A Review of the Chemistry and Dynamics of Pyrotechnic Whistles

Matthew L. Davies
Health and Safety Laboratory, Harpur Hill, Buxton, Derbyshire, SK17 9JN, UK

ABSTRACT

Although the first efforts in understanding pyrotechnic whistles began over fifty years ago, there is still no firmly established mechanism that accurately describes their operation. This review describes the progress made and the current state of knowledge of combustion phenomena in whistle devices. In addition, investigations into identifying alternative safer fuels and additives to increase the striking audio-visual features of these devices are also reported. Finally, it is concluded that despite these great advances in understanding pyrotechnic whistles, there is still some doubt as to their true operating mechanism.

Keywords: pyrotechnic whistle, combustion mechanism, oscillatory combustion, acoustics

Introduction

Although most pyrotechnic items produce some audible effect, for whistles, sound is the primary effect. The first published description of pyrotechnic whistles is that of Amédée Denisse;[1] one British Authority[2] says they were first used at the Crystal Palace displays in London. Whilst no specific date is given, it is likely to be in the early 1850s. In any case, it seems safe to say that whistles are a development of the late nineteenth century and were very popular by the beginning of the twentieth century. The original compositions were based on potassium picrate mixed with an oxidiser, usually potassium nitrate, to control the burning rate and reduce the likelihood of explosion. Picrate whistles are still made in some countries.[3]

Many authors[4,5] have described the use of picrate whistles (and coloured stars made with picric acid) as too shock-sensitive to be used in fireworks mortar shells. However, for many years, the Italo-American manufacturers used enormous numbers of picrate whistles as shell garnitures.[3] Nowadays, picric acid (a close relative of TNT) and its salts are rarely found in any kind of commercial product in Europe or the US as they have a reputation for being very hazardous. One of the earliest "shock-safe" alternatives, potassium chlorate–gallic acid, is more sensitive to friction than potassium picrate.[3] Whistle compositions are almost as explosive as flash powder in the loose powder form; the original "whistling chasers" used a loosely loaded whistle composition for the report and a pressed composition for the acoustic effect.

The use of picric acid has many drawbacks. Firstly, heavy metal picrates are sensitive primary explosives comparable to the materials found in blasting caps. For this reason, picric acid should not come into contact with the brass sieves, lead ramming blocks and similar tools commonly used in firework factories. Iron and steel are also to be avoided because of the spark hazard. Instead, a dedicated set of aluminium tools is the only practical option for working with picrates.[3] Secondly, the price of picric acid has risen sharply in recent years due to the decline in its use, and a technical grade is usually not available. Finally, picric acid and soluble picrates are powerful yellow dyes, which are messy to handle, and they have a bitter taste (the name picric is derived from Greek and means bitterness). As stated by Lancaster, "*Picric whistles are not popular with firework makers mainly because no-one cares to work with them.*"

Contemporary whistle compositions are made of a benzoate or similar fuel and a perchlorate oxidiser, usually the potassium salt in both cases. Current whistle compositions are still sensitive to shock and friction and must be handled with care.

Serious incidents involving whistle composition and whistle devices are known.[6] The first was an explosion of approximately 3 kg of a loose charge (composition unknown), which destroyed processing equipment at a government explosives manufacturing facility in New South Wales, Australia. The second incident occurred when a consolidated column of whistle composition (about 20 g) in a metal cylinder exploded in a soldier's hand, fragmenting the cylinder and severing a number of his fingers. There is also a recorded case of a fireworks demonstrator being killed when a pyrotechnic whistle that was being deliberately operated in a vest he was wearing (and located over his heart) exploded.

Fortunately, many different aromatic compounds have been found that will burn in a suitably oscillatory manner when combined with a chlorate or perchlorate oxidiser. Cost and availability are of paramount importance for commercial firework production. Gallic acid is still in use and the Chinese reportedly use phthalate salts but today the most common whistle fuels are sodium salicylate and the benzoates of sodium and potassium. The potassium perchlorate–potassium benzoate mixture is probably as safe as any composition in this class.[7] Sometimes, catalysts, such as iron oxide or other transition metal compounds are added to these whistle compositions to alter the pitch or increase performance.[8] It has become popular in the last 10 years to add titanium to whistles, which produces a "silver tail" without much change in the sound. Degn[9] was the first to introduce this effect in 1973.

Whistle tubes are not pressed completely full; an empty space about half an inch long (13 mm) is customary at the open end to produce the sound. The sound will vary somewhat with the length and diameter of the tube, but only a limited amount of tuning can be achieved, about 0.5 to 5.0 kHz,[10] depending on chimney length. Tubes of larger diameter produce a louder noise but a point of diminishing returns is reached very quickly. Large whistles are more likely to explode and are much more destructive when they do so. Therefore, whistling components, both in consumer and in display fireworks, rarely exceed half inch inside diameter. Whistles may be combined with practically any other type of firework and are especially popular in fountains, wheels and aerial shells. Benzoate and salicylate whistle compositions are characterised by low cost, high-energy output, and (except when they contain metal powders) low light output. These properties have made them increasingly popular as propellants in some tube items and as bursting charges in aerial shells.

Few investigators have contributed to the current state of knowledge of the mechanisms involved in pyrotechnic whistle chemistry but three authors have made significant progress in the area. A review of their work is set out below.

Early studies

Maxwell[11] studied pyrotechnic whistles extensively and has written an authoritative treatise on their behaviour and the possible mechanism of sound production. Maxwell made most of his measurements with a 70:30 potassium perchlorate–potassium benzoate mix, but also investigated mixes of 60:40 potassium picrate–potassium nitrate, 25:75 gallic acid–potassium perchlorate and 70:30 potassium dinitrophene–potassium nitrate. His most important findings are summarised in Figures 1 to 5.

Figure 1 shows that the frequency of the main component of the sound falls continuously as the length of the tube above the burning surface increases. Maxwell constructed a constant-frequency whistle by applying the coachman's lamp principle. He used a telescoping case with the upper portion resting on a shoulder of the burning mix. As the mix was consumed, the upper case descended, maintaining a constant throat. Figure 2 shows that the mix burns faster at higher whistle frequencies and burns fastest if not constrained to whistle at all.

Acoustic output, shown in Figure 3, increases somewhat faster than the cube of the diameter. Maximum acoustic output for the potassium perchlorate–benzoate system, as indicated in Figure 4, occurs at critical proportions of the ingredients. The proportions do not produce the maximum burning rate but correspond closely to stoichiometry for the reaction:

$$4\ C_6H_5COOK{\cdot}3H_2O + 15\ KClO_4 \rightarrow$$
$$26\ CO_2 + 22\ H_2O + 15\ KCl + 2\ K_2CO_3$$

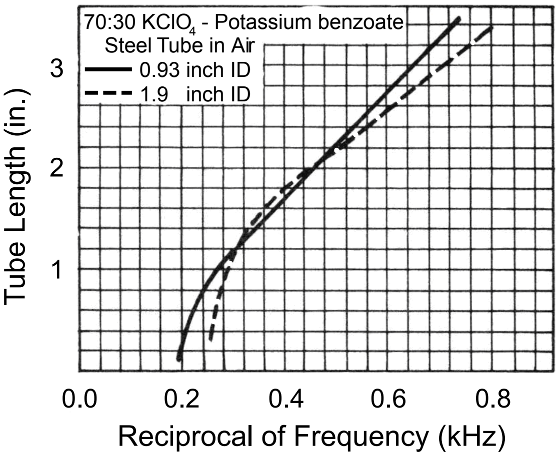


Figure 1. Effect of open tube length on whistle frequency.[11]

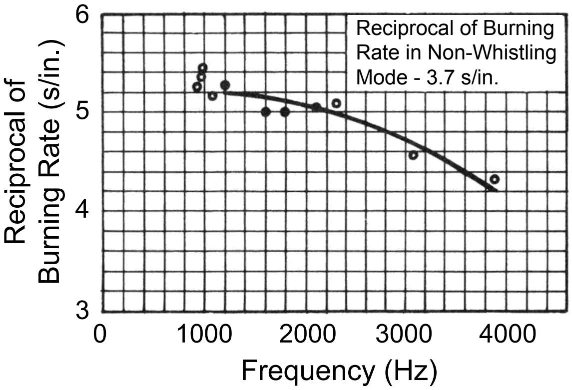


Figure 2. Effect of whistle frequency on burning rate.[11]

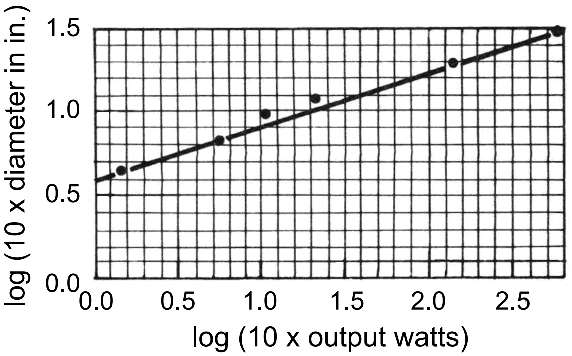


Figure 3. Effect of whistle diameter on acoustic output.[11]

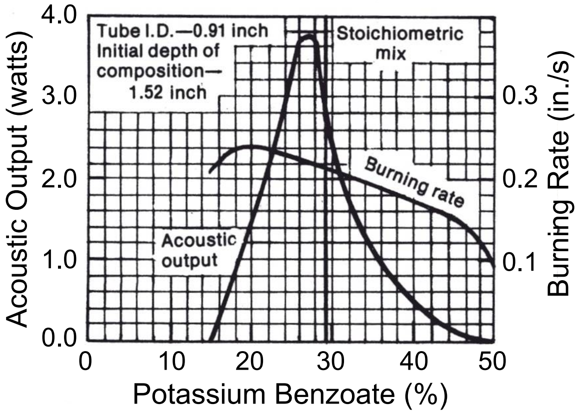


Figure 4. Effect of whistle composition on acoustic output and burning rate.[11]

A stoichiometric mixture is comprised of 70.8% potassium perchlorate and 29.2% potassium benzoate. Figure 5 shows that the burning rate of the whistle mix decreases as the surrounding pressure falls.

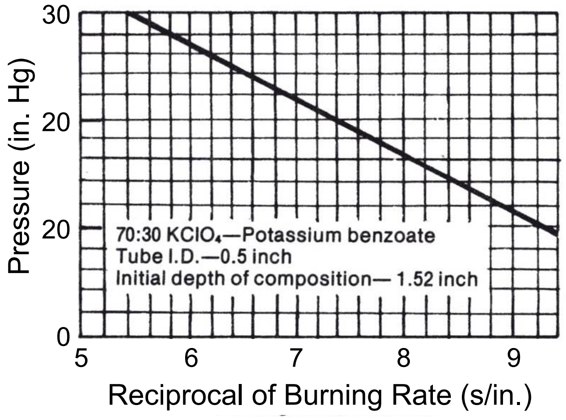


Figure 5. Effect of pressure on whistle burning rate.[11]

A Mechanism for Pyrotechnic Whistle Operation

Maxwell completed his work with an hypothesis for a possible mechanism of burning of pyrotechnic whistles. From the work described above, Maxwell proved that a whistling composition burns intermittently. Each time the composition surface is ignited, a pressure wave rises in the tube. When the pressure wave reaches the end of the tube, part of it passes out of the tube and part is reflected back into the tube as a rarefaction wave. When the reflected wave reaches the burning surface, the increased pressure causes the whistle composition to burn faster. This produces a pressure wave, which rises in the tube, beginning the process over again. Maxwell recognised that these waves of compression and rarefaction are what cause the composition to burn intermittently, but he stated that the exact mechanism is not clear.

This open organ pipe model appears to cause some confusion in later literature. The open organ pipe model represents a half-wave resonator with two low impedance boundaries[12] where the ratio of the upper harmonic to the fundamental frequency is termed the modal ratio, which follows a simple arithmetic progression. While the experimental data show such a relationship between the mode frequencies, they do not fit the half-wave resonator model, which yields unrealistically low acoustic propagation velocities when calculated as the product of wavelength and frequency, with the wavelength equal to twice the effective chimney length. This problem was addressed later by Wilson.[13]

A Mechanism for Pyrotechnic Whistle Combustion

A further point made by Maxwell in his article is that the variation in pressure on the burning surface is small (typically less than 7 to 14 kPa, i.e., 1 to 2 psi). This fluctuation cannot possibly account for the intense fluctuations in burning rate for a composition that is not abnormally sensitive to pressure when compared with propellants and other compositions.

Maxwell ascertained that spin had no effect on the burning rate, which suggests that whistles burn with a solid surface. In addition, he pointed out that whistling compositions are porous since they consist of consolidated crystals; this is confirmed by the fact that there is a complete lack of solid residue left in the burnt-out tube of a whistle. It is thus suggested that there is a connection between whistling power and the presence of a solid porous burning surface composed of fine crystals. Maxwell pointed out that the small crystals of chlorate, perchlorate or the salts of organic acids will decrepitate in a flame; this latter fact is also mentioned by Lancaster.[5]

On the basis of these observations, Maxwell suggested the following "mechanism" for the combustion of pyrotechnic whistles:[11]

"*The combustion of a whistling composition, whether in a tube or in the form of a pellet, involves the explosion of crystals as an essential part of the process. If the composition is not contained in a suitable tube, these crystals will explode in a random fashion and the products of combustion will flow from the surface at a uniform rate and no definite note or indeed any sound of appreciable intensity will result. If however, the composition is contained in a suitable resonating tube, the flame will be forced in and out of the surface by alternate waves of compression and rarefaction and every time it is forced into the surface a fresh mass of crystals will explode.*"

Significant Advances

The results of this literature survey suggest that until Wilson[14] published his findings in 1998, little work had been conducted in the area of pyrotechnic whistle chemistry since Maxwell presented his comprehensive findings in 1952. Wilson's paper details experiments carried out at the Aeronautical and Maritime Research Laboratory, DSTO, Australia, where a working theory was developed to describe the combustion mechanism of pyrotechnic whistles. Also, in the interests of safety, an investigation was undertaken to determine the reasons why pyrotechnic whistles can explode during combustion.

Wilson and co-workers experimentally investigated a number of the possible causes of explosion of whistle compositions. These included: shock propagation, mechanical disintegration, pressure-induced deflagration through the voids and the "flash-down-the-side" phenomenon. Their findings are included here for completeness and to give an understanding of some of the properties of pyrotechnic whistles.

Shock Propagation

An exploding bridgewire detonator was initiated on the surface of a column of whistle composition that had been compressed in a brass tube. The entire mass was consumed in the resulting explosion but no indentation of the witness plate occurred, and the brass cylinder fragmented into large longitudinal shards, typical of a pressure burst. From this it was concluded that although the whistle could be initiated by shock and that it would release a large amount of energy, propagation by shock in the whistle composition (detonation) did not occur.

Mechanical Disintegration

Mechanical crush tests of whistling composition revealed that it exhibits similar physical integrity to gunpowder and is apparently physically stronger than many other pressed pyrotechnic formulations. The burning fronts of a number of whistles were each subjected to a single dynamic peak pressure pulse ten times the estimated peak sound pressure within the tube by firing flash composition (1 g) at a distance of 2 cm from the tube mouths of functioning whistles. If these articles were susceptible to explosion by this mechanism, a pressure pulse of this magnitude should have been sufficient to cause disintegration and explosion of the columns. Of the articles tested, none performed abnormally.

Pressure-Induced Deflagration

The rate of burning of many gas-producing pyrotechnic formulations increases as the pressure at the combustion front is increased. This is mainly due to preheating of the reactants ahead of the combustion front by product species flowing through the voids present in the consolidated composition. If the magnitude of the environmental pressure becomes sufficiently great, the burning rate may increase and result in explosion of the column. However, a series of tests showed that although a five-fold increase in the mass burning rate can be observed between 20 and 200 kPa(a) (3 to 30 psia), the gradient of the curve increases only marginally thereafter up to 700 kPa(a) (100 psia). This is consistent with $\alpha < 1$ in Vieille's burning rate equation[15] and shows that the composition tested is not abnormally affected by pressure applied statically to the combustion front[15]. Although this series of tests was not comprehensive (the authors concede that the results could be very different if the environmental pressure could be increased rapidly) they go on to show that the assumption of the existence of void space in whistle compositions is not necessarily valid.

Flash-Down-the-Side

The propensity for pyrotechnic whistles to explode can partly be explained by the observation that both whistle fuels, potassium benzoate and sodium benzoate, exhibit self-lubricating properties; the compounds consist of flat platelets, which exhibit a slippery feel. It has been well documented[16] that many consolidated pyrotechnic compositions, including flares, tracers and smokes, will explode if steps are not taken to ensure that combustion cannot take place between the outer surface of the composition and the wall of the container into which the composition is pressed. With whistle compositions containing about 30% by mass of the fuels described above, it is to be expected that their wall bonding properties might be considered poor when compared to other pressed pyrotechnic compositions.

Wilson carried out a series of experiments that involved thermally cycling a whistle tube and then applying a drift load until displacement of the composition occurred. He showed that the mean displacement load required was halved when the tube had undergone thermal cycling. Thermal cycling easily breaks the already weak bond, and this introduces a slight gap between the composition and its tube. At any stage during the combustion process, hot combustion products could be forced down this gap and combustion could occur on a greatly increased surface area resulting in explosion. That explosion would inevitably result due to failure of the wall-to-composition bond was experimentally demonstrated.[13]

Combustion Mechanism of Pyrotechnic Whistles

To investigate intermittent combustion phenomena, Wilson and co-workers, undertook a series of experiments whereby static pressure was applied to a burning whistle. The results indicated that the environmental pressure did not affect the combustion frequency over the range from 20 to 200 kPa(a) (3 to 30 psia). Additional observations from this work were that at sub-atmospheric pressures the whistles were observed to produce increased amounts of excess particulate carbon during the reaction. They also found that combustion was not reliably sustained at pressures below 20 kPa(a) (3 psig).

To investigate the effect of incident pressure waves on burning pyrotechnic whistle composition, Wilson[14] performed a second series of experiments whereby two whistles—designed to produce different frequencies—where placed in opposition to each other. He found that the incoming sound pressure waves of the high frequency article increased the combustion cycle rate at the burning front of the low frequency article, confirming Maxwell's assertion[11] that cyclic incident pressure waves are probably an important part of the combustion mechanism.

It was clear from the two sets of experiments that pressure waves (but not static pressure) could control the combustion frequency of pyrotechnic whistles, but still one factor—the total energy output—could not be explained by pressure alone. It was calculated that during each pressure pulse, created during whistle operation, 3.6×10^{-4} g of whistle composition was consumed. To understand how such a small mass of consolidated pyrotechnic powder, consisting of discrete particles of fuel and oxidiser, could react at a rate fast enough to produce the observed acoustic output, Wilson[14] examined the reaction chemistry.

From his experiments on the effect of spin, Maxwell[11] proposed that whistle compositions burn in the solid phase. If this is correct, it is highly unlikely that a reaction rate that produces pressure pulses of the observed frequency and magnitude could be established. Both potassium perchlorate and potassium benzoate decompose at similar temperatures, which means that once this critical temperature (about 450 °C) is reached in either cycle of the whistle system, the potassium perchlorate will release oxygen and the potassium benzoate will produce hydrogen and free carbon at the same time resulting in an explosive mixture being compressed at the combustion front by the incoming pressure wave. Clearly ignition and explosion of the mixture would follow, and the outgoing pressure wave would cause rarefaction and a temperature decrease at the combustion front with a consequent suppression of the burning rate. The cycle would then be repeated. Some experimental confirmation of this proposed mechanism is given by Wilson; principally he showed that the decomposition temperatures of the fuel and oxidiser must be closely matched for the composition to both burn and whistle. He has shown that carbon plays an important role in the acoustic and thermal efficiency of whistle systems by identifying that the gradual substitution of carbon by nitrogen in the aromatic ring of the fuel has the effect of reducing the acoustic output. As a final point, the ability of whistle compositions to form the proposed explosive fuel-to-oxygen mix under specific conditions of temperature and pressure could also contribute to their tendency to explode by the flash-down-the-side phenomenon, where the configuration of the burning surface is relatively uncontrolled.

Refining the Model

In a later article, Podlesak and Wilson[13] extended the previous work and proposed an hypothesis that attempts to account for the observed high levels of explosive and acoustic power of pyrotechnic whistles.

Quarter-Wave Resonator

The acoustic model proposed by Maxwell[11] is not exactly clear. At first, he likened the pyrotechnic whistle to an open organ pipe, which under commonly understood terminology would represent a pipe with an open-open boundary and therefore a half-wave resonator, but later he describes the acoustic pulse generation process as in an open-closed pipe, which is a quarter-wave resonator. The half-wave resonator would infer unrealistically low sound propagation velocities. To overcome this problem, Podlesak and Wilson[13] model the acoustic behaviour of the device using a quarter-wave resonator, where the reaction front of the burning pyrotechnic composition provides both a high acoustic impedance boundary and an acoustic energy source, and the open end, or mouth, of the whistle chimney provides a low impedance boundary. A half-wave resonator with a low impedance boundary at both ends yields a 1, 2, 3, 4 … modal ratio as in the observed harmonic frequencies. The modal ratio for a quarter wave resonator, however, normally follows a 1, 3, 5, 7 … relationship, but it can be shown[17] that nonlinear distortions in the acoustic wave output are capable of producing the observed 1, 2, 3, 4 … modal ratios.

Thermo-Acoustic Feedback Mechanism

Podlesak and Wilson[12] proposed a "thermo-acoustic feedback" mechanism for pyrotechnic whistle operation. This is based on previous evidence that the acoustic pressure wave trapped in the chimney controls the combustion process and that the energy of the combustion feeds back positively into the trapped acoustic wave.

Energetics

By comparison with flash composition, Wilson[13] showed that a pyrotechnic whistle device is a very efficient converter of chemical to acoustic energy. They also concluded that the mechanism of sound production from the consolidated burning front within an open tube is evidently different (producing a greater acoustic impulse) from that when the composition deflagrates in the normal sound-producing mode (i.e., when filled as a loose powder and ignited under confinement).

Having considered the consumption of mass and the fuel–oxidiser decomposition temperatures, Wilson[13] turned to looking at the decomposition products of selected pyrotechnic whistle fuels.

Thermal decomposition analyses in a reducing atmosphere were carried out experimentally by Wilson.[13] It was found that highly energetic fuel species were formed during the dehydration reactions. This is thought to be a key factor in the oscillatory burning environment in whistle compositions even though it has not been directly observed at the combustion front of a whistle device. The observation that the whistle fuels exhibit a lower onset decomposition temperature than the ignition threshold temperatures of their pyrotechnic compositions, suggests that the physico-chemical properties of the fuels might be altered within the reaction zone immediately before ignition of the fuel-oxidant mixture occurs. This is not an uncommon observation in pyrotechnics technology. It is normally an ongoing process occurring just ahead of the combustion front. The reactants are preheated as a result of the permeability of the consolidated whistle composition, particularly when combustion occurs under pressure. However, as mentioned earlier, whistle compositions have been shown to have low permeability due to the physical properties of the aromatic fuels.[14] This has the effect of restricting the mass of reactants to a very thin layer at the burning front.

Wilson's thermal decomposition analysis yielded the results shown in Table 1.

Table 1. Thermal Decomposition Analysis Results of Wilson.[14]

Reactant	Combustible Volatiles Present
Potassium benzoate	CH_4, C_2H_4, C_2H_6, C_3H_8, C_4H_{10}, C_6H_6, CO
Sodium salicylate	CH_4, C_2H_4, C_2H_6, C_3H_8, C_4H_{10}, C_6H_6, CO, C_6H_5OH

Complete details are given in Wilson's article,[14] which shows that the relative abundance of the species in Table 1 varied with decomposition temperature. An important result of this study was the finding that about 40% by mass of elemental carbon and carbon compounds was present in the condensed residue. When examined under a Scanning Electron Microscope (SEM), it was found that the residue was mostly in the form of carbon spheroids with a diameter of approximately 1 µm (Figure 6). The discovery that these carbon spheres were, in the most part, hollow led to speculation about the dynamics of the formation process. Although no direct evidence is given, Wilson[13] speculated that at the moment of destruction of the aromatic ring (when temperatures at the combustion front are high) the carbon thus released is probably in the finely divided form. This would result in a hot and highly reactive form of carbon and combustible gases. The carbon forms the hollow spheres and the hot hydrocarbon gases likely fill the sphere's voids. This new and relatively energetic mixture, when burning during the compression cycle in the oxygen gas (evolved from the decomposing oxidiser) might account for the observed acoustic efficiency and explosive power of pyrotechnic whistles.

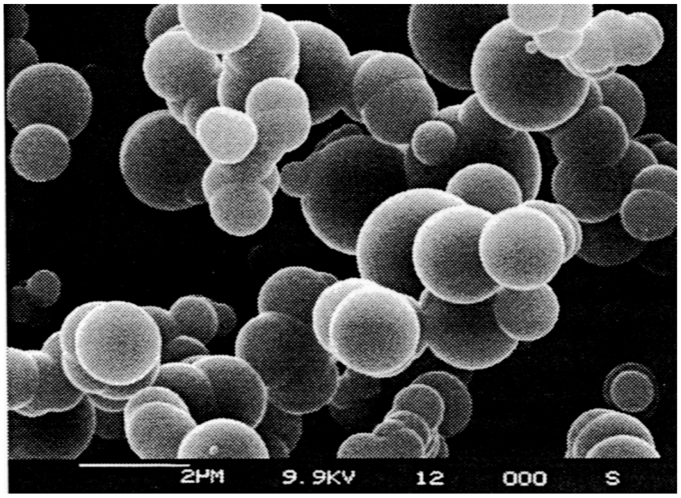


Figure 6. SEM electron micrograph of carbon spheres resulting from the thermal decomposition of whistle fuel in a reducing atmosphere.[13]

Some Other Aspects of Pyrotechnic Whistle Chemistry

Contributions from several other authors will now be considered. Their work has not been left until the end because it is considered to be less valuable; rather it is less critical, chronologically, in describing the advances made in understanding the chemistry and dynamics of pyrotechnic whistles.

Variations in the Performance of Pyrotechnic Whistles

All of the work described so far in this review has considered binary mixtures of pyrotechnic fuel and an oxidiser to produce the whistle effect. Hardt[3] reports that it has become common practice to add titanium to whistles, producing a silver tail without much change in the acoustic properties. Titanium does not cause a significant increase in the sensitiveness of finished benzoate or salicylate whistles, although it is especially important to be careful about friction when charging loose powders containing this metal.

The transition from a binary to a tertiary mixture demands a focus on safety concerns. As reported previously, the amount of energy stored in a pyrotechnic whistle composition is large, and under the correct conditions it is possible to increase the burn rate such that a transition from normal burning to a rapid deflagration occurs. Therefore, in *practical* applications, only large diameter powders (such as the reported titanium additive) are added to whistle compositions. Domanico *et al*.[8] investigated the effects of adding a third component to a binary whistle composition using very finely ground materials. They emphasise that this is done for scientific purposes only and that many of the compositions used were “very sensitive to ignition”, although they fail to explain whether this enhanced sensitivity is demonstrated through a friction or impact mechanism. They are so sensitive that they are not suitable for commercial purposes. Additional work would need to be performed to take these formulations to a level where they could be used in a practical way.

Domanico and co-workers performed four sets of experiments. The first considered the effect of replacing a proportion (5%) of the potassium benzoate of the control mixture with an alternative organic fuel. The burn rate and the peak noise level were recorded (see Table 2). In all cases, the control had the highest noise level recording but did not exhibit the fastest burn rate. One organic fuel, stearic acid, gave a slower burn rate and a significantly smaller acoustic output, whilst the remainder of those tested burned faster and also gave lower acoustic output than the control composition.

Table 2. Organic Fuel Results from Reference 8.

Additive	Burn Rate		Peak All Band Pass Level
	(in./s)	(mm/s)	dB
Stearic acid	0.181	4.60	113.0
Control	0.207	5.26	120.7
Terphthalic acid	0.210	5.33	117.5
Red gum	0.227	5.77	118.7
Sucrose	0.250	6.35	119.2
Charcoal	0.270	6.86	119.2

The second set of tests carried out by the group showed the effect of replacing some of the potassium benzoate with inorganic fuels (Table 3). Again, nearly all of the additives increased the burn rate with the exception of manganese, whilst none had the effect of increasing the acoustic output.

Table 3. Inorganic Fuel Results from Ref. 8.

Additive	Burn Rate		Peak All Band Pass Level
	(in./s)	(mm/s)	(dB)
Manganese	0.207	5.26	119.5
Control	0.207	5.26	120.7
Magnesium (–50 mesh)	0.213	5.41	120.1
Iron powder (–20 mesh)	0.214	5.44	119.8
Cadmium	0.217	5.51	103.3
Antimony	0.222	5.64	119.3
Nickel	0.224	5.69	119.2
Zinc	0.227	5.77	120.7
Copper	0.230	5.84	119.1
Titanium	0.232	5.89	120.5
Aluminium (–60 mesh)	0.232	5.89	119.9
Iron-silicon (50/50)	0.247	6.27	120.3
Silicon	0.261	6.63	120.6
Iron (–325 mesh)	0.261	6.63	121.2
Boron	0.262	6.65	119.2

A third series of tests used different oxidisers as the additive. In a similar fashion to the previous results, nearly all had the effect of increasing the burn rate (see Table 4). An insignificant increase in acoustic output was observed in two cases where the burn rate was also increased. These were for the oxides of copper and iron (in a later section it will be shown that the oxides of copper and iron can act as catalysts in these compositions).

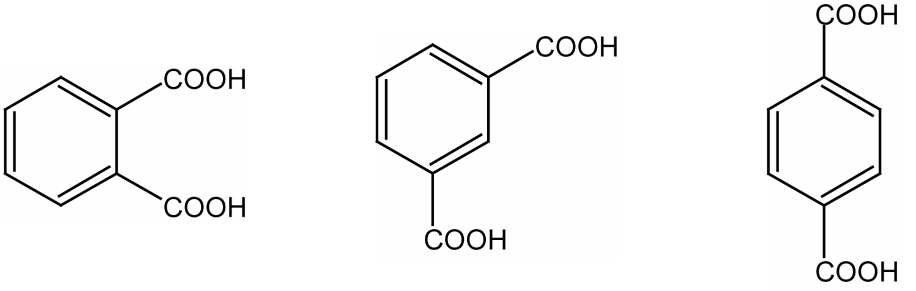
Table 4. Oxidiser Results from Reference 8.

Additive	Burn Rate		Peak All Band Pass Level
	(in./s)	(mm/s)	(dB)
Zinc oxide	0.199	5.05	119.7
Control	0.207	5.26	120.7
Cobalt oxide	0.242	6.15	119.8
Black Iron oxide	0.264	6.71	121.1
Titanium dioxide	0.272	6.91	119.1
Red iron oxide	0.274	6.96	120.9
Red copper oxide	0.275	6.99	120.8
Manganese dioxide	0.285	7.24	119.3
Lead dioxide	0.286	7.26	120.8
Lead trioxide	0.294	7.47	120.0
Black iron oxide	0.295	7.49	121.4
Black copper oxide	0.303	7.70	120.1

Domanico and co-workers also reported on the visual observations of tertiary mixtures. Each additive appeared to have a unique signature within the exhaust plume of the whistle. Colour additives were successfully used in combination with some of the tertiary mixtures to produce unique whistling devices. They showed that with the right proportions a whistle device can be manufactured that produces both noise and a colourful display of light.

Alternative Whistle Fuels

Amons[18] gives a basic account of the use of phthalic acid salts in whistle compositions. The author begins with a discussion on the basic properties of the materials and moves on to de-



a) Phthalic acid *b) iso-phthalic acid* *c) terephthalic acid*

Figure 7. The(a) ortho-, (b) meta-, and (c) para-isomers of phthalic acid.

scribe a series of experiments that use these alternative fuels. He then points out a few requirements for the successful use of phthalic acid salts in whistle compositions.

Whilst modern pyrotechnic whistles contain an aromatic carboxylic acid salt as a fuel with a suitable oxidiser such as potassium chlorate or potassium perchlorate, some reference works[5,20] have mentioned the salts of phthalic acids (alternatively benzene dicarboxylic acids). These are polybasic benzene carboxylic acids, which make them somewhat more complicated than their monobasic counterparts. The polybasic form has 3 isomers (Figure 7), each with different properties. The ortho isomer is phthalic acid, the meta form is iso-phthalic acid and the para isomer is terephthalic acid. The meta form was not investigated by Amons[18] because cost would prohibit its use as a pyrotechnic whistle fuel. When compared, terephthalic acid has the lowest solubility, which must be reckoned with when manufacturing the salt.

Potassium hydrogen terephthalate, which is only sparingly soluble in hot water, is used extensively by Chinese[20,21] manufacturers. As a consequence, it is less likely to absorb atmospheric moisture. Potassium hydrogen phthalate is another candidate for whistle fuel. It is readily soluble in water, which makes it easier to manufacture than the terephthalate salt.

The two salts described previously are formed by a partial neutralisation of the acid. A different salt is formed by complete neutralisation of the acid. In this instance, the ortho isomer is unusable as it absorbs moisture strongly. Even with the salt of the para isomer, neutralisation in excess acid is recommended to reduce moisture absorption problems. These salts make good whistle fuels but they have more affinity to absorb moisture than the hydrogen phthalates formed by partial neutralisation. This is critical since even a small amount of absorbed moisture can have a significant effect on performance.[19]

When the performances of phthalic acid salts as whistle fuels were compared to conventional compositions, Amons found that the particle size specified for traditional mixes was not appropriate when used in 8- and 10-mm inside diameter whistles tubes. The composition did not burn with a whistle; rather, a sputtering sound with intermittent whistling was observed. This observation seems to be more significant with mixtures containing stoichiometric quantities of ingredients; it was less significant with excess oxidiser. The irregular burning was overcome to a certain extent by the addition of a suitable catalyst such as iron(III) oxide or copper(II) oxychloride. Performance was also shown to improve by further refining the particle size of the fuel, but a catalyst may still help to improve performance further.

Phthalic acid salts, though more costly to manufacture, have significant advantages over their benzoic acid cousins. Potassium hydrogen terephthalate has a low hygroscopicity, which reduces the chances of poor performance if it is stored in damp conditions. It is also much easier to reduce potassium hydrogen terephthalate to a fine powder (the ortho form is more difficult in this respect). But, perhaps the most significant finding of Amons' report is that the alternative whistle composition potassium perchlorate–potassium hydrogen terephthalate is much less sensitive to friction (by about half) than the traditional potassium perchlorate–potassium benzoate mixture.

Curious Observations

In a communication to this journal Weinman,[21] described a "screeching" sound heard during the burning of bulk whistle composition (such practice is common at facilities that use pyrotechnics and require destruction of excess inventory). This observation was also made by Öztap [23] and Wilson.[6]

The disposal was carried out following a standard procedure. A trail of the excess composition was laid out on the ground? 3 m long, 50 mm wide and 7 mm thick and ignited from one end. The expected "whoosh" sound was not observed but was instead replaced by a sound, which was said to mimic that of a high-pitched whistle but with lower intensity. This observation strongly suggests that this technique should not be used to destroy unwanted whistle compositions.

A further "curious observation" was that made by Webb,[24] who noted that a whistle can be heard even when a thin layer of composition is coated on the inside of a tube and initiated.

These observations seem to contradict the proposed mechanisms that have been described in previous sections. However, the incidents have not been investigated beyond these first initial tests, and it is quite likely that there is some unrelated explanation for the observed phenomena. Nonetheless, these are curious observations worthy of further investigation.

Concluding Remarks

Preliminary investigations to ascertain the functioning properties of pyrotechnic whistles were carried out by Maxwell over 50 years ago. From his studies, Maxwell determined relationships between:

- Frequency and tube length
- Frequency and composition
- Acoustic output and tube diameter
- Acoustic output and ingredient ratios
- Sound quality and tube diameter

He also established the effect of frequency and the effect of lowering the ambient pressure on burning rate. In completing his authoritative elucidation on pyrotechnic whistles, Maxwell proposed a mechanism by which pyrotechnic whistles might be expected to burn. Although Maxwell made some attempt to explain the combustion mechanism of pyrotechnic whistles in terms of "the explosion of crystals," it is not a satisfactory explanation of either the reaction dynamics or the reaction chemistry.

The work was taken up by Wilson some years later and shortly thereafter Podlesak developed an acoustic model which showed that acoustic pressure doubling at the reaction front may be critical to the coupling between acoustic waves trapped in the whistle chimney and the combustion process. Temperature and pressure switching is currently believed to control the decomposition rates of the whistle fuel and oxidant. This results in a two-stage combustion cycle. The first quiescent stage involves the decomposition of fuel to form highly reactive species in an oxygen-poor atmosphere through acoustically-lowered pressure and temperature. These highly reactive species might take the form of hollow carbon spheres and hydrocarbon gases, which fill the voids of the spheres during this quiet phase of the combustion cycle. The second active stage involves the rapid combustion of the new fuel species in an oxygen-rich atmosphere through acoustically-elevated temperature and pressure. The energy released in the active cycle feeds back positively into the acoustic wave trapped in the chimney, but its final amplitude will be governed by the balance of energy injected by the combustion and the radiation and visco-thermal losses. A further limiting factor in the acoustic output is that the amplitude of the internal wave cannot exceed vacuum conditions during the pressure doubling of the rarefaction phase. Further investigations are required to confirm the mechanism proposed by Podlesak and Wilson.

In addition to the mechanisms of combustion, other aspects of pyrotechnic whistle operation have also been reviewed here. Domanico et al. showed that tertiary mixtures of whistle composition could be made that produce colourful displays of light without adversely affecting the acoustic output. Amons investigated alternative fuels that could help to improve the safety of these devices. Finally a review of a communication from Weinman showed that despite all of the intense research by the aforementioned investigators, the various theories of the dynamics and chemistry of pyrotechnic whistles is still widely open for debate.

Acknowledgments

I would like to thank Mike Wilson, of Pains Wessex Australia, and Rutger Webb of TNO Prins Maurits Laboratory, The Netherlands, for helpful discussions during the preparation of this review. I would also like to thank The Combustion Institute for allowing me to reproduce Figures 1 to 5 of this paper from Maxwell's 1952 article and DSTO, Australia for allowing me to reproduce Figure 6.

References

1) A. Denisse, *Feux d'artifice sifflants*, Poulenc frères, Paris, 1888.

2) A. Brock, *A History of Fireworks*, Harrap, London, 1949.

3) A. P. Hardt, *Pyrotechnics*, Pyrotechnica Publications, Post Falls, ID, USA, 2001.

4) G. W. Weingart, *Pyrotechnics*, 2nd ed., Chemical Publishing, NY, USA, 1947, p 14.

5) R. Lancaster, *Fireworks, Principles & Practice*, 3rd ed., Chemical Publishing Co., New York, 1998.

6) M. A. Wilson, Private communication, 2004.

7) T. Shimizu, *Fireworks: The Art, Science and Technique*, Pyrotechnica Publications, Austin, TX, USA, 1981.

8) J. A. Domanico, G. V. Tracy, M. N. Gerber, "Pyrotechnic Whistle Performance Variations", *Proc. 22nd Int'l Pyrotechnics Seminars*, CO, USA, 1996, pp 489–495.

9) R. Degn, "Pyrotechnic Whistle and Method of Making", US Pat 3,712,223, Jan 23 1973.

10) F. Ryan, "The Production of Music with Pyrotechnic Whistles", *Journal of Pyrotechnics*, No. 7, 1998, pp 1–10.

11) W. R. Maxwell, "Pyrotechnic Whistles", *4th Symposium on Combustion* at MIT Cambridge, MA, USA, 1952. Reprinted in *J. Pyro*., No. 4, 1996, pp 37–46.

12) N. H. Fletcher and T. D. Rossing, *The Physics of Musical Instruments*, Springer Verlag, NY, 1991.

13) M. Podlesak and M. A. Wilson, "A Study of the Combustion Behaviour of Pyrotechnic Whistle Devices (Acoustic and Chemical Factors)", *J. Pyro*., No. 17, 2003, pp 19–34.

14) M. A. Wilson, *The Combustion and Explosion of Pyrotechnic Whistling Composition*, Report DSTO-TR-0717, Aeronautical and Maritime Research Laboratory, Defence Science and Technology Organisation, Melbourne, Australia, 1998.

15) A. Bailey and S. G. Murray, *Explosives, Propellants & Pyrotechnics*, Brassey's New Battlefield Weapons Systems & Technology Series, Vol. 2, Brassey's (UK), 1989.

16) M. Podlesak and M. A. Wilson, "Study of Explosive and Combustion Behaviour of Pyrotechnic Whistle Devices – Acoustic Factors*", Proc. Symposium on Explosives and Pyrotechnics*, April, 1999, Philadelphia, PA, USA.

17) J. W. S. Rayleigh, *The Theory of Sound*, Vol. 2, Dover, NY, 1945.

18) R. Amons, "Consideration of Alternate Whistle Fuels", *J. Pyro*., No. 6, 1997, pp 65–67.

19) J. A. Conkling, *Chemistry of Pyrotechnics Basic Principles and Theory*, Marcel Dekker, NY, 1985.

20) R. Dilg, "Whistle While You Work*" American Fireworks News*, No. 74, 1987, p 4.

21) Private communication between R. Amons and A. Hahma, reported in reference 15.

22) L. Weinman, "A Curious Observation during the Burning of Bulk Whistle Composition", *J. Pyro.*, No. 17, 2003, p 79.

23) S. Öztap, "The Pyrotechnic Whistle and its Applications", *Pyrotechnica XI*, June, 1987.

24) R. Webb, TNO Prins Maurits Laboratory, Private communication, 2004.
