Pyrotechnic Flash Compositions*

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Pyrotechnische Blitzsätze

Blitzsätze werden sowohl bei der zivilen Feuerwerkerei verwendet als auch für pyrotechnische Artikel in der Technik wie z.B. Knallsignale, Kampfsimulations- und Übungsmunition, Vogelschreckmunition und Tränengasmunition. Die besondere Gefährlichkeit bei der Herstellung und Anwendung dieser Sätze resultiert aus dem Zusammentreffen von hoher Empfindlichkeit und starker Explosionswirkung. In der vorliegenden Arbeit werden die charakteristischen Sicherheitsdaten einiger Blitzsätze beschrieben (thermische und mechanische Empfindlichkeit und Empfindlichkeit gegen Detonationsstoß). Insbesondere wird die Explosionsstärke der Blitzsätze verglichen mit Werten einiger handelsüblichen Sprengstoffe. Weiterhin wird ein Vergleich zwischen $KClO_4$/Al-Mischungen und TNT angestellt aufgrund von Stoßwellenmessungen.

Compositions pyrotechniques pour production d'éclairs lumineux

Les compositions produisant des éclairs lumineux sont utilisées pour les feux d'artifices mais aussi sur un plan technique lorsqu'il s'agit d'engendrer des bruits impulsionnels, de simuler l'ambiance du champ de bataille, pour les munitions d'exercice, pour les tirs destinés à èpouvanter les oiseaux ou pour les munitions lacrymogènes. Le danger particulier que présentent la fabrication et la mise en œuvre de telles compositions résulte de la combination de leur sensibilité élevée et de l'intensité des effets produits par leur explosion. La présente étude décrit les données caractéristiques du point de vue sécurité de quelques compositions de ce type (sensibilité thermique et mécanique, sensibilité aux ondes de détonation). En particulier on compare l'intensité des effets produits par l'explosion de ces compositions avec les valeurs résultant de la détonation de quelques explosifs classiques du commerce. En outre, on compare leur sensibilité à l'onde de choc avec celle des compositions à base de $KClO_4$ et d'aluminium et avec celle de la tolite.

Summary

Flash compositions are used in fireworks as well as in pyrotechnic articles for technical purposes like report signals, battle simulation and practice devices, birdscaring ammunition and anti-riot-devices for instance. The special hazards in manufacture and use of these compositions result from the combination of both a high sensitivity and a strong explosive effect. The paper presents the safety characteristic data of some flash compositions (thermal and mechanical sensitivity and sensitivity to detonation shock). In particular, the explosive strength of flash compositions is compared with some values found for commercial explosives. Furthermore a comparison between a $KClO_4$/Al-mixture and TNT is made on the basis of shock wave measurements.

1. Introduction

In pyrotechnics there is a small group of mixtures with really explosive-like character. We are referring to the so-called flash compositions. They belong to the most dangerous category of pyrotechnic compositions according to the governmental safety regulations and to those of the industrial injuries insurance. Of course they differ from real high explosives in efficiency. On the other hand they have a much higher probability of being initiated independent of their individual sensitivities to thermal and mechanical stress and to detonation shock. Other then usual high explosives, they are not composed homogeneously, but are built up from different components: oxidizing and combustible substances and additives.

Flash compositions are mostly mixtures of potassium perchlorate and aluminium powder. More seldom chlorates are used in combination with aluminium. These mixtures are found in many fire-crackers, stun grenades, simulation devices, riot control items or military training ammunitions.

A second group of flash compositions are mixtures of barium peroxide as oxidizer and metal powders like magnesium, aluminium or zirconium as combustible substances; e.g. photoflash mixtures are made of these components.

In display fireworks, but also for simulating explosives in military training devices, there is often used a third group of flash compositions based on barium nitrate, aluminium powder and sulphur. This mixture is not quite as effective as the above mentioned ones, but very easy to ignite by sparks or flames. Unfortunately, maybe because of the sulphur content, it is also sensitive against electrostatic discharges and self-ignitable with certain amounts of moisture.

Besides that, pyrotechnic mixtures are composed of substances which can be bought easily from stores selling chemicals, paints, herbicides or fertilizers without any restriction. The manufacture of these mixtures is quite dangerous as demonstrated by a considerable number of accidents in the industrial production as well as in the illegal making. The reason for that is – as mentioned above – the high sensitivity against thermal and mechanical stress.

2. Experimental Determination of the Sensitivity of Explosive Substances to Thermal and Mechanical Stress and to Detonation Shock – Test Methods and Evaluation of the Results

The safety characteristic data which are divided into three sensitivities to thermal stress, to mechanical stress

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and to detonation shock were determined using the common test methods[1] of BAM. In detail the safety characteristic data are:

Sensitivity to thermal stress
- ignition temperature
- ignitability by sparks, black powder fuse, gas flame and red-hot steel rod
- combustion time in a red-hot steel bowl
- limiting diameter in the Koenen test

Sensitivity to mechanical stress
- sensitivity to friction
- sensitivity to impact

Sensitivity to detonation shock
- lead block expansion
- behaviour in a 1″ steel tube
- behaviour in a 2″ steel tube
- behaviour in a 4″ steel tube

With the object of getting a single number which may simply represent the degree of hazard of explosive substances, a system of combining the diverse safety characteristic data has been developed earlier in the BAM. This system was found to be especially useful for the comparison of pyrotechnic compositions and is comprehensively described elsewhere [2,3].

The decisive procedure of the system is: if one allots a certain, standardized number of points to the single test results obtained, the addition of these points gives a certain value for each type of sensitivity. The sum of the three values of sensitivity characterizes the degree of hazard of a pyrotechnic composition. If k_{th} denotes the value of the sensitivity to thermal stress, k_m the value of the sensitivity to mechanical stress and k_d the value of the sensitivity to detonation shock, the number of the hazard G (the hazard number) of the pyrotechnic composition is

$$G = k_{th} + k_m + k_d$$

Here it should be emphasized that the test methods “Limiting Diameter in the Koenen Test” and “Lead Block Expansion” are not only methods to determine the sensitivity of a substance. In a high degree those methods are reflecting the explosive effect, too.

3. Sensitivities to Thermal and Mechanical Stress

In order to give an idea of what level of sensitivity we are speaking about, it is necessary, to look at some data which are obtained in the laboratories of the Bundesanstalt für Materialforschung und -prüfung (BAM) and the Chemisch-technisches Institut (CTI) concerning the mechanical and thermal sensitivity of high explosives and pyrotechnics[4–6].

A simple comparison of these data is given with the overview in Table 1.

Naturally, the sensitivity of a pyrotechnic composition depends on the percentages of its components. This holds for the overall hazard – the hazard number G – as well as for the three individual sensitivities to thermal stress, mechanical stress and detonation shock. Figure 1 shows the situation in the binary system potassium perchlorate-aluminium for the values k_{th}, k_m and k_d representing the different sensitivities.

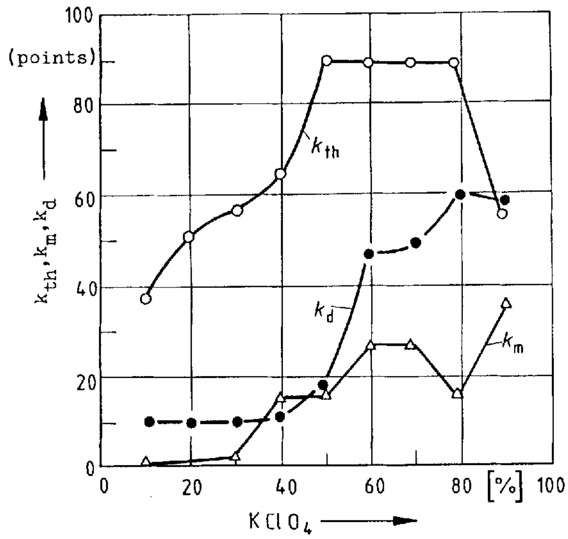

Figure 1. Values of k_{th}, k_m and k_d versus chemical composition of $KClO_4$/Al-mixtures.

In Fig. 2 the hazard number G of the same system is plotted versus the percentage of the oxidizer. The lower and

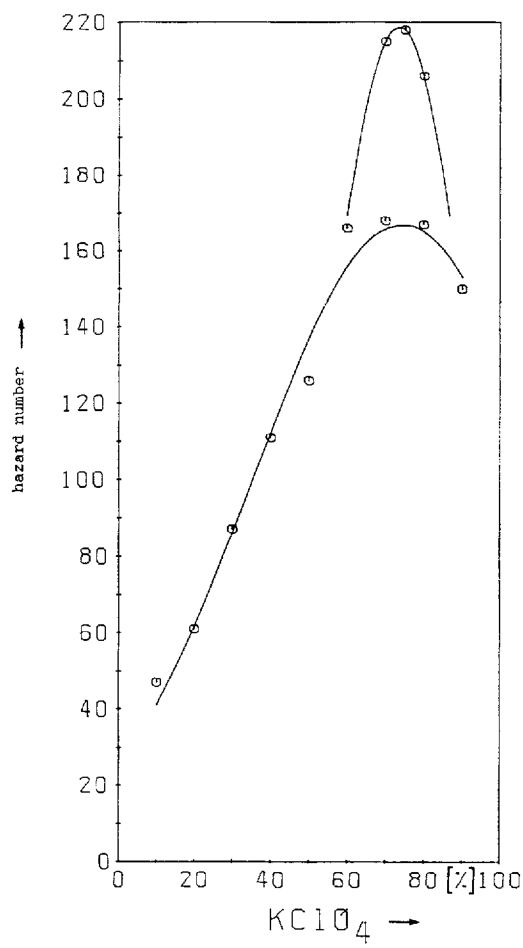

Figure 2. Hazard number versus chemical composition of $KClO_4$/Al-mixtures. (Two different types of components.)

Table 1. Some Safety Characteristic Data of High Explosives and Pyrotechnics

Explosive or pyrotechnic composition mass fractions [%]		Ignition temperature [°C]	Friction sensitivity [N]	Impact sensitivity [J]
TNT		295–300	>360	15
Hexogen (RDX)		220–230	120	7.5
PETN		202–205	60	3.0
NH_4ClO_4		–	>360	25
Flash 1: $KClO_4$/Al	= 70/30	>360	60	15
Flash 2: $KClO_4$/Al	= 75/25	>360	120	5
Flash 3: $Ba(NO_3)_2$	64	ca. 240	160	8
Al	20			
S	16			
Flash 4: $Ba(NO_3)_2$	66	>360	160	6
Al	25			
S	9			
Flash 5: BaO_2/Al	= 80/20	>360*	360	>50

* Ref. 6.

the upper curves were obtained with different types of the two components perchlorate and aluminium illustrating the strong influence of the purity and the physical properties (grain size etc.) of the components.

4. A Comparison of the Explosive Strength of Commercial Explosives and Flash Compositions

It is mainly determined by the explosive strength and the ability to propagate an initiated explosion if an explosive is of any value as a blasting agent. Thermochemical data may be used to get an idea of the expected strength or power, with the reservation that the kinetics are of influence, too.

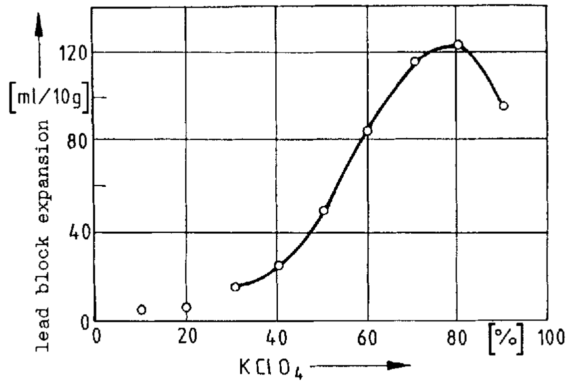

Figure 3. Explosive power (lead block expansion) versus chemical composition of $KClO_4$/Al-mixtures.

The heats of explosion of explosives and pyrotechnic compositions are within the same range, but the explosive strength of pyrotechnic compositions measured as lead block expansion according to Trauzl is found to be considerably smaller. Some values are listed in Table 2.

Some comments on the thermochemical data shall be added: Usually the heats of explosion (energies, constant volume) are calculated as proper thermochemical quantities of fast explosive reactions which may be considered to run under constant volume because of their high reaction velocity. However, the reaction velocities of pyrotechnic compositions are quite different and the test methods to determine the safety characteristic data represent the conditions of constant pressure as well as of constant volume. Therefore, the heats of reaction (enthalpies, constant pressure) are used to be compared with safety characteristic data or the resulting hazard numbers.

The standard heats of reaction ΔH^0_{298} were calculated with assumed reaction products which yield to a maximum

Table 2. Heat of Explosion and Explosive Strength (Lead Block Expansion) of Some Explosives and Pyrotechnic Compositions respectively

Explosives			Pyrotechnic compositions		
name	heat of explosion [kJ/kg]	lead block expansion [ml/10 g]	components [%]	heat of explosion [kJ/kg]	lead block expansion [ml/10 g]
RDX	6025	480	potassium perchlorate/aluminium (70/30)	9300	115
picric acid	5025	315	ammonium nitrate/aluminium (80/20)	6821	370
TNT	5066	300	ammonium perchlorate/milk sugar (80/20)	4176	339
PETN	5895	523	potassium perchlorate/milk sugar/sulphur (60/30/10)	3819	205
nitrocellulose	4052	420	barium nitrate/aluminium/sulphur (70/10/20)	3103	82
lead styphnate	1549	130	potassium chlorate/milk sugar (70/30)	3378	235
geosit 2	4292	310	guanidine nitrate (100)	2856	157
nitroglycerin	6322	520	guanidine nitrate/aluminium (80/20)	5785	374
blasting gelatine	6473	600	barium peroxide/iron (90/10)	174	0
tetryl	5527	410	strontium nitrate/aluminium (70/30)	7948	23

of heat (absolute) for each of the different compositions. The respective reaction products were found empirically. The standard heats of formation of the inorganic compounds were taken from Ref. 7, those of milk sugar and guanidine nitrate from Refs. 9 and 10 respectively.

Of course the explosive strength of binary pyrotechnic mixtures changes with the percentages of the components. Figure 3 shows the lead block expansion in the system potassium perchlorate-aluminium as an example.

5. The Propagation of the Initial Explosion

It is mainly a specific material property whether an explosion is propagated in an explosive substance from the point of ignition/initiation to the remaining substance or not. In case an explosive substance is basically able to propagate an initial explosion, it depends on other conditions if a propagation really will occur. In the first place these are the kind of ignition/initiation, the strength of the confinement and the quantity as well as the arrangement of the explosive substance.

Figure 4. 1″ steel tube tests with a potassium perchlorate/aluminium mixture (70/30) ignited by an electric match.

Figure 5. 1″ steel tube test with a potassium perchlorate/aluminium mixture (70/30) initiated by a blasting cap.

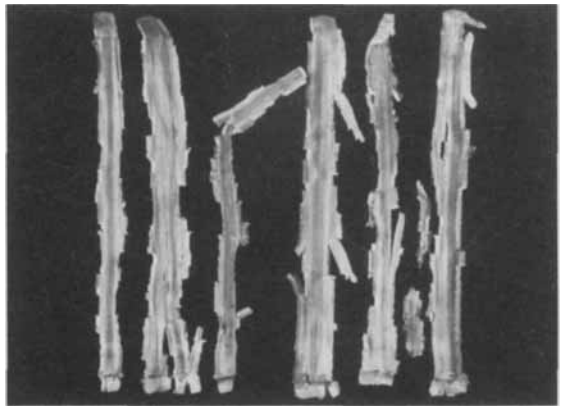

Figure 6. 1″ steel tube test with TNT initiated by a blasting cap.

In the Federal Republic of Germany the following tests are used to determine the ability to propagate an explosion, carried out in three steps: sensitivity to detonation shock

- in a 1″ steel tube (34 mm outer diameter, 300 mm of length) using a PETN blasting cap no. 8,
- in a 2″ steel tube (60 mm outer diameter, 500 mm of length) using a booster charge of 50 g hexogen with 5% wax and
- in a 4″ steel tube (114 mm outer diameter, 1000 mm of length) using a booster charge of 100 g hexogen with 5% wax.

Figures 4–6 show some test results.

The photographs easily illustrate that the pyrotechnic composition is able to fragmentate the confinement similar to the high explosive if initiated, and that even a weak thermal ignition may cause an explosive reaction of the flash composition.

6. Blast Effects from Flash Compositions

The destructive effects of potassium perchlorate/aluminium-mixtures are well known from several serious accidents in the pyrotechnic industry.

Figure 7. Test house before the experiment.

Figure 8. Test house during the experiment.

The following three photographs show an experimental explosion carried out the seventies by the BICT. 5 kg of a mixture of 70% potassium perchlorate and 30% aluminium were exploded in a building constructed of bricks. The photographs have been taken before, during and after the explosion and are kindly made available to the authors by R. Wild, the author of the original test report (Figs. 7–9).

Furthermore Wild[8] measured pressure time histories exploding the same potassium perchlorate/aluminium-mixture in quantities from 50 g to 500 g. The relations between quantity, distance and peak pressure (side on pressure) and the corresponding TNT equivalence are listed in Table 3. The TNT equivalences based on the peak pressures range from 0.55 to 1.3 for the relatively small quantities and short distances investigated.

According to calculations done by Wild the energy of the shock wave amounts to 7% up to 15% of the total heat of explosion.

All in all these results show that pyrotechnic flash compositions are undoubtedly able to destroy buildings or rooms of buildings.

Figure 9. Test house after the experiment.

Table 3. Results from Blast Wave Measurements with a Mixture of 70% $KClO_4$ and 30% Al (R. Wild[8])

Distance [m]	Pressure [mbar]	TNT Equivalency
	50 g	
1	604 ± 72	0.6
1.5	363 ± 33	0.84
2	264 ± 8	1.1
	100 g	
1	1126 ± 79	0.76
2	421 ± 12	1.3
3	213 ± 15	1.3
	200 g	
1	1880 ± 180	0.8
2	552 ± 11	1.05
3	287 ± 17	1.1
	500 g	
3	328 ± 23	0.55
5	185 ± 15	0.92

8. Conclusions

In general, pyrotechnic compositions are more sensitive than commercial explosives regardless the type of stress. On the other hand, their explosive strength is considerably smaller. But some of the pyrotechnic compositions come close to the explosive effects of commercial explosives, flash compositions for example.

In the Federal Republic of Germany the manufacture, processing, storage and use of explosives including pyrotechnic compositions are subjected to rigorous regulations, but it must be emphasized that especially the components of pyrotechnic compositions are easily to buy without any restrictions and can be mixed and processed without special technical equipment.

The present contribution gave a short summary of the methods applied to determine safety characteristic data of explosive substances and compared some selected explosives and pyrotechnic compositions by that data. Further the influence of the ratio of mixture on the hazard of binary pyrotechnic compositions was shown.

Then, usual explosives and pyrotechnic compositions were compared by their explosive strengths as well as by their heats of explosion. The influence of the kind of ignition (initiation) and of the confinement was presented exemplarily.

Finally the efficiency of potassium perchlorate/aluminium-mixtures was demonstrated by photographs showing the results of an experimental explosion in a building constructed of bricks.

The conclusion is, that the public security may be considerably endangered by the abuse of pyrotechnic compositions. Since those mixtures are rather sensitive, the endangering is not only given with the criminality itself, but also during the illegal making and processing. Therefore, it should be considered if a control of the selling and handing over of the components of pyrotechnic compositions is practicable and desirable.

9. References

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