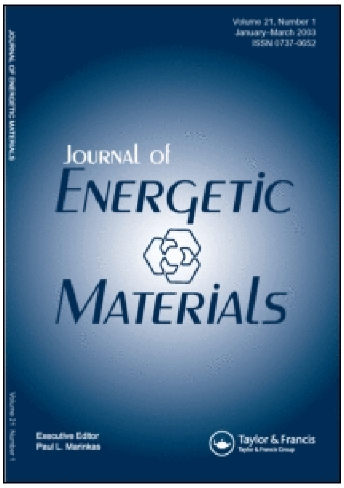

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SIGNAL TRANSMISSION TUBING WITH LOW INCENDIVITY FOR USE IN METHANE/AIR ENVIRONMENTS

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ABSTRACT

Signal transmission tubing has become the major initiation system for blasting operations in many countries. Conventional tubing based on Al/HMX has been found to be highly incendive in methane/air mixtures. Results for this and other compositions are presented, and the major mechanisms of methane ignition are discussed. Techniques for the formulation of non-incendive explosive compositions are utilised, resulting in signal tube compositions with very low incendivity. Important principles identified are the removal of hot solid reaction products, attainment of oxygen balance and the inclusion of flame inhibiting compounds such as alkali metal salts. These are incorporated in the preferred composition based on HMX/$KClO_4$. Ideal detonation analyses and flame studies by high speed photography are consistent with the principles of formulation for low incendivity.

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INTRODUCTION

The use of signal transmission tubing in initiating systems for blasting[1] has grown enormously since its invention twenty five years ago[2], to the extent that older initiators have now largely been eclipsed in many countries. A major factor in the adoption of signal tubes is the inherent safety of these non-electric systems[3]. One area of blasting which has, however, remained the domain of electric detonator systems is that of gassy underground mining. In particular, mining operations which encounter the potentially explosive situations of high methane concentrations, (often coupled with secondary coal dust explosive situations), have required unique blasting practices. Explosive systems for use in these environments have necessarily undergone careful formulation and design and have been subject to rigorous testing to ensure that they are of low incendivity in a methane/air mixture[4-7].

Conventional commercial signal transmission tubing comprises a hollow polymeric tube containing a dusting of explosive composition adhering to the inner wall. Typically the inner diameter is around 1 mm and the outer diameter is about 3 mm. The tubes are characterised by a low linear loading of explosive composition, typically around 15-20 mg/m, resulting in the tube wall usually being intact after firing. The usual explosive composition is a mixture of flaked aluminium (Al) and fine β-HMX (ca 20 μm). The propagation velocities for this composition are typically 1900-2100 m/s. These systems have been described by several authors(8,9,10)

Such tubing has been tested in a methane/air mixture and the exiting reaction products have been found to be highly incendive. We present and discuss these results and the formulation and performance of alternative reactive compositions to Al/HMX which have significantly reduced incendivity. The major mechanisms for the cause and suppression of methane ignitions are discussed, and thermodynamic and experimental studies on the preferred composition are presented, along with conclusions drawn about the nature of the low incendivity obtained.

INCENDIVITY TESTING

Test methods for the determination of the safety of explosive products in gassy environments have been in existence since the last century. Most coal mining countries have testing galleries for this purpose(11), utilising different geometries and charge configurations. Generally the most incendive concentration of methane in air, namely 9%, is used. For the purposes of testing signal tubing we used a configuration which fired the tubing open-ended into a 9% methane/air mixture. This simulates a worst case scenario of a complete tube rupture . The gas chamber was steel-lined and measured approximately 711mm x 267 mm x 51 mm. This is the same configuration used in the offical U.K. test for permitted electric detonators(12).

INCENDIVITY OF SIGNAL TUBING

Several compositions were loaded into conventional commercial tubing at typical coreloads of 10-25 mg/m and tested for incendivity as described above. The standard Al/HMX composition gave a very high frequency of ignitions of the methane/air mixture. while the removal of Al reduced this somewhat. Pyrotechnic compositions based on BaO_2 for use in low velocity tube systems(13) were also tested and found to be highly incendive. The incendivity of tubing containing PETN was comparable to that of HMX. The results are shown in Table 1. Propagation velocities were measured using optical fibres and a multichannnel electronic timer.

TABLE 1
Incendivity of Various Signal Tube Systems in 9% Methane/Air Mixtures

Composition (% m/m)	Propagation Velocity (m/s)	Ignitions/ No. Tested	Ignition Rate (%)
Al/HMX (8/92)	2000	70/115	61
HMX (100)	1850	30/77	39
Al/BaO_2 (15/85)	800	29/34	85
Si/BaO_2 (25/75)	600	59/82	72
PETN (100)	1900	3/12	25

The general principles of methane/air ignition by explosives have been summarised by Urbanski(4) and Fordham(5). Three major mechanisms of ignition that have been identified are:

(1) Shock initiation, either by direct action or by reflections from solid surfaces.

(2) Ignition by hot solid particles.

(3) Ignition by hot gaseous products, ie the "explosion flame".

Shock Initiation: From Table 1, it is clear that the incidence of ignitions is unrelated to the propagation velocity (and hence shock pressure) of these systems. The end pressures measured on signal tubes are typically in the range 0.5-15 MPa(8), which is orders of magnitude lower than typical detonation pressures of explosives which do not ignite methane/air mixtures(4). The charge masses in the tubing systems are also several orders of magnitude lower than the masses normally used in the test configuration. From these considerations, it appears highly unlikely that shock initiation, either by direct or reflected action, is a major contributory mechanism to the ignition process.

Hot Solid Particles: The removal of Al, and hence hot Al_2O_3 reaction products, from the Al/HMX system does produce a significant reduction in ignitions. Furthermore, the Al/BaO_2 and Si/BaO_2 systems are seen to be highly incendive. These systems almost exclusively produce solid reaction products. Clearly, the production of hot solid particles does appear to be a contributing factor to the incendivity.

Hot Gaseous Products: The HMX and PETN systems are seen to retain a somewhat high incendivity despite the absence of hot solid reaction products. It is concluded that these ignitions are caused by the exiting gaseous products or "explosion flame".

FORMULATION OF NON-INCENDIVE COMPOSITIONS

Urbanski(4) discusses the work of several authors on the formulation of explosives which have a very low tendency to ignite methane/air mixtures. Although a general principle is the reduction of the "power" or total energy of the explosive, there are other factors which appear to be more relevant to the low energy case of signal tubing.

The addition of salts has been used extensively in the formulation of methane-safe explosives, and in particular, potassium and sodium chlorides have been found to be highly effective. The inhibitory action of alkali metals and their salts, as well as that of halides, on methane and other hydrocarbon flames is an extensive field of study(14-18). The inhibitory effect of these compounds has been demonstrated to be chemical in nature as opposed to being merely a result of dilution. It is generally accepted(14,15) that they reduce the concentration of active flame species such as H, OH and O, thus interfering with chain branching reactions. There is also clear evidence(15,16) that these are homogenous gas phase reactions.

Aside from the consideration of inhibitory additives; the composition, temperature and duration of the explosion 'flame' entering a methane/air mixture are clearly vital factors determining its incendivity. Urbanski(4) classifies explosives on the basis of flame studies into two groups: those having a secondary flame and those with only a primary flame. The former group comprises fuel rich compositions, which, upon contact of the reaction products with atmospheric oxygen, give rise to a secondary flame due to the combustion of species such as CO, H_2, CH_4, etc. The latter comprises compositions with adequate or surplus oxygen for complete combustion within the explosive itself. Several studies are cited which have demonstrated secondary flame formation from fuel rich explosive compositions, and have shown that these compositions are highly incendive in flammable atmospheres. More recent work(19,20) supports this.

Combining the principles above, oxidisers based on potassium were mixed with secondary explosives in ratios which approached oxygen balance and yielded robust propagation in signal tube systems. The incendivity of the exiting reaction products in methane/air was tested as before and the results are summarised in Table 2. It is clear that a marked decrease in incendivity is obtained.

FURTHER STUDIES ON THE HMX/$KClO_4$ SYSTEM

The HMX/$KClO_4$ system was chosen for further study because of its robust propagation and higher thermal stability.

The system was analysed on the ideal detonation code IDeX(21) and compared

TABLE 2
Secondary Explosive/Oxidiser Composition

Composition (%m/m)	Oxygen Balance (%)	Propagation Velocity (m/s)	Ignitions/No. Tested	Ignition Rate (%)
HMX/$KClO_4$ (60/40)	5.5	1770	6/183	3.3
HMX/$KMnO_4$ (60/40)	-6.9	1800	1/40	2.5
HMX/KNO_3 (60/40)	2.9	1550	0/31	0
RDX/$KClO_4$ (60/40)	5.5	not measured	0/19	0

to the more incendive systems of Al/HMX and HMX. The predicted ideal detonation properties, based on 12 mg/m of HMX for each composition, are shown in Table 3 and compared with experimental results. Pressures were measured in an end-on configuration using a Piezotronics 113A23 quartz transducer.

TABLE 3
Results from the IDeX Code

Composition (% m/m)	Density (g/cm^3)	IDeX Ideal Velocity of Detonation (m/s)	Measured Velocity of Detonation (m/s)	IDeX Ideal Detonation Pressure (MPa)	Measured Detonation Pressure (MPa)
Al/HMX (8/92)	0.010	2650	2000	23	7
HMX (100)	0.009	2590	1850	19	5
HMX/$KClO_4$ (60/40)	0.015	1900	1770	25	7

It is clear that the non-ideality of processes occurring within the tubing result in significantly lower actual velocities and pressures, however the trends are consistent and some useful conclusions may be drawn from the ideal predictions. The predicted detonation product spectra following expansion to atmosphere are plotted in Figure 1. The production of uncombusted CO and H_2 is seen to follow the order of the actual relative incendivities of the compositions, ie Al/HMX > HMX > $HMX/KClO_4$. The formation of solid (undesirable) Al_2O_3 in the case of Al/HMX and the (inhibitory) KCl in the case of $HMX/KClO_4$ are also shown. Examination of the fired tubing in a scanning electron microscope, shown in Figure 2, revealed the formation of evenly distributed solid KCl crystals of the order of 0.1-2 µm, suggesting condensation from the vapour phase.

High speed photographic studies were done on the end spit of tubing into air, using an Imacon 790. Two composite sequences are shown in Figure 3, using an interframe time of 20 µs. The duration of the light emission from the Al/HMX tubing was seen to continue well beyond 720 µs, while the light from the $HMX/KClO_4$ system disappeared after 360 µs.

This was compared to the duration of light emission from the propagating tubing (ie the primary explosive "flame"), which was measured at right angles to the direction of propagation(8). For Al/HMX this was found to be ca 80 µs, while for $HMX/KClO_4$ it was ca 360 µs. These studies provide clear evidence for the occurrence of secondary combustion in the case of Al/HMX and for the absence of any such further combustion in the case of $HMX/KClO_4$.

CONCLUSIONS

The principles of reducing the incendivity of explosive reaction products to methane/air environments have been examined and the following have been seen to be important in the case of low energy signal tube systems:

1. The removal of hot solid reaction products
2. The move towards an oxygen-balanced formulation, thus eliminating secondary combustion and considerably shortening the duration of the explosion flame.
3. The use of alkali metal compounds, preferably in conjunction with halides.

These principles have been incorporated into a composition based on $HMX/KClO_4$, which yields signal tubing with robust propagation and low incendivity.

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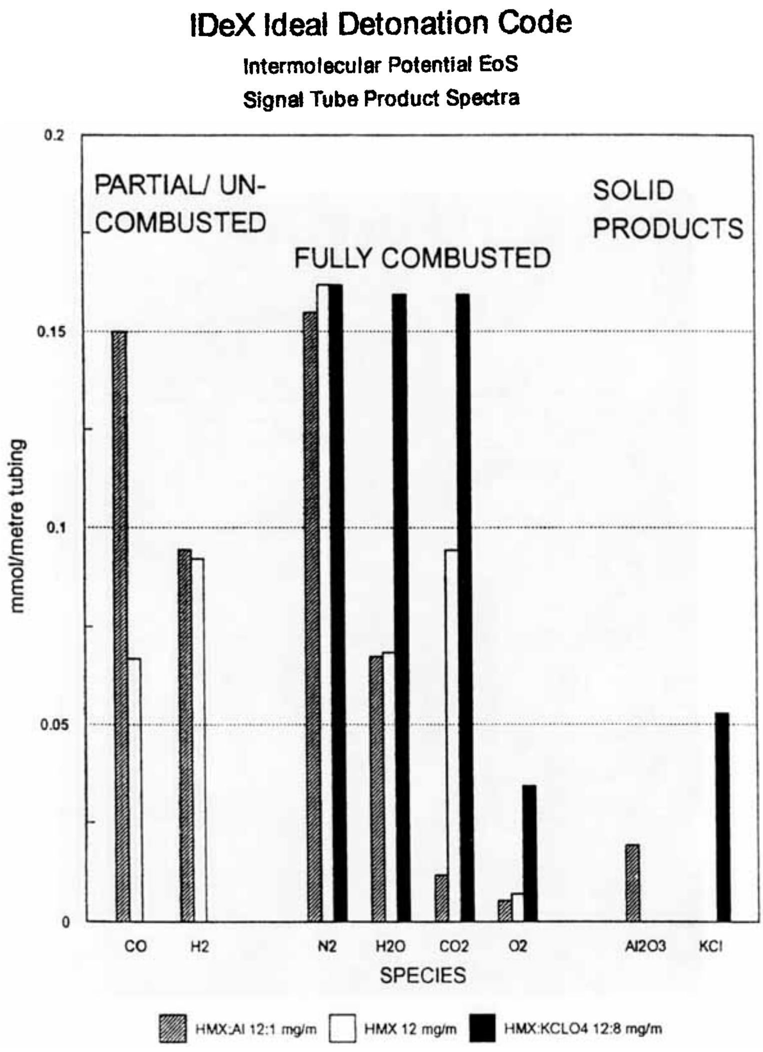


FIGURE 1

Ideal Detonation Product Spectra from Signal Tubing

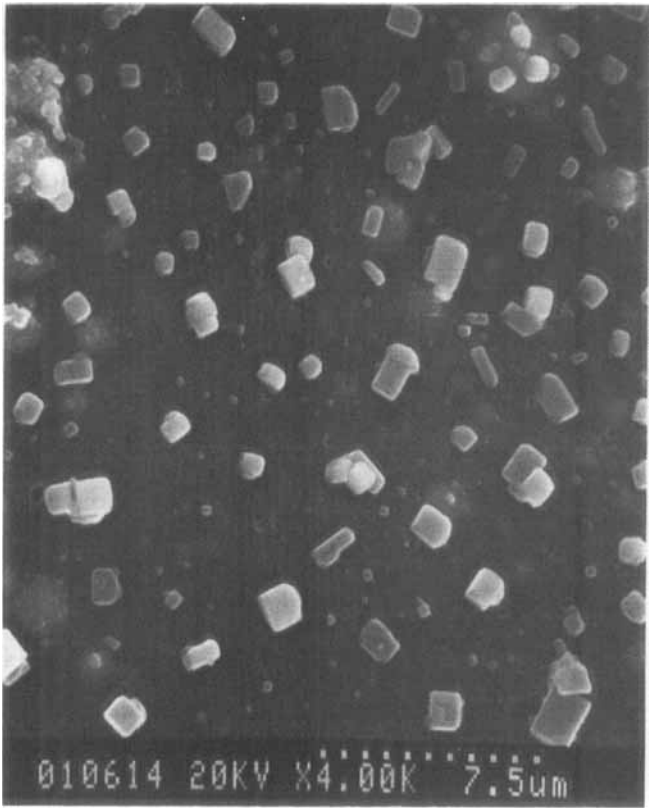
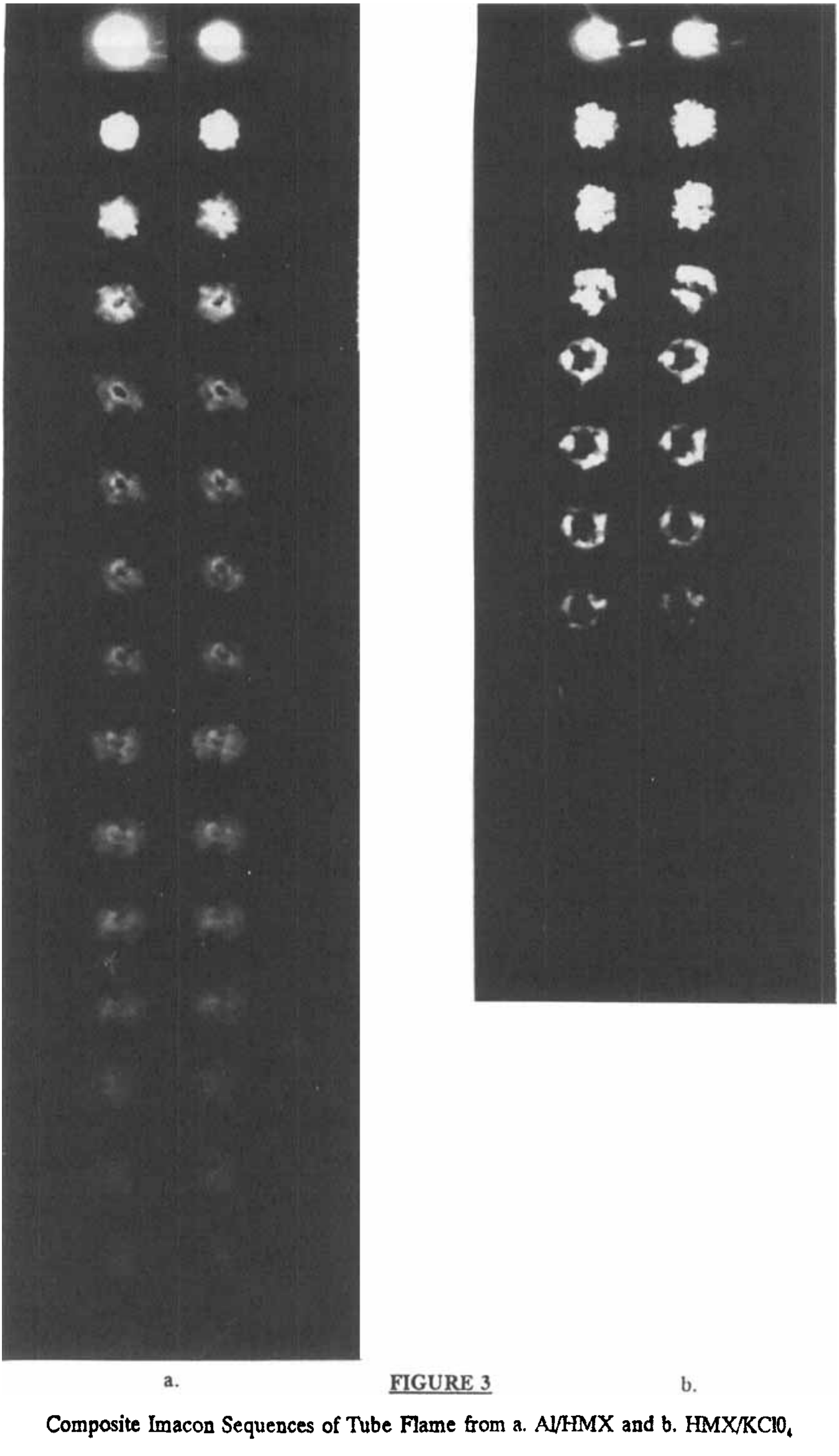


FIGURE 2

Scanning Electron Micrograph of KCl
Residues from HMX/$KClO_4$ Tubing



a.

FIGURE 3

b.

Composite Imacon Sequences of Tube Flame from a. Al/HMX and b. HMX/$KClO_4$

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