and gaseous products such as hydrocarbons, polycyclic aromatic hydrocarbons, chlorinated hydrocarbons, hydrochloric acid and oxides of carbon, and sulfur. While this assumption can be used as a basis for assessing the toxicological and environmental effects of fireworks it must always be borne in mind that unexpected chemical species may be produced.

Some of the constituents of fireworks are toxic. Unfortunately, literature relating to fireworks manufacture does not tend to cover this aspect in much detail and a concise and comprehensive coverage of the subject is lacking. Hardt[33] and Kosanke[34] provide an indication of the toxicity/hazard associated with some pyrotechnic reagents but do not enter into discussions on the toxicity of combustion products. Cegiel[28] refers to the Pyrotechnics Industry Association (VPI) in Germany, which set up a ‘Pyrotechnics Datapool’ in 1992. The aim was to collate information on the manufacture, application, recycling and disposal of pyrotechnics. The datapool is reported to contain information on the combustion of pyrotechnics and could be a valuable resource when considering environmental effects. However, access to the data is by association membership only and, to date, the author has been unable to gain access.

Military research into the toxicological and environmental effects of pyrotechnics has developed over recent years and may be a useful source of information in the future. However, it must be noted that not all the chemicals or compositions for military use would have firework equivalents and that any conclusions drawn from the data would need to be reviewed carefully.

More readily available journals on toxicology such as Sax[35], NIOSH-RTECS[36], and chemical company web sites[37] cover a very wide range of industrial chemicals, including precursors of pyrotechnic compositions but, as has been stated previously, the exact combustion products can be unclear which makes research into and assessment of hazards from pyrotechnic combustion products difficult.

Based on the reactants and products referred to in this paper, Table 6 lists compounds that have prescribed exposure limits taken from reference texts[37-40]. Mercury compounds have been omitted because it is believed that these compounds are rarely used in fireworks today. The Table includes chemicals based on their toxicity, it does not necessarily include:

- chemicals that are respiratory hazards due only to dust inhalation as these are discussed later in the paper
- chemicals that are unstable or react quickly with atmospheric chemicals (air, water etc.), because it has been assumed that such chemicals will have reacted and formed more stable compounds before display operators, spectators or local residence are exposed.

As can be seen from Table 6 the number of toxicologically dangerous chemicals used or produced by fireworks appears to be relatively large. The Occupational Exposure Level (OEL) data indicates that some of these chemicals are dangerous in small quantities and can cause significant physiological effects. Lead and chromium compounds, and hydrogen sulfide should be treated with particular caution not only because of their toxic action on humans but also due to their very toxic effects on aquatic organisms. In addition, there are a number of chemicals in the Table which may need careful assessment due to the possibility of causing tumorigenic, mutagenic or cancerous effects.

The physiological effects of perchlorate contamination have only recently been identified[39] which means that the toxicological effects are still unclear. However, the large amount of potassium perchlorate used in firework compositions and the potential effects warrant its inclusion in this paper. While toxicological studies are incomplete, the USA has established a tentative Reference Dose (RfD) of 0.9 µg/kg/day. The provisional action level for drinking water is 18 ng/ml, although certain states are expected to move to an action level of 4 ng/ml. These measures are being taken to prevent hormone imbalances due to the effects of perchlorate on the thyroid gland.

Dioxins are of particular environmental concern due to their accumulation in fatty tissues and very slow breakdown rate. Ingestion of low levels of polychlorinated dibenzo para dioxins (PCDD’s) and equivalent furans (PCDF’s) by small organisms results in larger doses for predators further up the food chain. The World Health Organisation (WHO) states that a Tolerable Daily Intake (TDI) for these chemicals is 1-4 picogrammes per kilogram body weight[40]. Current exposure in industrialised countries is in the range 1-3 picogrammes per kilogram. A report[41] indicates that average Americans currently have a body burden of these chemicals of 13 ng/kg which is less than 10 times lower than the levels believed to cause serious physiological effects such as chlor-acne, cancer, learning disorders, diabetes and sperm loss.

PCDD's and PCDF's are produced in small quantities naturally (volcanic action), but the main source is human activity. They are generated by incomplete combustion of chlorinated compounds at temperatures below 1000°C[40]. Fleischer[10] demonstrates that these types of chemicals can be generated by fireworks and therefore they are a legitimate environmental concern. As has already been discussed, small increases in background levels of these chemicals can result in serious effects on higher mammals.

Table 6: Toxicity of firework compounds and their combustion products											
Name of chemical	Formula	Data source reference	Airborne dust data			Airborne limits		Comments			
			Dust hazard	Total respirable (mg/m^3)	Total Inhalable (mg/m^3)	OEL (mg/m^3)	OSHA PEL (mg/m^3)	Carcino-genic etc.	Effects	Organs affected	Ecological info
Aluminium	Al	38	Y	4	10						
Aluminium salts (soluble)		38				2					
Aluminium chloride	Al_2Cl_3	37				2			destroys mucus membranes. Causes burns.	lungs	
Aluminium oxides	Al_2O_3	37,38	Y	4	10	2-10	5-15		irritant to mucus membranes	lung bones	
Ammonium carbonate	NH_4CO_3	37							irritant to mucus membranes		
Antimony (III) sulfide	Sb_2S_3	37,38				0.5	0.5	Possible	irritant to mucus membranes	behavioral, heart lungs stomach	
Barium salts [soluble)		38				0.5					
Barium chlorate	$BaClO_3$	37				0.5	0.5		May be fatal if inhaled, ingested or absorbed through skin. Irritant to mucus membranes	Heart nerves kidneys bone spleen liver blood	
Barium chloride	$BaCl_2$	37				0.3-0.5	0.5		irritant to mucus membranes	Heart nerves kidneys bone spleen liver blood	
Barium nitrate	$Ba(NO_3)_2$	37				0.4-0.5	0.5		irritant to mucus membranes	Heart nerves kidneys bone spleen liver blood	
Barium oxide	BaO	37				0.5	0.5		destroys mucus membranes. Causes burns.	Heart nerves kidneys bone spleen liver blood	
Barium sulfate	$BaSO_4$	38	Y	4	10						
Carbon black	C	38				3.5					
Carbon dioxide	CO_2	37,38				9000	9000				

Table 6: Toxicity of firework compounds and their combustion products												
Name of chemical	Formula	Data source reference	**Airborne dust data**			**Airborne limits**		**Comments**			
			Dust hazard	Total respirable (mg/m³)	Total Inhalable (mg/m³)	OEL (mg/m³)	OSHA PEL (mg/m³)	Carcino-genic etc.	Effects	Organs affected	Ecological info
Carbon Monoxide	CO	37,38				20-57	55		Can cause rapid suffocation		
Coal dust	C	38	Y	2							
Copper	Cu	38	Y		1	0.2					
Copper acetoarsenate	$3CuO.As_2O_3$	38				0.1			V Toxic		
Dioxins and Furans	Various	40							Tolerable Daily Intake (TDI) = 1-4 picogram/kg body weight.	Over-exposure can cause chloracne, cancer, reduced immune system, reduced testosterone levels	Accumulates in fatty tissue. Threat to larger predators
Hexachloroethane	C_2Cl_6	37,38	Y	4	10	10-49	10	possible	irritant to mucus membranes	Nerves liver kidneys	
Hydrogen chloride	HCl	37,38				1-2			destroys mucus membranes. Causes burns.	All that it contacts	
Hydrogen sulfide	H_2S	37,38				7-30	15		irritant to mucus membranes	lungs stomach kidney	V toxic to aquatic organisms
Iron oxide (as fume)	Various	38				5	10				
Iron particulates	Fe	38	Y	4	10						
Lead (IV) oxide	PbO_2	37,38				0.04-0.2		possible	irritant to mucus membranes. Congenital malformation. Cumulative effects	nerves blood kidney	V toxic to aquatic organisms
Lead	PbO_2	37,38				0.05-0.1	0.2	possible	irritant to mucus membranes. Congenital malformation. Cumulative effects	nerves blood kidney	V toxic to aquatic organisms

Table 6: Toxicity of firework compounds and their combustion products											
Name of chemical	Formula	Data source reference	**Airborne dust data**			**Airborne limits**		**Comments**			
			Dust hazard	Total respirable (mg/m^3)	Total Inhalable (mg/m^3)	OEL (mg/m^3)	OSHA PEL (mg/m^3)	Carcino-genic etc.	Effects	Organs affected	Ecological info
Lead Red (Minium)	Pb_3O_4	37,38				0.04-0.2		possible	irritant to mucus membranes. Congenital malformation. Cumulative effects	nerves blood kidney	V toxic to aquatic organisms
Magnesium oxide	MgO	37,38	Y	4	10	5-15	15	tumori-genic	irritant to mucus membranes	nerves lungs	
Nitric acid	HNO_3	38				5	5		destroys mucus membranes. Causes burns.	All that it contacts	
Nitrogen dioxide	NO_2	38				5.7					
Nitogen monoxide	NO	38				31					
Polyvinyl chloride	$(C_2H_3Cl)_n$	37,38	Y	4	10	4-10		tumori-genic	irritant to mucus membranes		
Potassium benzoate	$KC_7H_5O_2$	37							irritant to mucus membranes		
Potassium carbonate	K_2CO_3	37							irritant to mucus membranes		
Potassium chloride	KCl	37							irritant to mucus membranes	heart lungs	
Potassium dichromate	$Cr_2K_2O_7$	37,38				0.1	0.1	Yes	V Toxic. Destroys mucus membranes. Causes burns/ulceration.	lungs kidney blood	V toxic to aquatic organisms
Potassium hydroxide	KOH	37,38				0.5-2			destroys mucus membranes. Causes burns.	All that it contacts	
Potassium perchlorate	$KClO_4$	37,39							irritant to mucus membranes. Affects hormone production.	Thyroid blood	Uncertain at present. USA have a tentative action level of 18ng/ml in drinking water

Table 6: Toxicity of firework compounds and their combustion products											
Name of chemical	Formula	Data source reference	Airborne dust data			Airborne limits		Comments			
			Dust hazard	Total respirable (mg/m^3)	Total Inhalable (mg/m^3)	OEL (mg/m^3)	OSHA PEL (mg/m^3)	Carcino-genic etc.	Effects	Organs affected	Ecological info
Potassium thiocyanate	KSCN	37							irritant to mucus membranes	nerves lungs stomach	
Silver nitrate	$AgNO_3$	37,38				0.01		mutagen	destroys mucus membranes.	eyes nerve blood lungs	
Sodium hexafluoroaluminate (cryolite)	Na_3AlF_6	37				2	2.5		destroys mucus membranes. Causes burns.		
Sodium oxalate	$Na_2C_2O_4$	37							destroys mucus membranes. Causes burns. Possible congenital malformation	kidneys nerves eyes blood	
Sodium salicylate	$NaC_7H_5O_3$	37							irritant to mucus membranes. Possible congenital malformation	lungs reproductive organs	
Strontium chloride	$SrCl_2$	37							irritant to mucus membranes		
Strontium hydroxide	$Sr(OH)_2$	37							destroys mucus membranes. Causes burns.	All that it contacts	
Sulfur	S	37							irritant to mucus membranes		
Sulfur dioxide	SO_2	37				5-13	13	Tumori-genic. Possible Carcinogen	irritant to mucus membranes	blood	
Sulfuric acid	H_2SO_4	37				1			destroys mucus membranes. Causes burns.	All that it contacts	
Titanium dioxide	TiO_2	37,38	Y	4	10	4-10		Possible	irritant to mucus membranes		

4 Ground contamination

Specific research into the effects of firework fallout onto soils is very limited. Cegiel[28] states a number of solid firework combustion products and produces a generalised discussion on their probable effects on the environment. He concludes that risks to health are minimal. Schneider[39] discusses contamination by perchlorate and concludes that normal firework operation, even on a site used frequently for firework displays, does not cause significant perchlorate contamination, probably because most perchlorate is consumed when the fireworks function. This means that contamination can only be caused by fireworks or their sub-units (stars, whistles etc.) which do not ignite. Since most perchlorates are quite soluble in water it is unlikely that these chemicals would build up in the soil, although contamination of water courses may occur.

Most soil contamination literature relates to contamination by industrial pollutants, some of which are also found in firework compositions, or are generated by fireworks when they burn. Soil Guideline Values (SGV's) have been developed in the UK[42] for a limited number of contaminants which include chromium, nickel, lead and mercury, more chemicals will be evaluated in due course. These values aim to indicate the levels of contamination at which it is considered that exposure would become 'unacceptable'. It is implicit in this description that contamination below the SGV does not necessarily mean that there is no risk to health or the environment. SGV's have been produced for 3 types of land use, residential, allotment, and commercial or industrial. The levels are most conservative for contaminated land which is to be used for growing food (allotment). In this case the levels for chromium, lead and mercury are 130, 450 and 15 mg/kg soil(dry), respectively.

Dutch guidance[43] give values for a wider range of chemicals than in the UK and stipulates an intervention value and a target value, Table 7 summarises the values for some of the compounds that are used in, or generated by fireworks.

Table 7: Intervention and target values for soil contamination in The Netherlands

Compound	**Contamination level [mg/kg dry matter]**	
	Target value	**Intervention value**
Barium	200	625
Chromium	100	380
Copper	36	190
Lead	85	530
Mercury	0.3	10
Thiocyanates	-	20
Polycyclic aromatic hydrocarbons	1	40
General chlorinated hydrocarbon	0.001-0.01	1-60
Polychlorinated biphenyls (CB's etc)	0.02	1

5 Water contamination

There is little published in the literature on the environmental effects of firework combustion products on water courses. Aochi et al.[44] discuss the products generated from the explosion of aluminium/potassium chlorate compositions in water, but the experimental arrangement was specialised and no discussion of environmental effects were given.

Most water contamination literature relates to contamination by industrial pollutants, some of which are coincidentally found in firework compositions, or are generated by fireworks when they are ignited. Dutch guidance[43] give intervention and target values for groundwater contamination, Table 8 summarises the values for some of the compounds used or generated in fireworks. Comparison of Table 7 and Table 8 shows that levels permitted in groundwater are generally much lower than for soil contamination. This is probably due to the ease with which soluble contaminants can enter the food chain.

Table 8: Intervention and target values for groundwater contamination in The Netherlands

Compound	Contamination level [mg/kg dry matter]	
	Target value	Intervention value
Barium	50	625
Chromium	1	30
Copper	15	75
Lead	15	75
Mercury	0.05	0.3
Thiocyanates	-	1500
Polycyclic aromatic hydrocarbons	0.0002-0.1	0.05-70
General chlorinated hydrocarbon	0.01-0.25	0.5-1000
Polychlorinated biphenyls (PCB's etc)	0.01	0.01

To date, a detailed study of a man-made lake at Walt Disney's EPCOT Center in Florida over a 10 year period provides the most comprehensive study of the effects of firework fallout on water courses[29]. It is estimated that over 2000 firework displays were fired over the lake during the monitoring period (1982-1992). Results indicated that the heavy metals barium, strontium and antimony were deposited in the lake, predominantly in their water insoluble forms (oxides, sulfates etc.). There was a close correlation between the amount of antimony found in the lake and the estimated quantity contained in the fireworks that were fired. As a results it is suggested that this metal could be used as a marker to monitor firework activity in areas where they are fired infrequently. It was estimated that the total masses of antimony, barium and strontium in the lake were 9400, 84000 and 18500 kg, respectively. Such levels do not appear to have affected the ecology of the lake, probably because the metals are predominantly removed from the food chain due to their insolubility. The paper concludes that for water courses exposed to infrequent firework fallout the risks to the environment are minimal. PCDD's and PCDF's were excluded from this study but may provide another means of monitoring fireworks pollution.

A paper in 'Earth Island Journal'[45] states, however, that the fallout of metals from fireworks into watercourses may lead to accumulation of these metals over a number of years which could lead to contamination problems in the future. The chemicals bio-accumulate causing a gradual build up in the body which may take many years before showing symptoms.

6 Air pollution

A number of papers have been published on airborne pollution in relation to firework displays. Most concentrate on the behaviour of particulates and their effects on the population, while others report on the presence of specific chemicals.

Perry[46] identified 13 elements in the atmosphere from firework displays (Table 9), after the Independence Day Celebrations in the USA in 1990. However, there was no discussion of their effects on the environment or the population.

Table 9: Airborne elements associated with firework displays in Western Washington State on Independence Day 1990[46]

Element	Measured airborne levels [ng/m^3]		Ratio [4 July level/Background]
	Typical background level	Level on 4 July	
Strontium	0.5	9.0	18.0
Potassium	500	900	1.8
Vanadium	1.0	8.0	8.0
Titanium	2.5	15	6.0
Barium	1.0	30	30.0
Copper	1.5	4.5	3.0
Lead	2.0	8.0	4.0
Magnesium	4.0	45	11.3
Aluminium	20	100	5.0
Sulfur	350	500	1.4
Manganese	1.0	3.5	3.5
Zinc	4.0	8.0	2.0
Soot	450	1000	2.2

The occurrence of vanadium is surprising as it is not used in fireworks, however, similar results have been obtained in a pyrotechnic study dealing with indoor firework displays at the Houston Astrodome[47]. Other papers on air pollution in confined areas[30,31] have identified the elements Sr, K, Ti, Ba, Pb, Al and C. Chung et al.[31] comment that barium was produced predominantly in its water soluble forms at levels of up to 10mg/m^3, this is 20 times greater than the OEL and could cause respiratory problems etc. The levels of potassium salts, which could settle on surfaces in enclosed areas, were found to be sufficient to cause dermal irritation.

Cegiel's assessment of the quantity of firework combustion products produced outdoors[28] suggests that 54% are produced from blackpowder, and that the chemicals are 44% gaseous and 56% solid. It is estimated that the gaseous contribution from firework displays to the total gaseous emissions each year is less than 0.0006% and that solids (as barium) would generate only 0.03% of the limit value of 1500 mg/kg of soil. This limit value is at variance with the levels stated in Table 8 [625 mg/kg action level), but even on this basis the barium contribution equates to only 0.07% of the action level. It seems reasonable to concur with the conclusion in the paper that, generally, firework emissions are an insignificant contributor to soil pollution. Clearly, where fireworks are fired in an area many times a year the likelihood of contamination would be increased.

Particulate studies are a major area of air pollution study and are often segregated into 'total inhalable dust' and 'respirable dust'. The former represents dust that can enter the nose and mouth and is available to be breathed in, the latter is the fraction of dust which is small enough to travel into the gas exchange area of the lungs. To be respirable it is normal to assume that the particle size of the dust is 10 microns or less. Any dust that can travel into the gas exchange area of the lungs has the potential to affect respiratory function purely by its physical presence, rather than from any chemical interaction with the body. The following are listed in UK guidance[38] and have total inhalable and total respirable dust limits of 10 mg/m^3 and 4 mg/m^3, respectively:

Aluminium	Aluminium oxides
Barium sulfate	Carbon black
Hexachloroethane	Iron
Magnesium oxide	PVC
Titanium oxide	

Papers discussing particulate formation as a result of firework celebrations such as Guy Fawkes night[48] in the UK (5 November), Independence Day[46] in the USA (4 July), and New Year Celebrations in Germany[49] and Hawaii[50,51] show that when large numbers of fireworks are fired there is a rapid rise in the quantity of particulates in the air.

Colbeck[48] records an increase in the number of particles from a background level of < 1000/cm^3 to 27000/cm^3 during a celebration evening and Bach et al.[51] reported that particulate levels in Hawaii exceeded the 100 $\mu g/m^3$ air quality limit by between 17% and 173%. Wiedensohler[49] noted a marked rise in particulates in the 30 minutes around midnight on New Years Eve from 30 $\mu g/m^3$ to 235 $\mu g/m^3$ which was associated with a corresponding rise in NO concentrations from 4 ppb to 14 ppb. The NO level indicated high temperature combustion which would be associated with firework ignitions. The increase in particulates tended to occur in the respirable size range (< 10 micron). Smith[50] estimates that the majority of the increase occurs in the 0.3-2.0 micron range which is in agreement with the other papers cited.

Perry[46] monitored the movement of particulates from firework displays over a 2 day period and found that, in the dry calm conditions that prevailed at the time of the measurements, the dust cloud drifted 100 km and reduced in concentration by a factor of 10 each day. It was estimated that the particulates could stay in the air for up to a week unless they were removed by strong winds and/or precipitation.

The elevated particulate concentrations in Hawaii[50,51] were associated with an increase in respiratory problems. Those with existing respiratory weakness exhibited a 24% reduction in respiratory function and the admission to local hospitals as a result of breathing problems increased by 113%. While normally healthy people seem to be able to cope with the heightened particulate levels it is clear that those with respiratory weakness or asthma are at risk. Smith[51] also reports that a sulfur dioxide concentration of 1 ppm in the presence of sodium chloride produces a restriction in airflow in the lung and that potassium chloride (a product of firework combustion) is a factor of 1.4 times as effective at producing this phenomenon.

Given the large amounts of sulfur dioxide and potassium chloride formed when fireworks are used, and the particulate data outlined previously, it seems reasonable to conclude that, particularly in calm dry weather, firework displays can produce respirable particulates in combination with sulfur dioxide to produce air mixtures which put susceptible portions of the population at risk. Precautions should be taken to minimise the risks as for as is reasonable.

Studies into PCDD/F’s[10, 52, 53] have shown that they can be produced by fireworks. However, it is unclear whether they contribute substantially to the environmental burden. It seems likely that fireworks are a minor contributor to pollution by these chemicals unless many displays are fired in the same area. A far more plausible contributor would be the bonfires which often accompany firework displays.

7 Noise pollution

One of the more obvious forms of firework pollution occurs when they explode causing a loud noise which can cause distress to animals and people. A report on firework displays at a Disneyland theme park[45] comments on the negative aspects of fireworks for local residence and refers to complaints of repeated excessive noise and smoke. The same paper states that, in that location, the authorities were unable to take action unless noise levels exceed 60 dB for 10 minutes. Since no individual explosion lasts more then a fraction of a second no action could be taken. The article clearly demonstrates that in some instances noise regulations are not written with firework displays in mind.

Comparison of noise levels in Honolulu over the New Years Eve period[51] with the day and night time permissible noise limits throughout the USA showed that the maximum permissible level was at Anaheim and Boston College Park (60 dB(A)) whereas the maximum and minimum noise values encountered in Honolulu on New Years eve were 117 dB(A) and 89 dB(A), respectively. The vast difference between the permitted noise levels and those generated by fireworks would seem to be a clear area for concern.

The measurement and interpretation of noise levels has been discussed by a number of authors. Smoorenburg[54] comments on the wide range of different methods used to determine the risk of damage to hearing, while Lucchini[55] suggests that the range of frequencies of the noise as well as the overall sound levels need to be considered.

While Gjaevenes[56] suggests that hearing loss can result from exposure to specific fireworks, the levels at which it is considered that hearing damage can occur has varied over the years. Gupta[57] uses a peak level of 130 dB while Gjaevenes quotes a safe limit of 160 dB[58]. Studies on Chinese crackers by Smoorenburgh[59] suggest that a peak level of no more than 153 dB(lin) for 10 exposures at 2 m distance should be tolerated whereas Davis[53] reports that levels of 145 dB can cause damage from these fireworks.

An area of confusion when considering noise measurements is the weighting used for the measurements. The preferred unit of measurement for the European Standard (CEN) for Fireworks is the A-weighted impulse (dB(AI)), whereas the peak SPL (dB(lin)) is used in current legislation in the UK[60] and in the EC Directive on worker exposure to noise[61]. However, C-weighted noise measurements have also been used for noise information[62]. Because of the frequency distribution of firework noise it is unlikely that measurements in dB(C) would vary greatly from those of peak SPL and dB(lin). Wharton[63] discusses the relationship between dB(AI) and dB(C) for firework noise and proposes a conversion in the following form:

$$\text{Mean dB(AI)} = \text{mean dB(C)} - 20 \text{ dB}$$

On this basis the proposed European noise limit of 120 dB(AI) equates well with the instantaneous noise threshold of 140 dB(C) used in UK legislation[64].

Research into the noise levels produced by fireworks have shown that the sound level produced varies significantly depending on the type of fireworks being used. Clearly, fountains and sparklers are not going to generate noise levels comparable with report rockets or shells. However, noise studies of a wide range of fireworks which are generally available in the European Union have been undertaken[63]. The study showed that the types of fireworks listed in Table 10 can generate noise levels equal to or above the instantaneous noise threshold level in the UK (140 dB(C)). At a distance of 15 m from the functioning firework.

The study also revealed that the maximum noise generated by 100 mm and 125 mm shells was produced by the lift charge igniting in the mortar tube rather than from the explosion of the shell in the air. Maglieri[65] reports that larger report shells (150 mm diameter) than those used in Wharton's study produced a larger noise from the shell burst rather than from the lift charge. His conclusion was that, for the fireworks monitored, the noise levels produced were below the damage risk criteria for impulsive type noises (160 dB) suggested by Kryter[66].

Table 10: Types of fireworks generating noise levels ≥ 140 dB(C) at 15 m from the firing point

Firework type	Typical noise output	
	[dB(C)]	Calculated dB(AI_{max})
Air bomb	140.0-141.8	120.0-121.8
Ground mine	141.7-142.9	121.7-122.9
Report rocket (perchlorate composition(15g))	140.4	120.4
75 mm diameter report shell	140.6-141.4	120.6-121.4
100 mm diameter report shell	140.1-140.4	120.1-120.4
100 mm diameter star shell	141.3-143.1	121.3-123.1
125 mm diameter star shell	142.8-146.9	122.8-126.9
Banger (nitrate composition(10 g))	141.4	121.4
Banger (perchlorate composition(5 g))	149.1-149.5	129.1-129.5

The papers discussed so far consider fireworks that were mainly available to the general public at the time that the papers were published, and that the fireworks functioned in the correct fashion i.e. shells exploding in the air after launch etc. Little work has been performed on large stores of fireworks in the event of uncontrolled explosions at ground level due to inadvertent ignition. A limited number of tests have been performed in the UK which involved large numbers of fireworks in storage[67] and where noise measurements were made (Table 11).

Table 11: Summary of fireworks loads used in storage trials[67]

Trial No.	Contents of container	No. transport cases	Gross weight [kg]	NEC (kg)	Max. noise value at 250m [dB(C)]
1	**BS category 3 selection box fireworks** (contain >85% BS category 2 fireworks). Assorted selection boxes readily available to UK general public.	72	1000	228	<100.0
2	**Mixture of UN1.3G and UN1.4G fireworks** (Proportion UN1.3 (by NEC) = 48%) Chinese cakes/crackle mines. Titanium gerbs. 2oz Sticked rockets. 2oz Rockets. 4oz Rockets. 4oz Sticked rockets. 30mm Comet candles. 30mm Bombette candles. 45mm Comet candles. 45mm Bombette candles. 60mm Candles [assorted). 75mm dia. colour mines. Star shells 75,100,125,150 & 200mm dia.	75	1683.8	822.7	132.8
3	**UN 1.4G shells** Boxes of 18 x 125mm dia. star shells with flash composition burst charges	270	4050	2600	137.1

The results indicated that for large stores of small fireworks (Test 1), the noise pollution was likely to be minimal because the firework effects were contained within the storage building (ISO transport container) and are unlikely to generate noise levels hazardous to health. For stores of more energetic fireworks (Tests 2 & 3) where the effects cause the storage building to fail, the noise levels would exceed the 140 dB(C) instantaneous noise threshold at distances in the range 100-200 m, indicating that a significant noise hazard exists.

8 Social effects

The preceding sections indicate that fireworks are used extensively and present a number of environmental issues relating to their compositions, their toxicity or the effects they produce (smoke, dust, noise etc.). Other aspects of environmental pollution occur not only because of the parameters outlined above but also due to the quantities that need to be manufactured, transported or stored. The aim of this section is to highlight the effects of accidents that can occur during manufacture, transport or storage of bulk quantities of fireworks rather than accidents that occur as a result of firework displays.

The author has only found one detailed reference to a firework accident during transport[68]. A truck carrying 3.1 tonnes of fireworks collided with the central crash barrier which resulted in spark generation which ignited the load. A fire and explosion ensued which killed the driver. It is believed that the main explosion was caused by a number of 150 mm diameter report shells which generated sufficient overpressure to break windows up to 200 m away. A newspaper[69] reported that the area resembled a ‘moonscape’ and that the road needed to be temporarily closed. Two other transport related accidents are listed by Shaluf et al.[70], one was a road accident in Peking in 1998 which resulted in 40 deaths, the other was a rail accident in Allahabad, India in 1974, 42 people died. While the lack of reports suggests that transport accidents involving fireworks are infrequent, the potential to cause death and disruption to the social environment (roads, housing etc.) is clearly demonstrated.

Because of the damage caused by explosions it is not always clear whether accidents on firework manufacturing sites occur as a result of the manufacturing process or while the fireworks are being stored. Weeth[71] reports a number of firework accidents that occurred as a result of manufacture. 130 people died in the 6 accidents listed and over 540 were injured. In one instance an 8 story building was destroyed as a result of the explosions. Many of these accidents were due to illegal manufacture which probably accounts for the high mortality since it is unlikely that recognised safety procedures would have been implemented. However, explosions in authorised manufacturing plants also cause fatalities. An accident in Michigan USA in December 1997[72] resulted in 7 deaths. The explosion was heard 20 miles away and the plant was levelled to the ground. Debris was scattered hundreds of yards and people had to be treated for smoke inhalation. The examples cited demonstrate that immediate damage to the environment extends to the man made environment and can cause disruption to local infrastructure.

Similar effects to those found at manufacturing sites have been reported in firework storage accidents. In the UK in 1998 a complex of eight ISO-containers of fireworks were destroyed after a fire started in one store which led to a violent explosion in a store adjacent to it[73]. The complex was destroyed and fire spread to process and office buildings. A 10 kg steel fragment was propelled 140 m before it fell through the roof of a house. Other debris was found up to 212 m from the explosion point and windows were broken up to 100 m away. It has been estimated that the blast from the explosion was equivalent to a TNT charge with a mass in the range 200-250 kg.

An incident very similar to that reported in the UK occurred in Perth, Australia in 2002[74]. A fire in one area of the complex resulted in the explosion of adjacent ISO containers of fireworks culminating in a major explosion estimated to be equivalent to 227-409 kg TNT. Buildings in the immediate vicinity of the explosion were totally destroyed, 2 houses within 300 m suffered extensive structural damage and properties within 1000 m experienced shattered windows, displaced doors and damaged ceilings. Window damage was recorded up to 4.5 km away. Shrapnel from the explosions was found up to 510 m away and the roof of one container (380 kg) was propelled 295 m. In both incidents secondary fires were generated by the initial explosions which compounded the atmospheric pollution generated. Fortunately no one was killed in either of these incidents

The violence of the explosions in the 2 previous examples was far in excess of that expected from stores of fireworks. The effects were more like a high explosive detonation than the sequential ignition of individual fireworks that was expected. Detonation type explosions were also observed in Enschede, The Netherlands, in 2000. A fire in a firework storage complex resulted in major explosions which killed 22 people and injured hundreds more[75]. The complex and 400 homes were destroyed and many more damaged. The aftermath left a crater 1.35m deep and 13m in diameter. Glazing damage at different distances indicated that the explosion was equivalent to the explosion of 4000-5000kg of TNT. Investigations by the Dutch authorities[76,77] have shown that close to the fire during the incident the levels of particulates, carbon monoxide and heavy metals were high. Levels of particulates, heavy metals, volatile organic compounds and dioxins were only slightly above ambient levels in the ensuing few days. Away from the incident site contamination levels were approximately equivalent to ambient levels. It was concluded that, with the exception of short-term bronchial irritation, the health risks from the incident were minimal. This was supported by blood and urine samples taken from local residence which showed no systematic increase in levels of heavy metals commonly used in fireworks manufacture.

The examples given demonstrate that even when fireworks are not being fired deliberately there is a potential environmental risk.

9 Conclusions

The preceding discussions have highlighted a number of areas of environmental concern related to fireworks usage. It can be concluded that:

1. Many firework compositions and their combustion products contain toxic and environmentally damaging chemicals.

2. The scale of the effects on the environment or on human physiology is related not only to the quantity of the residues from fireworks but also the frequency of the displays and the interaction of the chemicals with the body or the environment. Certain chemicals are not removed from the environment very quickly and concentrations can build up to dangerous levels on a cumulative basis. Other chemicals form species which are essentially insoluble in water and effectively removed from the food chain. Many are readily soluble and migrate throughout the ecosytem. Clearly, those that are ‘mobile’ (soluble in water or fine dusts) are likely to have the most immediate effects whereas the effects of relatively ‘static’ chemicals such as heavy metals or PCCD’s, which accumulate over time, may not be observed for a number of years.

3. The transient nature of firework displays and the infrequent use of particular sites suggests that, generally, contamination is unlikely to be a problem. Even in catastrophic incidents such as Enschede, where large quantities of stored fireworks were consumed in one area, it has been shown that pollution levels were not affected. Where displays occur repeatedly at the same venue it would be prudent to monitor for specific element such as PCCD’s or antimony in order to get an indication of the levels of pollutants.

4. Noise pollution is a significant problem in two ways. Firstly firework operators at displays or residents close to explosions at large firework stores may be exposed to noise levels which could cause hearing damage. It should be ensured that operators have the correct hearing protection and that the emergency procedures for manufacturing, storage or transport of fireworks are adequate to prevent people from approaching too close the site.
   Secondly, noise pollution causes nuisance to local residents. While this may not cause physical injury it could lead to psychological problems if the noise is repeated often. At the very least it can generate negative feelings towards fireworks which may affect commercial aspect of the fireworks trade. It would seem prudent to ensure that efforts are made to reduce noise levels to a minimum to reduce these effects.

5. Particulates from fireworks can cause nuisance problems or serious illness. It is clear that fireworks produce many particulates in the resipirable size range (< 10 µm) and that sections of the population who have respiratory weakness suffer as a result. These effects are probably heightened due to the presence of sulfur dioxide and potassium chloride. Normally healthy populations do not exhibit symptoms but may become firework averse if repeated particulate problems occur.

6. Research to date has shown that environmental or physiological effects from accidental ignition of large quantities of fireworks in storage etc. are restricted to the local area. No evidence has been found to suggest that isolated incidents of this type have caused permanent environmental damage.

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Fireworks Selection for Future Testing

1 Introduction

Within the framework of the CHAF project a number of tests with fireworks on different scales shall be performed and it will be essential to have a systematic methodology for the selection of the fireworks at hand. Such a methodology should guarantee that tests will be chosen to cover all major effects and ranges of effects relevant to the understanding of the bulk reaction of stored fireworks. The methodology shall help in justifying a chosen test selection by a test hypothesis, which shall be confirmed or withdrawn, and a logical structure of tests which relate to each other.

In the section for Deliverable D4-1, types of fireworks available in Europe with examples of the types of composition found in these articles have been described, and in the following section (Deliverable D4-2) mechanisms for the propagation reaction between fireworks are discussed. The information given in these section forms the basis for the selection methodology for future testing as it is presented here.

2 Discussion

Fireworks range in hazard from innocuous novelty items such as party poppers through to articles having a major hazard such as report shells. Between the two extremes lie articles with a gradation in hazard. Many of the more hazardous fireworks are only available to professional fireworks personnel; however, there are fireworks that are available to the general public which may pose a considerable hazard when stored in large quantities. For more hazardous fireworks there may be methods of reducing the hazard by modifying packaging, such as inert spacers to reduce the pyrotechnic density within the package. Such solutions are outside of the scope of this report. However, this may well be relevant to testing in later work packages.

In the context of Deliverable D4-2, the study on reaction mechanisms between fireworks, three predominant propagation mechanisms have been identified. These are shock initiated reaction propagation, heat initiated reaction propagation, and propagation through projection. For the analytic study of the critical conditions in a reaction between fireworks articles these three mechanism shall form the principle categories for testing.

Within each of the three test categories the fireworks selection shall be refined by considering which pyrotechnic composition can be expected to respond in the most sensitive way to an initiation by shock, heat, or friction, respectively. I. e. in a second step the three Tables given in Deliverable D4-2 on the sensitiveness of the pyrotechnic compositions with regard to different initiation sources will be analysed.

From this it is obvious that articles that contain large amounts of flash compositions pose a major hazard in bulk storage. These items are of interest in the practical phases of this project. Less hazardous items will also be of interest in assessing the change from 1.3 to 1.1 and 1.4 to 1.3 type responses in testing. It will be particularly important to characterise these materials for future guidance on large-scale storage of fireworks.

To find a firework that meets the HD 1.3/1.1 interface may still necessitate a flash report composition either in a smaller device or a firework with a different construction such as a Roman candle or rocket. Alternatively, a different composition type in a shell may afford the required hazard reduction for testing. In either case it is likely that the material will require a composition that can propagate the reaction via both shock wave initiation and by flame, to be able to display HD 1.1 and HD 1.3 type response in the UN series 6 tests.

Large fountains or similar fireworks based on blackpowder compositions are very likely to provide both HD 1.3 and HD 1.4 results in the UN series 6 tests depending on composition. Higher energy compositions such as those in waterfalls are more likely to give a HD 1.3 response while smaller fountains will almost certainly provide a result of HD 1.4 firework. Package density will also play a role in the propagation or rather the speed of propagation within the transport packages. This may lead to a method of varying the response to the UN series 6 tests and this issue will need to be addressed in selecting the fireworks for the tests.

The selection of the size of an article, but also the selection of variants of the packaging as stated above, have to be made according to a test hypothesis or question posed to the test. That is, the question could be whether shock initiation is efficient enough to lead to mass explosive behaviour for articles selected beforehand, i. e. the 1.3/1.1 boundary is traversed towards HD 1.1. As an example, Roman candles could be selected with a fraction of flash-report composition and some special type of packaging. The calibre may then be chosen such that the amount of flash composition is high enough to expect propagation of an explosion in the package to propagate from article to article, perhaps despite some space being present in the packaging.

To summarise, the selection process will start with forming major categories relating to the principle propagation mechanisms, then involve the selection of pyrotechnic compositions which possess a high sensitivity with regard to the predominant initiation source of each category, and finally the selection of fireworks types and calibres which are expected to show the behaviour formulated in a test hypothesis. The detailed selection is being developed and will be presented in work package 6.