The Chemical Transformation of Fireworks in the 19th Century.

Barry Thomas Sturman
B.Ap.Sc (Chem.), M.Ap.Sc. (Chem.) W.A.I.T.,
M.A. Monash University

A thesis submitted for the degree of Doctor of Philosophy at
Monash University in 2017
School of Philosophical, Historical and International Studies

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Abstract

Fireworks in Europe underwent a remarkable transformation during the 19th century. A full range of colours was introduced, supplemented by white sparks, flashes and novel sound effects. This thesis explains the transformation of fireworks in 19th century Europe by showing that it was the result of the introduction of new materials into the chemical mixtures used in the fireworks. It explains why those materials were introduced in the 19th century, and not earlier, by arguing that a material cannot be applied in technology unless it is known, that it is known to have potentially useful properties, that no properties are known that would preclude the material from practical application and that it is available in sufficient quantity and at an affordable price. The possibility of the application of a material is not sufficient; there must also be social circumstances that make such an application worthwhile. Social circumstances of 19th century Europe were particularly conducive to efforts to improve fireworks. Many more people that ever before had time and money to spend on non-essential activities, including fireworks. As well as the obvious application in firework displays (popular as part of the entertainment provided at pleasure gardens) improved fireworks were of interest to theatrical entrepreneurs, who used them as stage effects, and to military men, who used them as signals. The unique historical combination of these circumstances and the availability of the necessary materials as a result of the activities of chemists and the development of chemical-based industries explains the transformation of fireworks in 19th century Europe. A significant discovery of this project is that much of the work was carried out and documented by amateur pyrotechnists, who flourished during the first three quarters of the century. Amateur pyrotechny, like photography, natural history and other science-based hobbies, was possible because some people had the resources to spend on leisure activities, were sufficiently well-educated to acquire and communicate the necessary knowledge. Furthermore, the necessary materials, which were available to all who could afford to buy them. Chemists indirectly made the transformation of fireworks possible by providing the new materials, but for the most part the explanation of the effects produced by fireworks was beyond the capabilities of 19th century science. It is argued that for this reason the direct contribution of chemists to the chemical transformation of fireworks was insignificant compared to the contributions of amateurs and military men. The contributions of professional pyrotechnists are difficult to assess, as they mostly did not write about their work and were inclined to keep new developments secret, but the evidence is that during the early part of the transformation the professionals adopted innovations made by amateurs and the military. This changed in the last quarter of the century, when new regulations placed restrictions on amateurs, and firework manufacture had to be carried out under license on a formally structured basis. Late 19th century pyrotechnic innovations were disclosed in patents rather than in books by amateurs.

Declaration

This thesis contains no material which has been accepted for the award of any other degree or diploma at any university or equivalent institution and that, to the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

Publications during enrolment

1. Sturman, B. "A Critique of Simon Werrett's Account of the Introduction of Potassium Chlorate into Pyrotechny." *PGI Bulletin (Bulletin of the Pyrotechnics Guild International, Inc.)*, no. 183 (2013), pp. 54-65.
2. Sturman, B. "The Early Use of Potassium Chlorate in Pyrotechny: Part I. John Forster and the First Chlorate-based Colored Fire." *PGI Bulletin (Bulletin of the Pyrotechnics Guild International, Inc.)*, no. 184 (May/June 2013), pp. 40-50.
3. Sturman, B. "The Early Use of Potassium Chlorate in Pyrotechny: Part II. John Forster, Sarah Hengler and the Original Chlorate-based Green Fire." *PGI Bulletin (Bulletin of the Pyrotechnics Guild International, Inc.)*, no. 185 (July 2013), pp. 70-78.
4. Sturman, B. "The Early Use of Potassium Chlorate in Pyrotechny: Part III. Applications of Early Chlorate-based Coloured Flame Compositions ". *PGI Bulletin (Bulletin of the Pyrotechnics Guild International, Inc.)*, no. 186 (October/November 2013), pp. 61-75.
5. Sturman, B. "The Early Use of Potassium Chlorate in Pyrotechny. Part IV. Martin Websky's Colored Flame Compositions of 1831." *PGI Bulletin (Bulletin of the Pyrotechnics Guild International, Inc.)*, no. 187 (January 2014), pp. 36-44.
6. Sturman, B. "The Early Use of Potassium Chlorate in Pyrotechny. Part V. Moritz Meyer and his Application of Chemical Theory to Pyrotechnics." *PGI Bulletin (Bulletin of the Pyrotechnics Guild International, Inc.)*, no. 188 (March/April 2014), pp. 46-61.
7. Sturman, B. "A Firework by Any Other Name." *Fireworks*, no. 65 (Spring 2014), pp. 42-43.
8. Sturman, B. "The Early Use of Potassium Chlorate in Pyrotechny. Part VI. Moritz Meyer's Work on Coloured Pyrotechnic Flames." *PGI Bulletin (Bulletin of the Pyrotechnics Guild International, Inc.)*, no. 189 (May/June 2014), pp. 42-55.
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10. Sturman, B. "The Early Use of Potassium Chlorate in Pyrotechny. Part VII. F. – M. Chertier and the Development of Chlorate-based Coloured Fires in France." *PGI Bulletin (Bulletin of the Pyrotechnics Guild International, Inc.)*, no. 193 (March/April 2015), pp. 29-46
11. Sturman, B. "Thomas Kentish: A Victorian Amateur Pyrotechnist." *Fireworks*, no. 69 (Spring 2016), pp. 31-33.
12. Sturman, B. "Notes on Frederick James Bishop (1862-1957) Pyrotechnist." *Fireworks*, no. 70 (Summer 2016), pp. 26-28.
13. Sturman, B. "On Chertier's Copper." *PGI Bulletin (Bulletin of the Pyrotechnics Guild International, Inc.)*, no. 199 (October 2016), pp. 39-56.
14. Sturman, B. "Artists in Fireworks: Joseph and George Southby. Part 1. Joseph Southby.' *Fireworks*, no. 71 (Summer 2017), pp. 42-44.
15. Sturman, B. "An Early Spanish Account of Coloured Fires." *PGI Bulletin (Bulletin of the Pyrotechnics Guild International, Inc.)*, no. 200 (December 2016/January 2017), pp. 35-46.

Student signature: [redacted] **Date: 21 March 2017**

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the student and co-authors' contributions to this work.

Main Supervisor signature: *(Insert electronic signature)* **Date:**

Acknowledgements

I thank the following people for their assistance with this project.

My supervisors, David Garrioch and Michael Hau, provided invaluable insights, advice and encouragement.

Seamus O'Hanlon, Agnieszka Sobocinska, Paula Michaels and Adam Clulow gave helpful advice and criticism as members of milestone review panels.

The Document Delivery library staff at Monash University (Pauline Middleton, Claudia De Salvo, Kimberley Ferrier, Catherine Hocking, Glenda Hill, Amanda O'Shaughnessy, Janine Zimmer) were extremely helpful in securing obscure material remarkably quickly and efficiently.

Megan Deacon of Monash University provided helpful advice on copyright matters.

Sascha Burnside of the School of Philosophical, International and Historical Studies efficiently ensured that I maintained compliance with the administrative requirements of the University.

Dr Ken Kosanke of Whitewater, Colorado, U.S.A. generously conducted some pyrotechnic experiments for me, as indicated in the text. Such experiments would have been impossible for me to do without contravening local explosives regulations.

Mr Michael S. Swisher of Bayport, Minnesota, U.S.A. kindly provided scans of several ancient pyrotechnic documents that were not available through the resources of the library. He also encouraged me to publish articles based on this project in the *Bulletin of the Pyrotechnics Guild International, Inc.*

Damian Cairns, Special Collections Librarian of the Macmillan Brown Library, University of Canterbury, New Zealand went to a lot of trouble to provide photographs of an ancient book held in the library but not available for interlibrary loan.

Jayne Shrimpton's specialized knowledge of historical costume provided valuable chronological insights into some old photographs of people mentioned in this project.

Margaret Chapman, Jeannie Johnston and Carloyn Golowka generously shared genealogical information about members of their families encountered during the research for this project.

Gary Hicks kindly provided the original source of some information about a relevant historical character mentioned in his book *The First Adman: Thomas Bish and the Birth of Modern Advertising.*

Sandra Hempel provided helpful discussions of a relevant historical character mentioned in her book *The Inheritor's Powder: A Tale of Arsenic, Murder, and the New Forensic Science.*

Ken Kosanke, Bonnie Kosanke and Robert Winokur, my co-authors of the *Encyclopedic Dictionary of Pyrotechnics and Related Subjects*, have graciously accepted my neglect of the second edition of that work for the duration of this project. Ken also provided editorial comments on one or two sections of the text of Chapter 9.

I specially thank my beloved wife Susan, who encouraged me to take up postgraduate studies in my retirement and patiently tolerated my spending many long hours at the computer.

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Chapter 1: Introduction.

This thesis explains the changes in fireworks that took place in Europe between the middle of the 18th century and the end of the 19th. Those who think of fireworks as childish and unacceptably dangerous things that provide ephemeral, wasteful entertainment for the unsophisticated would consider this subject unworthy of attention, but the history of the technical development of fireworks provides insights into how new materials can contribute to technical innovation. Furthermore, the historian David Edgerton has recommended that attention be paid to the details of the histories of specific technologies. This project is part of a growing body of scholarship that does exactly as Edgerton suggested. [1]

The present enquiry focuses on the technical changes in fireworks over the 19th century. It is not an investigation of the place of fireworks in 19th century life, nor is it a contribution to the history of popular entertainments. It investigates a process of technological innovation that happened when an ancient technical craft was transformed by new materials made available by developments in chemistry. Some of those chemical developments are discussed in detail, but the project is essentially a case study of the role of materials in technological innovation.

At the beginning of the 19th century European fireworks were not greatly different from those of the previous few centuries, but by the end of the 19th century they had been transformed. A European firework expert of the 17th century miraculously transported to a firework display at the start of the 19th century would have been in broadly familiar territory, but an expert from the beginning of the 19th century would have been awestruck to experience a display at the end of that same century. The types of fireworks would have been familiar: rockets soared into the air and transformed into cascades of falling stars, mortars thundered fire and smoke as they flung shells high into the air, each projectile ominously trailing dull sparks as it rose and rose, then exploding to fill the sky with fiery stars and comets. Jets of sparks turned spinning fire-wheels; pictures and patterns outlined in points of fire crackled out of the darkness. All this would have been familiar – but what a difference in the performance! The familiar yellow, orange and dim-red tones of the sparks were now supplemented by dazzling silvery-white, and the few vague, dull tints of long-familiar firework flames were replaced with brilliant colours. Whole landscapes would be illuminated with coloured light. Even the sounds were different. The thud of exploding gunpowder would still be heard, but there were also explosions of a distinctly different tone, louder and sharper, accompanied by a flash of white light. The percussion of the explosions was supplemented by weird, shrill whistles, louder than any musical instrument, mysteriously generated by chemicals burning in little paper tubes. The performance of fireworks had become so impressive that there was no longer any need to provide the sumptuous architectural backdrops that had been so important in the displays of old.[2]

Figure 1.1 shows a firework display fired in London in 1814. The centrepiece is a purpose-built architectural edifice; the colours of the fireworks are limited to fiery shades of yellow to orange-red. It might be argued that this was because it was conventional to depict fireworks in this way, but why would that convention have arisen, if not because that was what people remembered when they recalled a firework display? Any assertion that the colours were imposed by limitations in print technology is easily refuted by noting the brilliant colours of items of clothing depicted in prints of this period (notice the jackets of the soldiers in the lower left, distinctly blue even though it is night-time).

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[1] David Edgerton, "Innovation, Technology or History What is the Historiography of Technology About?," *Technology and Culture* 51, no. 3 (2010), p. 697.

[2] For the similarity of early 19th century European fireworks to those of preceding centuries, see Franz Eduard Moritz Meyer, *Die Feurewerkerei in ihrer Anwendung auf Kunst, Wißenschaft und Gewerbe* (Leipzig: Johan Ambrosius Barth, 1833), p. 1. For the 19th century changes, see Alan St Hill Brock, *A History of Fireworks* (London: George G. Harrap & Co. Ltd, 1949), chapter XIII, pp. 151-164.

Figure 1.1. Early 19th century firework display. [3]

Figure 1.2 shows a display fired in London, some 105 years later, after the changes explored in this project. The fireworks are multi-coloured; a huge spray of silvery-white plumes dominates the left-hand side of the picture. No architecture is to be seen. Why did these changes happen? At first the answer seems obvious: in the 19th century fireworks were well-established in European life, just as they had been for four or five centuries. In the 19th century more people than ever before had the time and money to participate in non-essential activities, some of which involved fireworks. Fireworks were seen in a variety of settings ranging from great public displays for occasions of state, regular shows at metropolitan and regional pleasure gardens, formal displays at the great homes of the wealthy, down to the enthusiastic and often over-exuberant setting off of small fireworks by the common people on occasions such as Guy Fawkes' Day in Britain, Bastille Day in France and Sylvester in Germany. Increased demand led to competition between manufacturers of fireworks, and this naturally led them to attempt to gain market share, either by cutting prices or by offering novel, more impressive products. The appearance of new and improved products is only to be expected, but that is not the whole story.[4]

[3] http://www.georgianindex.net/G_peace/GJulbile.html Accessed 25 February 2017.

[4] For fireworks in European life, see Anonymous, "Art de l'artificier," in *Encyclopédie méthodique; ou, par ordre de matières; par une société de gens de lettres, de savans et d'artistes.* (Paris: Panckoucke, 1782); L., "Artificier," in *Dictionnaire technologique, ou nouveau dictionnaire universel des arts et métiers, et de l'économie industrielle et commerciale par une société de savans et d'artistes* (Paris: chez Thomine et Fortic, 1822); John MacCulloch, "Pyrotechny," in *The Edinburgh Encyclopaedia*, ed. David Brewster (Edinburgh: William Blackwood, 1830); Julian Robert John Jocelyn, "The connection of the Ordnance Department with National & Royal fire-works, including some account of Sir Martin Beckman, Colonel Henry John Hopkey, & Sir William Congreve (2nd Baronet.)," *Journal of the Royal Artillery* 32 (1906); Alan St Hill Brock, *Pyrotechnics: The History and Art of Firework Making* (London: Daniel O'Connor, 1922); *A History of Fireworks*; George Plimpton, *Fireworks: A History and Celebration* (Garden City, NY: Doubleday & Company, Inc., 1984); James Riddick Partington, *A History of Greek Fire and Gunpowder* (Baltimore: The Johns Hopkins University Press, 1999); Chris Philip, *A Bibliography of Firework Books: Works on recreative fireworks from the sixteenth to the twentieth century* (Winchester: Chris Philip, in association with St Paul's Bibliographies 1985); Geron Sievernich and Hendrik Budde, *Das Buch der Feuerwerkskunst: Farbenfeuer im Himmel Asiens und Europas* (Nördlingen: Delphi (Greno Verlagsges. m b.H.), 1987); P. Bracco and E. Lebovici, *Ruggieri: 250 ans de feux d'artifice* (Paris: Denoël, 1988).

Figure 1.2. Early 20th century firework display[5]

Some people certainly made and displayed fireworks primarily to make money. Others were more interested in the aesthetic, artistic and creative aspects of fireworks, and sought improvements independently of economic considerations. Practitioners in any creative field continually strive for novelty, variety and excellence. Thus, two independent but complementary reasons can be discerned for the changes in fireworks over the course of the 19th century: commercial competition and artistic ambition. Both of these must, however, have been present for as long as people have been making fireworks and staging firework displays, so why did the changes not take place long before the 19th century?

These questions were addressed in the late 1940s by the English pyrotechnist Alan St Hill Brock (1886-1956) and the American chemist and historian of chemistry Tenney Lombard Davis (1890-1949). Brock wrote: 'The modern era of pyrotechny began with the introduction of potassium chlorate...', and according to Davis 'The history of fireworks divides itself naturally into two principal periods, the period before the introduction of potassium chlorate and the period after the introduction of that substance.' [6]

The most recent detailed work on the history of fireworks has been done by Simon Werrett, who is primarily interested in cultural history. Werrett has written widely on historical aspects of fireworks, mostly with little attention to the technical aspects.[7]

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[5] Gordon Stowell and J. Edward Mason, *The Book of Knowledge*, 8 vols., vol. 3 (London: The Waverley Book Company Ltd, no date, but after 1953), facing p. 365.

[6] Brock, *A History of Fireworks*, p. 156; Tenney L. Davis, "The Early use of Potassium Chlorate in Pyrotechny: Dr Moritz Meyer's Colored Flame Compositions," *Chymia* 1 (1948), p. 75.

[7] For Werrett's writing on aspects of the history of fireworks, see Simon Werrett, "Explosive Affinities: Pyrotechnic Knowledge in Early Modern Europe," in *Making Knowledge in Early Modern Europe: Practices,*

In his 2010 book, *Fireworks Pyrotechnic Arts and Sciences in European History*, Werrett devoted four pages to coloured fires and two paragraphs to potassium chlorate, but made a number of factual errors. [8]

More significantly, he seems not to have understood the qualitative difference between the old coloured fireworks (and coloured alcohol flames) and the new firework colours that were made possible by potassium chlorate. In his 2010 book he traced a misleading trajectory of the development of coloured fires from the green alcohol flames popular in 18th century Russia, through Cutbush to the French pyrotechnist Claude-Fortuné Ruggieri (1777-1841). In another recent paper, in which he explicitly addressed colour in early modern fireworks, he wrote:

> That modern authors place so much emphasis on colored fire is due to the promotion of color in pyrotechny by writers working in the age of the Chemical Revolution . . . [9]

and:

> Just to be clear, this essay does not deny that there was a transformation in the ability to produce colors in fireworks in the nineteenth century. But people of earlier generations did not view their fireworks as weak or colorless affairs, even if later chemists, pyrotechnists and historians have represented them that way. [10]

Objects, and Texts, 1400-1800, ed. Pamela H. Smith and Benjamin Schmidt (Chicago: University of Chicago Press, 2007) pp. 68-89; "From the Grand Whim to the Gasworks: 'Philosophical Fireworks' in Georgian England," in *The Mindful Hand: Inquiry and Invention from the Late Renaissance to Early Industrialisation*, ed. Peter Dear, Lissa Roberts, and Simon Schaffer (Amsterdam and Chicago: Edita; University of Chicago Press, 2007), pp. 325-347; "Making Fire Work: Pyrotechnics and Natural Philosophy," *Endeavour* 32, no. 1 (2008), pp. 32-37; "The Finest Fireworks in the World: Chinese Pyrotechnics in Early Modern Europe," in *Variantology: On Deep Time Relations of Arts, Sciences and Technologies*, ed. Siegfried Zielinski and Eckhard Fuerlus (Cologne: Walther Koenig, 2008), pp 17-34; "Sparks of Life." *Cabinet Magazine Online*, Winter 2008/2009, no page numbers, http://cabinetmagazine.org/issues/32/werret.php Accessed 8th March, 2017.; "William Congreve's Rational Rockets," *Notes and Records of the Royal Society* 63, no. 1 (2009), pp. 35-56; *Fireworks Pyrotechnic Arts and Sciences in European History* (Chicago: University of Chicago Press, 2010); "The Power of Pyrotechnics," *History Today* 60, no. 11 (2010), pp.10-16; "Watching the Fireworks: Early Modern Observation of Natural and Artificial Spectacles " *Science in Context* 24, no. 2 (2011), pp.167-182; "Technology on the Spot: The Trials of the Congreve Rocket in India in the Early Nineteenth Century," *Technology and Culture* 53, no. 3 (2012), pp. 598-624; "Green is the Colour: St. Petersburg's Chemical Laboratories and Competing Visions of Chemistry in the Eighteenth Century " *Ambix* 60, no. 2 (2013), pp. 122-138; "Fireworks and Color in the Sixteenth and Seventeenth Centuries." *Early Science and Medicine* 20 (2015), pp. 458-77.

[8] Simon Werrett, *Fireworks Pyrotechnic Arts and Sciences in European History* (Chicago: University of Chicago Press, 2010), pp. 229-233; his treatment of potassium chlorate is on pp. 230-231. Werrett erroneously attributed the first mention in print of the use of potassium chlorate in coloured fires to the American chemist James Cutbush (1788-1823), whereas I have shown that the introduction of the new chlorate-based coloured fires began with the invention of a new red fire as a theatrical stage effect in London in the second decade of the 19th century. See B. Sturman, "Coloured Fire: The Development of Coloured Pyrotechnic Flames in Early Nineteenth Century Europe" (Monash University, 2011); "The Early Use of Potassium Chlorate in Pyrotechny: Part I. John Forster and the First Chlorate-based Colored Fire," *PGI Bulletin (Bulletin of the Pyrotechnics Guild International, Inc.)*, no. 184 (2013), pp. 40-50. Examination of the references cited by Werrett revealed that they did not support his claims See B. Sturman, "A Critique of Simon Werrett's Account of the Introduction of Potassium Chlorate into Pyrotechny," *PGI Bulletin (Bulletin of the Pyrotechnics Guild International, Inc.)*, no. 183 (2013), pp. 54-65.

[9] "Fireworks and Color," p. 458.

[10] Ibid., p. 462.

This project focuses on the 19th century transformation mentioned by Werrett and will argue that it was precisely because people of earlier generations were dissatisfied with the ability of their fireworks to produce colours that efforts were made to improve them. Such efforts were largely unsuccessful, because the necessary materials did not exist until the late 18th century. Werrett's account of materials previously used in pyrotechny in attempts to produce colour contains nothing that would not have been known to Brock and Davis. Yes, these materials were used to produce different colours, but, as will be explained in Chapter 2, the results were disappointing, not least to the pyrotechnists. The exception was the green alcohol flame, which Werrett has shown was in use in Russian firework displays in the 18th century. It was based on verdigris, which according to Werrett 'easily burns to give a green flame'. [11]

Verdigris does indeed impart a green colour to flames, but not as readily as might be concluded form Werrett's comment. There is evidence of its use in pyrotechny from the 13th century, but for reasons given in Chapter 2 the results were mediocre; indeed, as Werrett correctly wrote elsewhere 'It was easy to tint flames green, but very hard to make a gunpowder mixture that burned with the same intense colour.' [12]

The green-coloured alcohol flames used in 18th century and early 19th century firework displays clearly provided some pleasing variety, but they were not nearly as bright as the coloured pyrotechnic flames that would later be produced, not with 'a gunpowder mixture' but with new pyrotechnic mixtures based on potassium chlorate. The new generation of green fires did not included verdigris at all, but a new chemical, barium nitrate. When these new green fires came into use, the once-admired green alcohol flames were relegated to funeral ceremonies, where the subdued and flickering colour they produced was seen as befitting the sombre occasion. [13]

The conclusions of this project are consistent with those of Brock and Davis, but give a much more detailed analysis than was provided by those two highly-esteemed authors. The arguments presented here oppose Werrett's implication that the changes in fireworks have been exaggerated. On the contrary, it will be shown that the changes were the real and transformational result of the introduction of new materials into the firework-maker's craft.

Knowledge of the existence and the properties of the materials that would eventually transform fireworks began in the late 18th century as a result of the efforts of chemists, but contrary to what might be expected, the introduction of the materials into fireworks happened long before chemists (or anyone else) could account for the remarkable effects that the new materials produced. These effects were discovered in some cases (the ability of various salts to impart different colours to flames) by exploratory experimentation by firework makers following up observations reported by chemists in their publications on the new materials. Other effects, such as the pyrotechnic whistle and the

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[11] For Werrett on the green alcohol flame, see *Fireworks*, pp.162-166, and "Green is the Colour", pp. 133-137. His claim about the overemphasis of coloured fires is in "Fireworks and Color." p. 458. His comment on burning verdigris is in ibid. p.469.

[12] For verdigris in 13th century green fire, see Partington, *A History of Greek Fire and Gunpowder* , p. 203. Werrett's remark about the difficulty of colouring the flame of a 'gunpowder mixture' is in Werrett, "Green is the Colour", p.134.

[13] For the relegation of the green flame to funeral ceremonies, see F.-M Chertier, *Nouvelles recherches sur les feux d'artifice*, 1 ed. (Paris: chez l'auteur, 1843), p. 478; Amédée Denisse, *Traité pratique complet des feux d'artifice* (Paris: chez l'auteur, 1882), p. 355 and Paul Tessier, *Chimie pyrotechnique ou traité pratique des feux colorés* (Paris: J. Dumaine, Lacroix et Baudry, 1859), p. 225.

beautiful phenomenon of 'glitter' seem to have been discovered by serendipity as firework makers tried promising new materials.

Foremost amongst these new materials, as emphasized by Brock and Davis, was potassium chlorate ($KClO_3$). This chemical supplemented the traditional saltpetre (potassium nitrate, KNO_3) as a source of oxygen in firework compositions. Appropriate mixtures of potassium chlorate and a suitable fuel (originally sulfur, S_8) produce flames having a chemical environment favourable to the generation of coloured light. Certain chemicals, when burned in such a flame, are transformed into gases that emit coloured light, for reasons that remained a mystery until the 20th century. Strontium nitrate ($Sr(NO_3)_2$) colours an appropriate flame red, barium nitrate ($Ba(NO_3)_2$), green. Other chemicals produce different colours. Later, after the new colours had become an expected part any firework display, the introduction of other new materials brought different effects: silvery-white sparks and sharp, lightning-like explosions produced by magnesium (Mg) and aluminium (Al), and screeching whistles generated by a burning mixture containing potassium picrate ($C_6H_2(NO_2)_3OK$). These new materials were simply not known anywhere until they were discovered in Europe. Without them, no real change in fireworks would have been possible, however strong the incentives for change might have been.[14]

1.2. The Role of Materials in Historical Explanation

In 1988 George Basalla wrote: 'the extent to which innovation is promoted by the introduction of new materials has been greatly exaggerated.' He gave examples of the introduction of new materials resulting in existing artefacts merely being replicated in the new material. This might make an artefact easier to make, or more durable, but does not change it in any fundamental way. A basket made of woven plastic does not have any huge advantage over one made of woven cane. Over time, better appreciation of the properties new material might lead to changes in design, but the process is slow.[15]

This project provides a counter-example of the introduction of new materials bringing about the transformation of a technology. While it is true that the fireworks themselves were similar (or even identical) in appearance and construction to those before the introduction of the new materials, and were manufactured in much the same way, the presence of new materials in the mixtures of chemicals

[14] Brock, *A History of Fireworks*, especially chapter XIII, pp. 151-164 ; B. Sturman, "Coloured Fire: The Development of Coloured Pyrotechnic Flames in Early Nineteenth Century Europe" (Monash University, 2011); "A Critique of Simon Werrett's Account of the Introduction of Potassium Chlorate into Pyrotechny", pp.54-65; "The Early Use of Potassium Chlorate in Pyrotechny: Part I. John Forster and the First Chlorate-based Colored Fire," *PGI Bulletin (Bulletin of the Pyrotechnics Guild International, Inc.)*, no. 184 (2013), pp. 40-50; "The Early Use of Potassium Chlorate in Pyrotechny: Part II. John Forster, Sarah Hengler and the Original Chlorate-based Green Fire " *PGI Bulletin (Bulletin of the Pyrotechnics Guild International, Inc.)*, no. 185 (2013), pp. 70-78; "The Early Use of Potassium Chlorate in Pyrotechny: Part III. Applications of Early Chlorate-based Coloured Flame Compositions " *PGI Bulletin (Bulletin of the Pyrotechnics Guild International, Inc.)*, no. 186 (2013), pp. 61-75; "The Early Use of Potassium Chlorate in Pyrotechny. Part IV. Martin Websky's Colored Flame Compositions of 1831," *PGI Bulletin (Bulletin of the Pyrotechnics Guild International, Inc.)*, no. 187 (2014), pp. 36-44; "The Early Use of Potassium Chlorate in Pyrotechny. Part V. Moritz Meyer And His Application of Chemical Theory To Pyrotechnics," *PGI Bulletin (Bulletin of the Pyrotechnics Guild International, Inc.)*, no. 188 (2014), pp. 46-61; "The Early Use of Potassium Chlorate in Pyrotechny. Part VI. Moritz Meyer's Work on Coloured Pyrotechnic Flames." *PGI Bulletin (Bulletin of the Pyrotechnics Guild International, Inc.)*, no. 189 (May/June 2014), pp. 42-55; "The Early Use of Potassium Chlorate in Pyrotechny. Part VII. F.-M. Chertier and the Development of Chlorate-based Coloured Fires in France." *PGI Bulletin (Bulletin of the Pyrotechnics Guild International, Inc.)*, no. 193 (March/April 2015), pp. 29-46.

[15] George Basalla, *The Evolution of Technology*, Cambridge History of Science (Cambridge: Cambridge University Press, 1988), pp.106-108.
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that went into the fireworks brought about revolutionary changes in their performance – changes that have been likened to the introduction of colour into motion pictures.[16]

The importance of materials in the history of technological and intellectual innovation has been discussed by historian Ursula Klein and her colleagues. For example, in a review of Hasok Chang and Catherine Jackson's book on the history of chlorine, Klein wrote:

> Historical studies of material substances thus can provide insight into a broad range of different practices and forms of knowledge of the past, cutting across the sciences, technology, medicine and the consumer market.[17]

Klein's observation is supported by accounts in scholarly journals showing how new materials transformed fields as diverse as anaesthesia, artist's pigments, dyeing, and paper-making. Books have been published on the histories of individual chemical substances including phosphorus and saltpetre, and there have been several historical studies of gunpowder and other explosives.[18]

Rochelle Forrester has argued that the whole course of technological development is determined by the chemistry of materials. This is a profound insight: when and where technological development started might well have been different, but the sequence of developments could have differed only in

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[16] The comparison to colour in motion pictures was made by Brock, *A History of Fireworks.* p. 160, and, as cited by Werrett, "Fireworks and Color." p. 461, in Alan St Hill Brock, "Fireworks," *Journal of the Royal Society of Arts* 99, no. 4852 (1951), p. 682.

[17] Ursula Klein, "Review of H. Chang and C. Jackson (eds.), An Element of Controversy: The Life of Chlorine in Science, Medicine, Technology and War. BSHS Mongraph Series, Vol. 13, London: British Society for the History of Science, 2007 " *British Journal for the History of Science* 42, no. 1 (2009), p. 129. See also Ursula Klein and E. C. Spary, eds., *Materials and Expertise in Early Modern Europe: Between Market and Laboratory* (Chicago and London: The University of Chicago Press, 2008).

[18] *Materials and Expertise in Early Modern Europe: Between Market and Laboratory*. Rochelle Forrester, *How Change Happens: A Theory of Philosophy of History, Social Change and Cultural Evolution*, 2nd ed. (Newlands, Wellington, New Zealand: Best Publications Limited, 2013). M. Goerig and J. Schulte am Esche, "History of nitrous oxide - with special reference to its early use in Germany," *Best Practice and Clinical Research Anaesthesioloy* 15, no. 3 (2001), pp. 313-338; Francis X. Whalen, Douglas R. Bacon, and Hugh M. Smith, "Inhaled anaesthetics: an historical overview," *Best Practice and Clinical Research Anaesthesioloy* 19, no. 3 (2005), pp. 323-330; Linda Stratmann, *Chloroform: The Quest for Oblivion* (Stroud, Gloucestershire: Sutton Publishing, 2003); J. R. Barnett, Sarah Miller, and Emma Pearce, "Colour and art: A brief history of pigments," *Optics & laser technology* 38 (2006)' pp. 445-453; Barbara H. Berrie, "Rethinking the History of Artists' Pigments Through Chemical Analysis " *Annual Review of Analytical Chemistry* 2012, no. 5 (2012), pp. 411-459; Agustí Nieto-Galan, "Between Craft Routines and Academic Rules: Natural Dyestuffs and the "Art" of Dyeing in the Eighteenth Century," in *Materials and Expertise in Early Modern Europe: Between Market and Laboratory*, ed. Ursula Klein and E. C. Spary (Chicago and London: The University of Chicago Press, 2008), pp. 321-353; Ursula Klein, "Review of A. Nieto-Galan, Colouring Textiles: A History of Natural Dyestuffs in Industrial Europe. Boston Studies in the Philosophy of Science, 217, Dordrecht, Boston and London, Kluwer Academic Publishers, 2001," *The British Journal for the History of Science* 37, no. 2 (2004), pp.214-215; Simon Garfield, *Mauve* (London: Faber and Faber Limited, 2000); Yeung Chung Lee, "Science-Technology-Society or Technology-Society-Science? Insights from an Ancient Technology." International *Journal of Science Education* (2009), pp. 1927-50; John Emsley, *The Shocking History of Phosphorus: A Biography of the Devil's Element* (London: Pan Books, 2000); David Cressy, *Saltpeter, the Mother of Gunpowder* (Oxford: The University Press, 2013); Brenda J. Buchanan, ed., *Gunpowder, Explosives and the State: A Technological History*, London and NewYork: Routledge, 2016; Patrice Bret, "Le dernier des procedees revolutionnaires: la fabrication et l'expertise de la poudre ronde (1795-1830)," *Annals of Science* 50, no. 4 (1993), pp. 325-347. Rae, Ian D., and James N. Whitehead. "Rackarock: On the Path from Black Powder to ANFO." in Gunpowder, Explosives and the State: A Technological History, edited by Brenda J. Buchanan, London and NewYork: Routledge, 2016, pp. 367-384.

minor detail. People naturally made their first tools with materials readily to hand (wood, bone, or stone); the next step would have been to notice and exploit those few metals (e.g. gold, copper) that occur naturally. Familiarity with native copper would have led to copper being recognized if it were accidentally produced when certain unusual rocks were exposed to a hot fire. Experience with copper-smelting would have led to the discovery of other easily smelted metals (e.g. tin) and alloys (bronze). Knowledge of smelting would eventually lead to the smelting of iron, a metal known to a lucky few from its occasional natural occurrence in meteorites but not easily extractable from its ores.[19]

People could, and some did, remain at each of these stages of technological development for a long time, and there is nothing to say that the next step had to be taken. Indigenous Australians lived for untold generations without metals, and it is only in the last five hundred years or so that anyone knew of metals apart from gold, silver, copper, tin, lead, iron, and mercury. There was nothing inevitable about the development of technology, but what was inevitable is the sequence in which the various materials are introduced, if they are introduced at all. No new material can be produced without the practical knowledge developed in the course of producing and using existing materials; and existing materials are necessary for the production of new ones. This refers to materials that are new to the human race – materials were often introduced by transmission from more materially advanced communities.

Bruno Latour has called contributors to historical change ‘agencies”. They include inanimate things, such as materials, as well as the people and social institutions more conventionally called ‘agents’. Latour claimed that ‘agencies’ have three aspects: ‘naturality’, ‘sociality’ and ‘semiotic construction’, and that these cannot be clearly differentiated. Put in plain words, and focussing on materials, this means that any material has three inseparable aspects: what it is, what part it plays in human society, and what people think of it. These aspects are different at different periods of history. Many of the materials discussed in this project simply did not exist on Earth until people produced them, so an important part of explaining how they came to be used is to show how and why they were produced at that particular time and place. Another aspect is how costly the materials were, in relation to the price that could be commanded in the market at that time for items that included those materials. [20]

The discovery (or creation) of the handful of new materials that would eventually transform fireworks began in the late 18th century. These new materials were among the great many discovered when chemists and natural philosophers analysed all manner of minerals and drew from them a range of metals, earths and salts with new and unexpected properties. The story of how that happened for some materials has been well told by historians of chemistry, but when and where the new materials were introduced into the craft of firework-making has not previously been discussed in detail. In teasing out the story we encounter people from different walks of life, and observe the effects of many of the well-known developments of the 19th century: changing modes of production (especially the rise of the chemical industry), the increasing numbers of people with time and money to spend on amusements, and the growing influence of science, particularly chemistry.

1.3. Firework Making and Chemistry

The relationship between firework making and chemistry forms a central theme in the project. Intuitively, the tale should be simple. Chemists discovered a new material, and described its properties. They noticed that some of those properties were of possible interest to firework-makers, and mentioned this in their publications. Firework makers picked up the opportunity, and tested the new material. Eventually, if the material did indeed have some advantages, and if its cost were not

[19] Forrester, *How Change Happens: A Theory of Philosophy of History, Social Change and Cultural Evolution*, pp.41-45.

[20] Bruno Latour, "On actor-network theory. A few clarifications plus more than a few complications," *Soziale Welt* 47 (1996), pp. 360-381.

prohibitive, it became part of the firework maker's set of ingredients and the art was advanced. In most cases the story is not nearly so straightforward.

I have discussed elsewhere the paradoxical role played by chemists in the development of coloured fires in the early 19th century. With hindsight, we can see that coloured fires became possible when 18th century chemists discovered the essential new materials and documented their properties. This was done because an important part of a chemist's work was to identify and characterize new materials. On the other hand, the actual application of those materials in coloured fires was delayed for decades, mainly because chemists taught that the key ingredient (potassium chlorate) was too dangerous for practical purposes. Chemists were thus at the same time unwitting facilitators and inhibitors of progress in pyrotechny.[21]

The meanings of the words 'firework', 'chemist', and 'chemistry' have changed over the centuries, and as recently as the 19th century their use was not always consistent and was sometimes different from our current usage, which itself is not completely uniform. Defining the meanings of certain words used in this project should avoid possible ambiguity and misunderstanding. *Pyrotechnics* is a branch of chemical technology that exploits the fact that certain mixtures of powdered solids can remain stable indefinitely and yet undergo a self-sustaining chemical reaction when ignited, producing useful or entertaining effects. Such a mixture is called a pyrotechnic *composition*. A *firework* is a device, incorporating one or more pyrotechnic compositions, used primarily for spectacular, entertaining or artistic purposes. *Pyrotechny* is the art and craft of making and displaying fireworks. A *pyrotechnist* is a person skilled in *pyrotechnics*, both in the broad sense of the term (as in 'military pyrotechnist') or in the restricted sense of one who is skilled in making and using fireworks.[22]

It is obvious that a firework-maker is someone who makes fireworks, but what is a *chemist*? Even now, the word can refer to a pharmacist as well as to a practitioner of *chemistry*, a relic of times when those occupations were not as distinct as they are today. *Chemistry* is the science of materials and their changes, so practitioners of such ancient crafts as metal smelting, glass-making, dying, bleaching, brewing, tanning, cooking, and the making of gunpowder and fireworks could plausibly be thought of as engaging in chemistry. These people had profound knowledge of the materials with which they worked and understood how to manipulate them to achieve the desired results, but to call them *chemists* would make the term too broad. These skilled manipulators of materials can be distinguished from the people described in this work as *chemists* in that they were concerned primarily, if not exclusively, with the materials of direct relevance to their craft, whereas *chemists* studied materials of all types, useful or not, and sought to classify them, and to understand their interactions and transformations. At the beginning of the 19th century such an understanding of the term 'chemist' would have been consistent with the contemporary textbooks of chemistry and would probably have been acceptable to people who identified themselves as chemists and who were so designated by others.[23]

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[21] Sturman, "Coloured Fire."

[22] See the relevant entries in K. L Kosanke et al., *Encyclopedic Dictionary of Pyrotechnics (and Related Subjects)* ed. K. & B. Kosanke, 3 vols., Pyrotechnic Reference Series (Whitewater, Colorado: Journal of Pyrotechnics, Inc., 2012). For technical details on pyrotechnics, see A. A. Shidlovski'i, *Principles of Pyrotechnics*, trans. Wright-Patterson Air Force Base Foreign Technology Division, Ohio **1974**, 3 ed. (Moscow: Mashinostoyeniye Press, 1964); Herbert Ellern, *Military and Civilian Pyrotechnics* (New York: Chemical Publishing Company, Inc., 1968); Kenneth L. Kosanke et al., *Pyrotechnic Chemistry*, ed. Bonnie J. Kosanke, Pyrotechnic Reference Series (Whitewater, CO: Journal of Pyrotechnics, Inc., 2004); John A. Conkling and Christopher J. Mocella, *Chemistry of Pyrotechnics: Basic Principles and Theory* 2nd ed. (Boca Raton, FL: CRC Press, 2011); Kosanke et al., *Encyclopedic Dictionary of Pyrotechnics (and Related Subjects)*.

[23] For the view that the chemically-based crafts and academic chemistry constituted various "cultures" of chemistry, see Nieto-Galan, "Between Craft Routines and Academic Rules", pp. 338-339.

A person could be at the same time a chemist and a practitioner of a chemically-based craft, just as a person might follow one or other of these callings exclusively. There were also intermediate cases, where a person was predominantly a craftsperson but took an interest in chemistry, and vice versa. Examples will be encountered in the following chapters.[24]

1.4. Artisanal and Scientific Ways of Knowing

The distinction between the knowledge possessed by practitioners of technical crafts and scientific knowledge has attracted the attention of scholars. For example, historian of science Myles W. Jackson has written on the craftsmanship involved in optical glass manufacture in the early years of the 19th century. It might seem that optical glass-making would be amenable to scientific analysis and that it would be a simple matter to duplicate the process, but Jackson showed that it was beyond even such a great experimental scientist as Michael Faraday (1791-1867). Faraday subjected samples of German optical glass to chemical analysis, and attempted to duplicate them, only to find that his product was distinctly inferior. The reason was that the German manufacturers had acquired, through practical experience, knowledge of subtle procedures necessary to obtain the extreme uniformity essential for fine optical glass. These artisanal aspects of the German glass-makers' craft were understood and appreciated by Joseph Fraunhofer (1787-1826), who was involved in establishing scientific procedures for the characterization and measurement of optical glass.[25]

Differences between artisanal and scientific knowledge have also been discussed by political scientist and anthropologist James C. Scott, who uses the ancient terms 'metis' and 'techne' to distinguish the two. Artisanal knowledge ('metis') typically involves knowing how to move the human body in specific ways to achieve the desired result (as the optical glass-makers in Fraunhofer's time knew how to stir the molten glass to make it perfectly uniform). Artisanal knowledge is traditionally acquired by undergoing training by a person who has mastered the necessary skills, accompanied by prolonged practice. It is possible to acquire artisanal skills by following written instructions, but success comes only after diligent practice. Success or failure is measured by the extent to which the product conforms to requirements and by the time and effort required to produce each conforming product. Scientific knowledge ('techne'), on the other hand, can be learned from books. The actual practice of science often involves artisanal skills – one cannot learn, for example, how to carry out volumetric analysis in chemistry without considerable practice to acquire the bodily movements involved in manipulating the burette, the pipette and the volumetric flask. [26]

In the case of pyrotechnics, the old firework-makers and gunpowder-men knew how to extract and purify saltpetre, how to refine sulfur and how to turn wood into charcoal. Having obtained their raw materials, they knew how to combine them and process them, and what extra materials to add, to obtain the effects they needed. These skills were passed from one generation of practitioners to the next by apprenticeship. A person who had mastered all the necessary skills, and was achieving satisfactory results, might reasonably be resistant to advice from a chemist who had no such skills.

[24] On the blurring of the academic and applied aspects of the study of materials in the eighteenth century, see Klein, Ursula. "Blending Technical Innovation and Learned Natural Knowledge: The Making of Ethers." Chapter 6 in *Materials and Expertise in Early Modern Europe: Between Market and Laboratory*, edited by Ursula Klein and E. C. Spary. Chicago and London: The University of Chicago Press, 2008, pp. 125-157.
[25] Myles W. Jackson, *Spectrum of Belief: Joseph Fraunhofer and the Craft of Precision Optics* (Cambridge, MA, USA and London, UK The MIT Press, 2000).

[26] James C. Scott, *Seeing Like a State: How Certain Schemes to Improve the Human Condition Have Failed* (New Haven, CT: Yale University Press, 1999).

On the other hand, the renowned French pyrotechnist Claude-Fortuné Ruggieri, writing in 1802, claimed that chemistry had much to offer the art.[27]

A few chemists took a keen interest in firework-making. The most well-known of these was Antoine-Laurent de Lavoisier (1743-1794), whose pyrotechnic work is discussed in Chapter 3. Chapter 7 discusses the contributions of the Prussian military chemist Franz Eduard Moritz Meyer (1798-1838) who, in the early 1830s, sought to place firework-making on a thoroughly scientific footing. The contributions of two scientific men (the British polymath John MacCulloch (1773-1835) and the Hessian chemist and social reformer Karl Georg Winkelblech (1810-1865)) who took it upon themselves to expound on firework-making, are reviewed in Chapters 7 and 9 respectively and it will be shown that their contributions were not as valuable as they apparently imagined.

1.5. Sources and Methodologies

The main limitation of the sources used in this project lay in the obscurity of many of the people involved, particularly the pyrotechnists. In some instances it was difficult (or even impossible) to find the dates of their birth and death; in others biographical information had to be laboriously inferred from casual remarks in their writing, or even from addresses given for self-published books. It was necessarily to rely primarily on their publications, and these have limitations. Some writers sought to exaggerate their contributions, and understandably almost all wrote to create a positive image of their work and its originality. Some could be discerned as having particular political or scientific agendas, and some may have had an interest in **not** revealing everything they knew. Some records are missing or were never produced: for instance, we cannot know in any detail what apprentice firework-makers of the 18th or 19th century learned about the materials and techniques used in the art.

Historical sources need to be assessed in the context of their times. To do this, it is helpful to know exactly what effects could have been produced by the materials and techniques disclosed in the historical texts. As a professional chemist and long-time firework enthusiast, I had the advantage of being able to assess the plausibility of historical claims about the effects produced by specific recipes in the light of today's knowledge, sometimes with the aid of thermodynamic modelling software, originally developed by the National Aeronautics and Space Administration for the evaluation of rocket propellants. Knowledge of whether or not the materials and recipes in historical sources could have been effective was an important advantage, which purely text-based scholarship could not provide. Furthermore, enough detail was provided in most original sources to allow the recipes to be duplicated and tested. Unfortunately, in Australia it is extremely difficult for even trained chemists to obtain the necessary chemicals and even if they could be obtained experiments with pyrotechnics and explosives are prohibited. I am fortunate in having pyrotechnically skilled friends in the United States of America, where there are no such restrictions, and one of these friends was kind enough to carry out some experiments, as mentioned and acknowledged in the text. Duplication and testing of historical recipes provided valuable insights into how the effects produced would have appeared to contemporary spectators.[28]

1.5.1 Miscellaneous Notes

1. The Internationa1 Union of Pure and Applied Chemistry requires that the name of the chemical element with symbol S and atomic number 16 be spelled 'sulfur'. Accordingly, I have used this spelling except where the original source uses 'sulphur' or when I am quoting from an historical document (even in translation) from a time when the spelling 'sulphur' was universal.

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[27] Claude-Fortuné Ruggieri, *Elémens de pyrotechnie, divisés en cinq parties; avec un vocabulaire des termes compris dans cet ouvrage*, 1 ed. (Paris: Barba, 1802).

[28] The software used was NASA Glenn Research Centre's *Chemical Equilibrium with Applications*. See https://www.grc.nasa.gov/WWW/CEAWeb/ (accessed 24th February, 2017).

2. All translations (unless otherwise stated) are my own.

1.6. Organization of Chapters

Chapter 2 begins by explaining the limitations of traditional firework materials. It then outlines the history of pyrotechnics from its beginnings in ancient China to transmission of knowledge of new ingredients from China to the West in the mid 18th century. It explains a demand for novel pyrotechnics in Europe with reference to the use of fireworks by the State; pyrotechnics for military signalling; firework displays at commercial venues; and pyrotechnic effects in the theatre. The reasons for seeking new effects in fireworks are discussed, and an explanation is given for why the most desirable new effect - bright, distinct colours - proved so elusive.

Chapter 3 shows that in 17th century Europe the materials used in fireworks were much the same as had been used since the earliest days. In the mid 18th century European missionaries to China brought back knowledge of new firework effects; these aroused interest in Europe and, as the materials involved were already well-known in Europe (but not previously applied to fireworks) they were soon incorporated into European practice.. Eighteenth century European attempts to make coloured fires are reviewed, revealing both the limitations imposed by the available materials and a surprising ignorance on the part of the pyrotechnists of the value of some materials that had long been used in other fields of technology.

Chapter 4 details the development of the new coloured fires that were central to the transformation of fireworks in 19th century Europe, beginning with the discovery by 18th century chemists of the chemicals essential for the new colours. The details of the initial discovery of the value of potassium chlorate in coloured fires (as discussed in my MA thesis) are mentioned only briefly. The role of potassium chlorate as a transformational material is emphasised: it allowed previously ineffective or marginally effective colour-producing agent to create brilliant, intense colours.

Chapter 5 reviews the introduction of three new firework ingredients that were not directly associated with the production of coloured fires. Magnesium and aluminium provided brilliant white flames and sparks, while potassium picrate introduced a completely new sound-effect: the pyrotechnic whistle. These materials had been known to chemists for decades, but were not available at affordable prices until much later in the century. The falls in price were brought about by the introduction of new technologies for their production when potential commercial applications became evident. Some of the new aluminium-based pyrotechnics were first disclosed as patents, indicating that innovation now had a strong commercial focus, quite different from the free disclosure of new information by amateurs that had characterised much of the development of coloured fires earlier in the century.

Chapter 6 focuses on the most surprising finding of this project: the role played by amateur pyrotechnists in the chemical transformation of fireworks. This could be seen as anomalous at a time when there was a distinct trend towards 'professionalization' in mainstream chemistry, but here we are dealing not with mainstream chemistry, but a traditional craft that drew on new materials that had become available through the efforts of chemists. There certainly were professional firework-makers, but there were also (and the evidence suggests many more) 'gentleman amateurs' who indulged in firework-making as a hobby. The boundaries between the two categories were porous: some amateurs turned professional, and some professionals were on friendly terms with amateurs and even employed them to assist with displays. Amateurs were particularly important in technical innovation because, in contrast to professionals, they could afford to be adventurous in trying new materials. The professionals were far more conservative – the inherent danger of the art made it prudent to err on the side of caution, especially when some of the new materials already had an evil reputation for causing spontaneous ignition. At least as important were the very different attitudes of professionals and amateurs to the dissemination of information. Professionals preferred to keep new developments secret, whereas amateurs earned status by publicizing the results of their efforts. Thus, almost all the information that we have about the development of coloured fires in the 19th century is in books

written by or for amateur pyrotechnists. These amateurs flourished at a time when the making and using of fireworks was officially prohibited, but that prohibition was so widely ignored that many were probably unaware of it. Later in the century, when prohibition was replaced by formal requirements for licensing of firework-makers under strict conditions, amateurs either abandoned the field or operated in a clandestine manner that precluded the free dissemination of information. None the less, several of the best books on firework-making appeared late in the 19th century, having most likely been in preparation before the new restrictions were enforced.

Chapter 7 addresses the role of the military in the transformation of fireworks. Writers on the history of fireworks in Europe have emphasized that from the earliest days the provision of firework displays for State occasions fell within the province of the armed forces. The military was important in that it provided technical training in pyrotechnics for its members and documented practical procedures that eventually permeated to civilian practitioners. The financial resources of the military also provided an incentive for civilians to develop pyrotechnic devices and materials of potential value to the military. No attention is paid here to the extensive work done since the mid 18th century on the technology of gunpowder. Improvements in gunpowder were of obvious importance to the military, and would have been useful to firework-makers, but they did not transform fireworks. That only happened with the introduction of completely new materials.

Chapter 8 explores the cost of materials as a limiting factor in the transformation of fireworks. Previous chapters mentioned examples of materials known to be potentially useful in fireworks but were far too expensive to be practical. This chapter reviews the costs of a range of firework ingredients over the 19th century, and accounts for the tendency for prices to fall by the economies of scale that follow when demand for a material justifies its manufacture in bulk. This happened for the materials of interest to firework-makers mostly when a material found applications outside firework-making. There were also examples of the demand for a material for fireworks becoming sufficient to justify an increase in production and a reduction in price. In other instances wide availability of a new material at a reasonable price led firework-makers to investigate its use in fireworks, and thus to discover some unexpected new effects.

Chapter 9 focuses on the role of chemists in the transformation of fireworks. Intersections between chemical science and pyrotechny are demonstrated, and evidence presented that by the end of the century the two fields had little influence on each other. Once the new materials had been absorbed into the traditions of the craft, pyrotechnists followed the old artisanal approach, relying on 'receipts' handed down from one generation of practitioners to the next. Academic chemists, preoccupied with more serious matters, took even less interest in pyrotechny.

Chapter 10 states the answers to the question posed at the start of the project: why were fireworks transformed during the 19th century in Europe? These answers turn out to be very simple: the transformation happened because fireworks were popular, people had time and money to spend on them, and novelty was expected and appreciated. At this period in history, and in this place, it was possible for fireworks to be transformed because the necessary materials were available for the first time ever, and at prices and in quantities that made their use in fireworks practical.

As well as answering the question that it set out to address, the project will reveal and explain the unexpected importance of amateurs in the transformation of fireworks, cast light on the role of the military in that transformation and shown that chemists played far less of a part than might have been imagined, given the chemical basis of the changes. It is suggested that the reason for the peripheral role played by chemists is that much of the chemistry involved in fireworks was beyond the capacity of the science of the day, and that chemists were preoccupied with other matters, more important to the advancement of the science. Finally, the changing costs of the relevant materials over the nineteenth century have been analysed in some detail and correlated with the application of those materials in the chemical transformation of fireworks.

Chapter 2: Limitations of Traditional Firework Materials. Fireworks in European History, and Drivers for their Improvement.

2.1 Limitations of Traditional Firework Materials

This project explains why, from the late 1760s and throughout the 19th century, a few Europeans tried to improve fireworks and ultimately succeeded. The key was the introduction of new materials: no matter how strong the drivers for change might have been, it was simply not possible to transform fireworks without those materials. Bruno Latour, as noted above, indicated three interactive aspects of historical 'agencies': the natural, the social and the semiotic. Recent historical treatments of fireworks have emphasized the last two and largely ignored the first, which this project will show was central. Assessing the 'natural' aspect of historical technologies requires specialized knowledge; without which it is impossible to separate the wheat from the chaff. For example, much could be written about the social and semiotic aspects of the quest for the philosophers' stone and the transmutation of base metals into gold, but it would be of little value unless it recognized the 'natural' aspect of the subject: there was no possibility that the quest could succeed. The fact that the seekers of the Stone could not have known that their quest was impossible is important, as are the reasons why they might have expected success; but it is vital to know that when they claimed success (as they sometimes did) they must have been mistaken – or fraudulent. What, then, needs to be said about the 'natural' aspects of pyrotechnics?[29]

Pyrotechnic compositions are mixtures of solid powders that are stable indefinitely until a part of the mixture is heated to a certain temperature, whereupon a chemical reaction propagates through the mixture with the release of heat. As discussed in the next section, the earliest pyrotechnic compositions were mixtures of saltpetre with sulfur and charcoal (a black, carbon-rich solid, of complex chemical composition and physical structure, made by heating wood). Saltpetre contains chemically-combined oxygen, some of which is released when the saltpetre is heated above a certain temperature. The released oxygen can then sustain the combustion of the sulfur and charcoal in much the same way as these materials burn in the oxygen present in the air, generating heat that decomposes more saltpetre, and so the process continues.

Compositions made from saltpetre, charcoal and sulfur are remarkably versatile. A range of effects can be achieved, depending on the proportions of the ingredients, the particle size and how intimately the ingredients are mixed. In the correct proportions (around 75% saltpetre, 15% charcoal and 10% sulfur), finely powdered and mixed extremely well, the mixture becomes 'gunpowder'. In this state it called 'meal powder' by firework makers, 'gunpowder' being reserved for the product obtained by prolonged milling of the dampened mixture, followed by compression into solid cakes that are then broken into granules and separated according to size. This gunpowder was used in firearms and is still used in fireworks as the propellant for shooting objects into the air and for bursting star shells. Similar mixtures, not as thoroughly mixed and with additional coarse charcoal, form the fuel for firework rockets and of the 'drivers' that turn firework wheels. Much the same mixtures, but again with the proportions and particle size adjusted to suit, are used in 'fountains' to project fiery jets of sparks, formed by droplets of molten dross, rich in potassium sulfide and unburned charcoal, which burn in the air. The effect may be enhanced by adding pulverized cast iron or steel filings.

All these effects are produced by hot solids or liquids, glowing orange-yellow to dim red by 'incandescence'. A very hot object is yellowish-white; as it cools it becomes in succession yellow, orange-yellow, orange, red and dull-red, before it no longer emits visible light. As the colours of a heated object progress from dull-red to white, the light becomes brighter. In theory it ought to be possible to make matter so hot that the light becomes bluish-white, then blue, and indeed this does

[29] Werrett, *Fireworks*. For recognition of the role of materials, but with inadequate technical knowledge, see "Green is the Colour."; "Fireworks and Color."

happen in stars (those studied by astronomers, not the 'stars' made by pyrotechnists). On Earth, solids and liquids turn to gas before that happens, and gases behave differently. This is because light is emitted when electrons vibrate, and, conversely, electrons vibrate when they absorb light. Beneath the surface of a solid or liquid, light emitted by one electron is absorbed by another, so that light and vibrating electrons are in equilibrium. Figuring out the implications of this for the colour of the light emitted at the surface of a hot object required the invention of quantum mechanics - one of the most profound consequences of people paying attention to something so familiar that it must have seemed quite beneath the notice of scholars: the colours of hot objects. Quantum mechanics accounts for the rules that relate the temperature of hot objects and the colour of the light that they emit.

These rules do not apply to gases. All the electrons in a gas are bound up in tiny, widely-spaced particles consisting of clusters of electrons around one or more atomic nuclei. Any light emitted by those electrons can easily escape from the gas without being re-absorbed and re-emitted over and over again. As the rules of 'incandescence' do not apply, a gas, in principle at least, might be made to emit light of any colour. This makes coloured flames possible, because a flame is simply a body of gas made very hot by chemical reactions. These reactions are nothing more than the re-arrangement of electrons around various atomic nuclei. Only a limited number of such arrangements can exist, and only some of them are stable. When a more stable arrangement is formed from a less stable one, the newly-formed arrangements of electrons and nuclei move faster. This is called 'release of energy' and is manifested in the material getting hot. What we call 'temperature' is related to the speed of the various groups of nuclei and electrons, collectively known as 'atoms' (if there is just one nucleus in a group) and 'molecules' (if there is more than one).

Some familiar flames, such as those of wood fires or candles, are yellowish-white because they contain very fine particles of solid carbon that are heated to incandescence by the chemical reactions that generate them. The flames of a kitchen gas stove are coloured shades of blue by light emitted by certain molecules produced in the burning of the gas. The emission of coloured light in this way can be exploited to make flames of any colour. Books have been written on the emission of light by atoms and molecules, but only a brief discussion is required here

In a hot gas, atoms and molecules are continually colliding and some of those collisions result in the electrons around one of the colliding objects being kicked into an unstable arrangement, while the other object slows down. Most of the time, the object with its electrons in an unstable arrangement collides with another object, resulting in that object speeding up and the electrons in the first object returning to a stable arrangement. Sometimes, before a collision occurs, the unstable arrangement of electrons spontaneously drops back to the stable condition by emitting light. At the temperatures involved in flames, the difference between the stable and unstable arrangement normally involves a change in the arrangement of just one electron. The colour of the emitted light depends on the two arrangements of the electron around the nucleus or group of nuclei. For example if the electrons in question are a group of 11 arranged around an atomic nucleus containing 11 protons (and normally 12 neutrons), we have a sodium atom (Na). The re-arrangement of electrons that happens when a single electron moves from the most common unstable arrangement of a sodium atom to the stable one results in the emission of orange-yellow light. This explains the long-familiar phenomenon that common salt thrown into a flame makes the flame turn yellow. Common salt is sodium chloride (NaCl); in the flame some of it breaks up into atoms of chlorine (Cl) and sodium, and the sodium atoms emit orange-yellow light as just described.

It might be expected that if one were to mix a sodium compound with gunpowder, it would make the flame turn yellow. This is indeed true; as we shall see, an eighteenth-century chemist worked out how to make a yellow flame by replacing the potassium nitrate in a firework mixture by sodium nitrate ($NaNO_3$). What about the other colours?

In the eighteenth century it was known that several substances make pretty colours when thrown into a fire, or put into a candle flame, or, even better, into an alcohol flame. Some compounds of copper, for example, can transform normally dull blue alcohol flames to a most beautiful green. As Simon

Werrett has shown, pyrotechnists in 18th century Russia enriched their displays with green flames produced when mixtures of copper (Cu) salts, sal ammoniac and alcohol were set alight. Sal ammoniac (ammonium chloride, NH_4Cl) when heated with copper compounds can transform them into copper chloride (CuCl), which is easily vaporized. This process had been known to untold generations of tinsmiths and metal-workers, who used sal ammoniac to clean their copper soldering 'irons' so that they could pick up and hold the molten solder. The green flame was used as an indication that the copper 'iron', having been dipped in sal ammoniac and re-heated, was hot enough to be 'tinned' with solder. . In 1661 the Anglo-Irish natural philosopher Robert Boyle (1627 – 1691) made a candle flame burn green 'somewhat to the wonder of the spectators' by placing under the wick of 'a strong and actually burning candle' some small grains of 'an easy preparation of copper, by the intervention of a little sal-ammoniac' Given that it is so easy to colour a flame green with copper, it is perfectly reasonable to expect that making a green firework flame would be a simple matter of mixing powdered copper, or some copper-containing chemical, with gunpowder or some similar mixture. Over the centuries many firework-makers tried, but the best they could achieve was a green-edged flame, or one having a tint most honestly described as 'greenish'. How could this be?

The reason was not discovered until well into the 20th century. It might be assumed that the green light from flames coloured by copper is produced by copper atoms in much the same way as sodium atoms produce yellow light, but it turned out that the green light did not come from copper atoms at all, but from molecules of a copper-containing gas called copper monohydroxide (CuOH). Unless this gas is formed in the flame, there is no green light. Copper monohydroxide contains hydrogen, so it needs a source of hydrogen for its formation. It is also rather unstable, so if the flame is too hot, it will not be formed. Fires, candle flames, coal–gas flames and alcohol flames all provide favourable environments for the formation of copper monohydroxide, which is why they are easily coloured green by copper. The flames of gunpowder-type mixtures are not in the least favourable to the formation of copper monohydroxide, so it is almost impossible for copper to colour them green.[30]

Much the same can be said about the production of a red flame with strontium (Sr) salts. These readily colour common flames red, and, just as for copper, the colour is not produced by the metal atom, but by a gaseous monohydroxide. Strontium monohydroxide (SrOH) is more stable than copper monohydroxide, and it is possible to get red flames from gunpowder-type mixtures containing strontium salts, but these still leave much to be desired.

In the late 18th century the range of coloured firework flames was quite small. Yellow could be made with sodium nitrate, white with potassium nitrate and sulfur, usually with the addition of antimony sulfide (Sb_2S_3) or one of the arsenic sulfides (As_2S_3 or As_4S_4) to make the mixture easier to ignite. Pale greenish-blues could be made with compositions containing zinc (Zn). Mixtures of saltpetre with resins (complex natural products containing carbon, hydrogen and oxygen, $C_xH_yO_z$) could produce pale pink and lilac shades, greenish tints could be made by adding crystallized verdigris (hydrated copper acetate, $Cu(CH_3COO)_2.H_2O$) to white-flame mixtures. That, along with coloured alcohol flames, was about as much as could be done with the materials at hand. A full range of intense, brilliant colours would not be possible until new materials were discovered that could make flames providing chemical environments favourable to the production of the various gases that could emit the desired colours. Of course at the time it was not known that this was what was being done. It was found by experiment that mixtures of hitherto unused materials could burn with brilliantly coloured flames.

In any field of technology, the introduction of new materials does not happen automatically. It happens in response to particular motivations in particular circumstances. What circumstances facilitated, and what hindered, the introduction of new materials into European fireworks between the

[30] E. M. Bulewich and T.M. Sugden, "Determination of the Dissociation Constants and Heats of Formation of Molecules by Flame Photometry. Part 3. - Stability of Gaseous Cuprous Hydroxide," *Transactions of the Faraday Society* 52 (1956), pp. 1441-1448.

late 1700s and the late 1800s? To answer that question, it is useful to begin at the beginning: the origin of fireworks in ancient China.

2.2. Fireworks in European History

Rochelle Forrester has argued that materials are introduced into technology in a sequence ultimately determined by their chemical properties. Before a material can be used, people must be aware of its existence and of any properties that could make it useful. This observation is not as trivial as it might appear. Forrester has shown that recognition of new materials and the acquisition of knowledge of their relevant properties depends on what materials and knowledge are already available at the time and that fundamentally limits the range of materials available to any society.[31]

A natural sequence of utilization of materials is discernible in the history of pyrotechnics. The earliest known pyrotechnic compositions were made, probably accidentally, in ancient China from naturally-occurring materials (saltpetre, sulfur, realgar (As_4S_4), charcoal), that were already being used for other purposes, principally in traditional medicine and in alchemical research; from time to time people must have noticed that certain mixtures of them burned much more vigorously than ordinary fires. Investigation of those mixtures led to their use in ways that can only be guessed. They might have added drama to the performance of a magician, or perhaps they were taken up by military men as incendiary weapons. Later, when the mixtures had been developed for use in entertainments and celebrations, their performance was enhanced by the introduction of materials that do not occur naturally but were already being made for other applications by the transformation of natural products. That was as about far as introduction of new pyrotechnic materials was taken in China.[32]

Early Chinese pyrotechnics have attracted the attention of authors because of the Chinese invention of gunpowder and rockets; their invention of fireworks has mostly been seen as a quaint aside to the gunpowder story or as a precursor to the invention of rockets. Simon Werrett has written of changing European perceptions of Chinese fireworks from the 16th century. He implies that Chinese fireworks were always superior to European ones, and that opinions to the contrary during the 19th century showed ‘an increasingly condescending view of Chinese art and culture’. As we shall see, there were real differences between Chinese and European fireworks over the centuries, arising mostly from the use of different materials. By the end of the eighteenth century, the few materials that had given the Chinese some unique firework effects had been absorbed into European practice. Between 1810 and 1821 the French pyrotechnist Ruggieri had the opportunity to examine some Chinese fireworks, and concluded: ‘These fireworks were no different from what the Chinese have been making for three or four centuries; and that convinced me that we in Europe are indeed superior to the Chinese.’ A more accurate assessment might be that by the early 19th century Europeans had no more to learn from the Chinese about the formulation of firework mixtures.[33]

Traditional Chinese firework mixtures were based on saltpetre, which occurred naturally in parts of China as white encrustations on the ground, easily collected by sweeping. Early Chinese accounts quoted by Joseph Needham et al. mention the use of saltpetre as a metallurgical flux and its property,

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[31]Forrester, *How Change Happens: A Theory of Philosophy of History, Social Change and Cultural Evolution*.

[32] Brock, *A History of Fireworks*; Tenney L. Davis, *The Chemistry of Powder and Explosives* (New York: John Wiley and Sons, 1941/1943; repr., Hollywood: Angriff Press, 1970); "The Early use of Potassium Chlorate in Pyrotechny: Dr Moritz Meyer's Colored Flame Compositions." Sturman, "Coloured Fire."

[33] Werrett, "The Finest Fireworks in the World: Chinese Pyrotechnics in Early Modern Europe." Claude-Fortuné Ruggieri, *Élémens de pyrotechnie, divisés en cinq parties; la première, contenant le traité des matières; la 2e., les feux de terre, d'air et d'eau; la 3e., les feux d'aérostation; la 4e., les feux de théâtre; et la 5e, les feux de guerre. Suivis d'un vocabulaire et de la description des principaux feux d'artifice qui ont été tirés à Paris depuis 30 ans, etc. ...* 3 ed. (Paris: Bachelier, 1821), pp. xxxiv. This passage is quoted by Werrett, "The Finest Fireworks in the World: Chinese Pyrotechnics in Early Modern Europe", p. 31.

when mixed with vinegar (dilute acetic acid, CH_3COOH), of dissolving metals and minerals. Chinese medical practitioners and alchemists left descriptions of the purification of saltpetre by crystallization from water and gave accounts of its disconcerting propensity to cause conflagrations when heated with combustible substances. For these developments to have happened there had to be people with the time and motivation to take notice of this peculiar natural salt, experiment with it, and record their results. These conditions were met in ancient China, where Taoist monks could devote much time to medicine and alchemy – arts that focussed, in different but related ways, with enhancing and prolonging human life by the use of materials, and which were supported and encouraged by the ruling elites.[34]

Needham and his colleagues have pointed out early Chinese references to the deflagration of mixtures containing saltpetre warning against making any such mixtures – not just because of the danger, but because conflagrations in an alchemist's workshop were scandalous, bringing the practitioner, the art of alchemy and even Taoism itself into disrepute. Based on evidence from Needham et al. and other scholars, Frank Winter et al. argued that the Chinese discovery of pyrotechnic mixtures and their subsequent development of gunpowder and rockets were accidental by-products of alchemical and medicinal experimentation, rather than the result of deliberate research directed to the production of explosives or missiles. This is hardly surprising; without the accidental discovery of pyrotechnic combustion there would have been nothing to suggest that such things were possible. Once the effects of saltpetre on combustion had been discovered, the way was open to practical applications. The Chinese were accustomed to using fire as a weapon of war, so it is plausible that it would have occurred to someone that the prohibited mixtures of the alchemists could be put to military use as incendiaries; attempts to optimize them for that purpose could have led to the discovery of mixtures that could burn sufficiently vigorously to project a jet of flame when ignited in a container. If the outlet were deliberately made smaller, to increase the intensity of the jet, the container would move in the opposite direction. If the outlet were smaller still, the container would burst with a loud noise. The Chinese developed these effects for military purposes and for entertainment.[35]

A list of materials mentioned in early Chinese writings on pyrotechnics would not be particularly useful for this project, because the military compositions included a bewildering array of substances apparently intended to make the smoke unpleasant or poisonous, and some ingredients (earthworm powder, snakeskin) seem to have been included for reasons of sympathetic magic. There is no oxidizing agent other than saltpetre; fuels included the naturally occurring minerals sulfur (long known for its yellow colour and its ability to burn with a dull blue flame, accompanied by a choking stench); realgar, a red sulfide of arsenic used in traditional Chinese medicine since before 100 BC; and the related golden-yellow mineral orpiment (As_2S_3), long-used in medicine and as a pigment.

[34]For early Chinese knowledge of saltpetre, see Joseph Needham et al., *Science and Civilisation in China*, vol. 5, Chemistry and Chemical Technology, Part 4, Spagyrical Discovery and Invention: Apparatus, Theories and Gifts (Cambridge: Cambridge University Press, 1980). For its use in fireworks and military devices, see Joseph Needham et al., *Science and Civilization in China*, vol. 5 part 7: *Military Technology; The Gunpowder Epic* (Cambridge: Cambridge University Press, 1986). For a succinct summary, see Joseph Needham, *The Guns of Kaifêng-fu: China's Development of Man's First Chemical Explosive* The Creighton Trust Lecture (London: The University of London, 1979). See also 'The Epic of Gunpowder and Firearms, Developing from Alchemy.' *Science in Traditional China: A Comparative Perspective*, Chi'en Mu Lecture Series (Cambridge, MA: Harvard University Press, 1981), Chapter 2.

[35]For accidents bringing discredit, see Needham et al., *Science and Civilization in China*, 5 part 7: *Military Technology; The Gunpowder Epic*, p.112. For Needham's assessment that civilian fireworks did not appear until the late 12th century, see ibid., pp. 131-134, also Needham, *Science in Traditional China: A Comparative Perspective*, p. 32. For the accidental discovery of pyrotechnic mixtures, see Frank H. Winter, Michael J. Neufeld, and Kerrie Dougherty, "Was the Rocket Invented or Accidentally Discovered? Some New Observations on its Origins," *Acta Astronautica* 77 (2012), pp. 131-137.

Charcoal was commonly used, both as an ingredient in its own right and as an essential component of gunpowder. All these materials remained in use in fireworks well into the 20th century.[36]

Fireworks and military devices based on saltpetre were known in India from an early date, and similar knowledge existed later in the Islamic world. European knowledge of the arts of firework-making and gunnery was probably acquired from the Arabs, but details remain obscure. Around the middle of the 13th century the English monk Roger Bacon mentioned the use of saltpetre in what we would now call firecrackers. He referred to

> 'that toy of children made in many parts of the world, namely an instrument as large as the human thumb. From the force of the salt called saltpetre, so horrible a sound is produced at the bursting of so small a thing, namely a small piece of parchment, that we perceive it exceeds the roar of sharp thunder, and the flash exceeds the greatest brilliance of the lightning accompanying the thunder'. [37]

At the other end of the spectrum of pyrotechnic devices, guns were being used in European wars as early as the 14th century. In 1532 the Emperor Charles V ordered the formation in his army of a body of 'fireworkers', distinct from the artillery, perhaps establishing the long tradition in Europe of the army providing fireworks for occasions of officially-ordered rejoicing.[38]

The earliest known book to deal exclusively with fireworks as a form of entertainment was published in Nurnberg in 1560. By the 18th century fireworks were a long-established part of European life. They ranged from firecrackers similar to those mentioned by Bacon to large rockets and shells used for official State celebrations. In between, there were smaller devices used as part of theatrical performances and others used (and sometimes made) by private citizens for family celebrations and entertainments. Amateur firework-making was sufficiently common to justify the publication of instructional books on the subject. Firework compositions were still based on saltpetre, and the usual fuels were mixtures of powdered charcoal and sulfur – the same fuels used in gunpowder. Over the years several new combustibles had been introduced to add variety to fireworks. Most notable were powdered cast iron (an alloy of iron (Fe) and carbon (C)) and lampblack (carbon-rich soot collected from the flame of burning oil), both used to make beautiful flower-like sparks. These were first introduced in China, and knowledge of them was brought to Europe in the 18th century as a consequence of European missionary enterprises in the Far East.[39]

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[36] For realgar in traditional Chinese medicine, see Jinzhu Wu et al., "The Medicinal Use of Realgar (As_4S_4) and its Recent Development as an Anticancer Agent," *Journal of Ethnopharmacology* 135, no. 3 (2011), pp. 595-602.

[37] Roger Bacon, *The Opus Majus of Roger Bacon*, trans. Robert Belle Burke, 2 vols., vol. 2 (New York: Russell & Russell Inc, 1962), pp. 629-630.

[38] Brock, *A History of Fireworks*, p. 31.

[39] Philip, *A Bibliography of Firework Books: Works on recreative fireworks from the sixteenth to the twentieth century*. For pyrotechnics in the theatre, see Philip Butterworth, *Theatre of Fire: Special Effects in Early English and Scottish Theatre*, ed. Glynne Wickham (London: The Society for Theatre Research, 1998); John A. Rice, "Operatic Pyrotechnics in the Eighteenth Century," in *Theatrical Heritage: Challenges and Opportunities*, ed. Bruno Forment and Christel Stalpaert (Leuven: Leuven Univerity Press, 2015), pp. 23-40. For 18th century amateur pyrotechny, see, for example, Grignon et Lalaing, *La pyrothecnie pratique: ou, Dialogues entre un amateur des feux d'artifice, pour le spectacle, & un jeune homme curieux de s'en instruire* (Paris: L. Cellot, & Jombert fils jeune, 1780). For Chinese spark-producing materials, see Pierre D'Incarville, "Manière de faire les fleures dans les feux d'artifice chinois," *Memoires De Mathematique et de Physique, Présentés À l'Académie Royale Des Sciences, Par Divers Savans, & Lus Dans Ses Assemblées.* 4 (1763), pp. 66-94; James Cutbush, "Remarks on the composition and properties of the Chinese fire, and the so-called Brilliant fires," *the American Journal of Science and Arts* 7 (1824), pp. 118-140.

2.2. Drivers for the Improvement of Fireworks in Europe

Michael Lynn has drawn attention to a remarkable change in the place of fireworks in European life during the 18th century: they became increasingly commercialized. Consequently, many more people had access to them and the meanings that people attributed to fireworks changed. A firework display was previously likely to have been seen as a gift from an all-powerful monarch to a subservient population; now, people could buy their own fireworks, and organize their own displays. The older meanings of fireworks as symbols of monarchical power remained, but new meanings were added as fireworks were 'used in a wider variety of social and political arenas'.[40]

Lynn implied a chain of causation from commercialization to changes in meaning to broader use, but is seems more likely that these were interactive and mutually reinforcing processes, fed by changes in society at large – especially by those changes referred to as 'The Enlightenment'. Be that as it may, the changes in the social and semiotic aspects of fireworks happened at a time when it became possible to change fireworks themselves by the introduction of new materials. The mid-century introduction of novel spark-producing compositions from China was soon followed by an attempt to bring the rapidly-developing science of chemistry into the service of the commercially-driven firework-maker. These developments will be discussed in the next chapter. For now, it is sufficient to note that the possibility of introducing new materials was itself a consequence of changes in European social conditions and attitudes.[41]

The 18th century introduction of novel sparkling firework compositions from China was contingent upon Europeans believing that they could learn from the Chinese – a belief that had arisen in at least two ways: International commerce had introduced Europeans to Chinese products that unequivocally demonstrated the superiority of some areas of Chinese technology, such as the production of porcelain. Europeans were also aware of favourable reports of Chinese technology by European missionaries sent to China – sent, paradoxically, in the belief that the Chinese needed instruction (albeit in theology rather than technology). The recognition of Chinese technological superiority in certain fields must have at least subliminally challenged European assumptions of their own superiority, assumptions founded primarily in the belief that Europeans enjoyed divine favour as a consequence of holding correct theological views. Perhaps that challenge was one more influence feeding into the intellectual and social changes in 18th century Europe. Europeans assumed that their religious views were superior to those of the Chinese, but they could not deny that Chinese ceramics, or their fireworks, for that matter, were superior to their own, and this might well have puzzled them.[42]

Apart from the meticulous hand skills required to make traditional Chinese firecrackers, Chinese achievements in pyrotechny were soon absorbed into European practice. Further improvements would require the introduction of materials that had not previously been used in fireworks in China or anywhere else. The possibility that completely new materials might be introduced into European fireworks arose because of new developments in what was beginning to be called chemistry - the study of materials and their transformation, not just for practical purposes but as an intellectual endeavour in its own right. The flourishing of chemistry was another aspect of European life arising from the changes denoted by the 'Enlightenment' and the 'Scientific Revolution'. Developments in chemistry fed back into the changing society in a positive way; chemistry was seen as beneficial, as a

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[40] Michael R. Lynn, "Sparks for Sale:The Culture and Commerce of Fireworks in Early Modern France," *Eighteenth-Century Life* 30, no. 2 (2006), pp. 74-97.

[41] Dorinda Outram, *The Enlightenment*, 3rd ed. (Cambridge: The Cambridge University Press, 2013), especially Chapter 8.

[42] D'Incarville, "Manière de faire les fleures dans les feux d'artifice chinois." For porcelain, see Janet Gleeson, *The Arcanum: Extraordinary True Story of the Invention of European Porcelain* (New York: Bantam Books, 1999).

potential provider of new and better medicines and for its perceived scope for improving chemically-based industries such as bleaching and dyeing. Its contributions to material culture and to the understanding of Nature became widely valued, in contrast to the satirical approach taken by Irish clergyman and writer Jonathan Swift (1667-1745) in the first decade of the century. By the end of the 18th century chemistry was not just a pursuit of savants. It had become a fashionable hobby for gentlemen – a development that helped establish commercial suppliers of laboratory equipment and, more importantly from the perspective of this project, of chemicals and mineral specimens.[43]

The emergence of chemistry as a fashionable hobby was but one manifestation of the fact that from the middle of the eighteenth century developments arising from changes in the economy and forms of production, international trade and imperial expansion left more Europeans than ever before with time and money to spend on entertainment and leisure activities of all kinds, including fireworks. As noted by Lynn, this was associated with the commercialization of fireworks and the emergence of people who earned a living from them. Competition between firework makers motivated them to seek ways of differentiating themselves and their products. One way to do this was to seek new firework effects, and, as will be seen in the next chapter, that is exactly what some of them did. The introduction of a new effect would have been particularly desirable at a time when there were expectations of novelty in many aspects of life, arising from increased awareness of exotic cultures and of products brought to Europe through imperial expansion and international trade. Furthermore, professional pyrotechnists would have been well aware that if one firework show looked much like another, patrons and spectators would soon loose interest. Enthusiasm for fireworks would be replaced by condemnation, with attention drawn to negative aspects such as cost, damage to property, injuries and bad behaviour of people in crowds. Such criticism had long been levelled at State-sponsored firework displays and an undercurrent of disapproval of fireworks remains to this day. Commercial providers of fireworks have to struggle against those who would forbid fireworks if they could and, failing that, strongly discourage their use. One way to resist such people was to maintain public enthusiasm for fireworks by introducing novelty. Furthermore, in the late 18th century and throughout the 19th, production of a new firework effect could have been expected to bring status and prestige to the maker, as well as giving a competitive advantage to both maker and exhibitor. Commercial considerations were favourable to the introduction of new effects.

Commercialism was not the only driver for new firework effects. Some firework-makers presented themselves as creative artists; presumably for some this was mere self-promotion to further their commercial endeavours, but pyrotechnists who genuinely aspired to artistry might well have been frustrated by the limitations imposed by the materials at their disposal. The relative lack of colour in fireworks, compared to other artistic media such as painting and stained glass, was an obvious shortcoming. This would be disputed by Simon Werrett, who has claimed that the importance of coloured fireworks has been exaggerated by modern authors. Direct evidence that pyrotechnists working before the development of modern coloured fires were indeed aware of the limitations of their coloured fireworks is to be found in a remark of the 18th century pyrotechnist John Maskall, who in 1786 wrote:

> There are yet wanting, Yellow Specchis for fixt Illuminations, Red and Green Specchis; Specchis of a full Blue, for those we have burn only of a light Sky Colour, which appears to me rather as the effect of the smoke proceeding from them, than any real tint of the flame.

[43] Swift depicted savants pursuing absurd projects, including the extraction of sunbeams from cucumbers, the reversion of human excrement into food, and the calcining of ice into gunpowder. See Jonathan Swift, *Gulliver's Travels*, 2 vols., vol. 2 (London: Jones & Company, 1826), Chapter 5. For an example of a commercial supplier of laboratory chemicals see Georges Kersaint, "Sur la fabrique de produits chimiques établie par Fourcroy et Vauquelin 23, rue de Colombier, à Paris," *Comptes rendus hebdomadaires des séances de l'Académie des Sciences* (1958), pp. 461-464; "L'usine de Vauquelin et Fourcroy (pour l'histoire de l'industrie chimique)," *Revue d'histoire de la pharmacie* 47, no. 160 (1959), pp. 25-30.

> Probably, Experiments may discover the other Colours, if it should be thought proper to try for them. [44]

The evidence presented by Werrett is perfectly consistent with the opinions of Chertier, Brock and others that the early pyrotechnists did indeed seek colours, and in fact achieved them to the extent permitted by the materials at their disposal. The results still left much to be desired, and efforts to improve them led to the introduction of new materials. This will be discussed in more detail in the next chapter.[45]

A completely different motivation to introduce new effects came from the use of pyrotechnic stage effects in the theatre. Werrett has correctly indicated that these effects included noise, smoke and smell as well as flames. None the less, flame effects were important and by the late 18th century their limitations were evident to creative stage designers and to competitive theatrical entrepreneurs. Ruggieri wrote of his father's introduction in 1787 of Bengal Fire as a stage effect; some 13 years later French art theoretician Henri de Valenciennes (1750 -1819) commented that the bluish-white colour of Bengal Fire made the conflagration depicted on the stage seem appropriately far away, and that even better effects might be achieved if the flames of Bengal Fire could be contrasted 'with those that are more red.' As discussed elsewhere, the desire of theatrical managers for a red fire effect was the major driver in the development of the new generation of coloured pyrotechnic flames.[46]

Yet another motivation to introduce new pyrotechnic effects was the use of fireworks as military signals. A range of distinct colours would greatly increase the information that could be transmitted; the role of the military in the transformation of fireworks is discussed in Chapter 7. Finally, awareness of the activities and statements of chemists made it seem possible that new materials might be capable of producing new firework effects. Without a belief in the possibility of change there would have been no point in pursuing it, no matter how desirable such change might have been.

The circumstances outlined in the preceding paragraphs made the period from the mid 18th century particularly favourable to the introduction of new materials into fireworks, but there were also other circumstances that worked against such a development. One of these has already been mentioned: disapproval of fireworks on the grounds of extravagance, wastefulness and danger. This could to some extent be countered by improving fireworks and thus can be included among the drivers for doing so. Here we see the same circumstance acting both as a driver for change and as an inhibitor. In its most extreme form, disapproval of fireworks can lead to official restrictions on their use and even to their prohibition, and this would reasonably be expected to inhibit research. The making and use of fireworks by private individuals was officially prohibited in Britain until 1860, but this was so widely disregarded that the original work on the new coloured fires happened in England in the first decade of the19th century. It is impossible to say whether the official prohibition had any effect on the development of fireworks. The impression given by the rare mentions of new fireworks in the contemporary literature is that they were seen in a positive light; there was nothing to indicate that experimenting with fireworks was illegal or deserving of condemnation.

Another circumstance that might be expected to have inhibited change is secrecy, as it made knowledge acquired by one person unavailable to others as a starting point for further development.

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[44] John Maskall, "Artificial Fireworks Vol. 2 " The Getty Research Institute, https://archive.org/details/artificialfirewo02mask p. 24. Accessed 8 March 2017.

[45] Werrett, "Fireworks and Color."

[46] Butterworth, *Theatre of Fire: Special Effects in Early English and Scottish Theatre*; Werrett, "Fireworks and Color." For Bengal fire, see Ruggieri, *Elémens de pyrotechnie, divisés en cinq parties; avec un vocabulaire des termes compris dans cet ouvrage*, pp 128-130. P. H. Valenciennes, *Élémens de perspective pratique, à l'usage des artistes, suivis de réflexions et conseils à un élève sur la peinture, et particulièrement sur le genre de paysage*, 2me. ed. (Paris: Aimé Payen, Libraire 1820), pp. 264-265; Sturman, "Coloured Fire."; "The Early Use of Potassium Chlorate in Pyrotechny: Part I. John Forster and the First Chlorate-based Colored Fire."

The patent system, which trades full disclosure of new technical information in exchange for a monopoly on its use for a specified number of years, is an attempt to overcome this problem. Secrecy might not always be an effective inhibitor of technological change. If a practitioner becomes aware of a new development, he or she can attempt to re-create it. If successful, the practitioner can use the result without restriction – the opposite to the situation when a patent exists. There was much debate in the 19th century as to whether patents enhanced, or inhibited, the progress of technology.

A major barrier to the introduction of new materials into fireworks was that some materials known to be effective were too expensive to be practical. This aspect of the transformation of fireworks by the introduction of new materials is the subject of Chapter 8. The next three chapters show how new materials were discovered and introduced into firework-making. Until the 1860s the new materials were associated with the production of colours; later, other materials were introduced that further transformed fireworks by permitting the production of bright white sparks and by introducing new sounds into the art.

Chapter 3: Materials: Part 1. Pyrotechnic Materials in Europe to the end of the 18th Century.

For many centuries after the first appearance of fireworks in Europe there were few additions to the range of materials already in use by the Chinese. For example, Table 2.1 lists firework materials mentioned by the French printer, engraver and pyrotechnist Jean Appier (also known as Hanzelet Lorraine, 1596-1647) in 1620:[47]

Name	Modern English Name	Main Use in Fireworks	General and Industrial Uses
Ambre blanc	White amber powder	Fuel	Waste product
Antimony	Antimony(III) sulfide	Fuel	Antimony ore
Argent vif	Mercury	Additive in fireball composition.	Mirror-making, medicine
Camphre	Camphor	Fuel	Medicine, insect repellent.
Charbon doux	Charcoal	Fuel	Fuel, metallurgy
Colophone	Pine resin	Fuel	Varnish, soldering flux
Eau de vie	Alcohol	Binder activator	Beverages, medicine, solvent.
Gomme adragant	Gum tragacanth	Binder	Medicine
Gomme arabique	Gum Arabic	Binder	Adhesive
Huille de lin	Linseed oil	Binder	Putty, wood preservatives
Huille petrolle	Petroleum oil	Fuel, mixing aid	Medicine
Limaille d'acier	Steel filings	Spark producer	Waste product
Limaille de fer	Iron filings	Spark producer	Waste product
Mastix	Mastic	Fuel, binder	Confectionary
Oliban	Frankincense	Fuel	Perfume, incense
Orpiment	Arsenic(III) sulfide	Fuel	Pigment
Poix refiné	Pitch, refined	Fuel	Waterproofing
Poudre	Gunpowder	Propellant	Military, sporting guns, blasting
Salpetre	Potassium nitrate	Oxidizer	Gunpowder, preserving meat
Soufre	Sulfur	Fuel	Gunpowder, medicine
Sublimé	Mercury(II) chloride	Additive in star composition.	Medicine
Vere (cristal) grossierement pillé	Glass (crystal), coarsely powdered	Additive in star and fireball compositions.	Waste product

Table 3.1. Firework ingredients listed by Jean Appier in 1620.

[47] For Appier, see Partington, *A History of Greek Fire and Gunpowder* , pp. 176-177. Jean Appier and Francois Thybourel, *Recveil de Plusiers Machines Militaires, et feux Artificials, pour la Guerre & Récréation* (Pont-à-Mousson: Charles Marchant, 1620). Livre V.

Nearly all of these ingredients either definitely were, or certainly could have been, known to the Chinese, centuries before, and most of them are recorded as having been used in Chinese fireworks. The inclusion of such apparently useless ingredients as mercury and mercury(II) chloride calls to mind certain Chinese military compositions, where they may have been included to make the smoke poisonous. Appier's mention of 'antimony' (presumably antimony(III) sulfide, Sb_2S_3, the mineral stibnite) deserves further comment. This material seems not to have been used by Chinese pyrotechnists, and indeed Needham found no records of any early Chinese technologists taking notice of antimony or of its ore for any purpose, despite the occurrence of large deposits of stibnite in China. The availability of a material is not sufficient for it to be brought into general use; its relevant properties must first come to the attention of an interested investigator, who must then choose to make the results known.[48]

An even more striking example of the neglect of a useful pyrotechnic material is provided by the metal zinc. As shown by Needham, zinc was known and used by the Chinese long before it was known in Europe. Despite this, no evidence has been mentioned of the Chinese having used zinc in fireworks. This is much more remarkable than their neglect of antimony; there was no interest in antimony in China for any application, and in any case the main role of antimony in fireworks (in the production of white flames) was already being played perfectly well by the two arsenic sulfides realgar and orpiment. In contrast, zinc was being manufactured on a large scale in China, and the characteristic blue-green flame produced when it burns must have been familiar to those involved with its smelting and casting. It is puzzling that zinc seems not to have been used at all by Chinese firework-makers, but this illustrates the important point that while a material must be known, and its properties recognized, before it can be used, a known material with relevant properties can still be neglected. Here we have an instance where a material was well known and widely used in China, but for unknown reasons its property of burning with a coloured flame was not used in Chinese fireworks. Its use in Europe will be discussed later.[49]

Appier mentioned a rather large collection of materials, but other 17th century European firework-makers found that a much smaller range met their needs. The English gunner and firework-maker John Bate wrote in 1635 that the principal ingredients were 'Saltpetre, Rochpeter [i.e. re-crystallized saltpetre], Sulpher, Charcoale, good Gunpowder, Filings of Steele, oyle of Peter [i.e. petroleum] and spirit of Wine.'[50]

Appier listed iron filings and steel filings separately. These do indeed give different effects, steel filings producing brighter and more 'branching' sparks that iron filings. This is a consequence of the greater carbon content of steel compared to (wrought) iron. Cast iron contains even more carbon than does steel, and its spark-producing qualities are correspondingly better. This was known to the Chinese, but possibly not as early as one might imagine, given that cast iron had been used in China from an early date. Cast iron is brittle and can readily be crushed into the sand-like form in which it is used in fireworks.[51]

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[48] Joseph Needham, *Science and Civilization in China*, vol. 5, Chemistry and Chemical Technology, Part 2, Spagyrical Discovery and Invention: Magisteries of Gold and Immortality (Cambridge: Cambridge University Press, 1974), pp. 190-191.

[49] Wenli Zhou, "Distilling Zinc in China: The Technology of Large-Scale Zinc Production in Chongqing During the Ming and Qing Dynasties (AD 1368-1911)" (University College London, 2012).

[50] John Bate, *The Second Booke Teaching most plainly, and withall most exactly, the composing of all manner of Fire-works for Tryumph and Recreation* (London: Ralph Mab, 1635; repr., Seattle: Shorey Book Store, 1972), p. 94.

[51] For the antiquity of cast iron in China, see Joseph Needham, *Science and Civilisation in China*, vol. 5, Chemistry and Chemical Technology ; Pt. 11, Ferrous Metallurgy (Cambridge: Cambridge University Press, 2008), pp 105 ff. For its brittleness, see ibid., p. 161.

Mixed with gunpowder, or with the three ingredients of gunpowder in appropriate proportions, and compressed into a strong tube having a restricted outlet, pulverized cast iron produces the effect long known as 'Chinese Fire': a huge jet of sparkling orange-yellow fire surmounted by hundreds of large, flower-like sparks that branch and divide, sometimes several times. 'Chinese Fire' so impressed the French Jesuit missionary Pierre Nicolas le Chéron d'Incarville, (1706-1757), who lived in China from 1740 to his death in 1757, that he wrote a detailed manuscript about Chinese fireworks. This was published in France in 1763; an illustrated English summary was published in 1764.[52]

D'Incarville also described another type of Chinese firework fountain in which the charcoal and cast iron had been replaced by lampblack, producing a unique spark effect subsequently known as 'Spur Fire'. D'Incarville's introduction of 'Chinese Fire' and 'Spur Fire' could well be the reason that Ruggieri formed his initial opinion, published in 1802: 'The Chinese today are perhaps superior in this art to the French and to the Italians, by the preciseness of their work and even more by their possession of some materials that we lack.' Both effects are extremely spectacular and would have made a great impression on anyone seeing them for the first time.[53]

D'Incarville wrote that the Chinese 'do not expect to have truly distinct colours' in fireworks. He noted that their compositions included 'some ingredients that give some shades of colours, such as orpiment gives a yellow colour, white lead and camphor a white fire, some people use indigo for blue, but I doubt this colour…they say that the mineral cinnabar gives a red fire..'[54]

The colour allegedly imparted to the flame by each of the materials mentioned is the same as the colour of the material itself. Orpiment is yellow, white lead and camphor are white, indigo is blue and cinnabar is red. Camphor burns with a whitish flame, and lead compounds can, under favourable circumstances, make white pyrotechnic flames. None of the other materials could produce coloured flames. There is no expectation in modern science of any correlation between the colour of a chemical and the colour that it might impart to a flame. The Chinese recommendation of these materials as colour producers may be a relic of their use to make coloured smoke puffs, in which the powdered material was dispersed into the air by exploding gunpowder, or simply an instance of the optimistic application of sympathetic magic. It is even possible that the original intent was to impart colour to the powdered compositions themselves, rather than to the flames. D'Incarville downplays the role of colour in Chinese fireworks. He seems to be reporting hearsay, not his own experience, in mentioning indigo and cinnabar. He says nothing about green.

It is appropriate to mention here a Chinese firework effect first reported to Europeans in the 17th century. The Portuguese Jesuit missionary Gabriel de Magalhães (*Magaillans*) (1609-1677), who was in China from 1640, wrote in 1668 of a firework display that he had witnessed in 'Su chuen' (Sichuan?) Province in 1644, when he was held prisoner by the rebel Zhang Xianzhong (Chang Hsien-chung (1606-1647)). He was particularly surprised to see a grape vine represented in coloured fire. As the device burned, 'all the time one could see the red of the clusters of grapes, the green of the leaves, the chestnut-brown colour of the vine, so well represented that one would have sworn that all these things were natural and not artificial.[55]

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[52] D'Incarville, "Manière de faire les fleures dans les feux d'artifice chinois." The English summary is Anonymous,"Manner of making Flowers in the Chinese Fire-works, illustrated with an elegantly engraved Copper-Plate. – From the fourth Volume [just published] of the Memoires presented to the Academy of Sciences", *Universal Magazine* 34 (January 1764), pp. 21-23.

[53] Ruggieri, *Elémens de pyrotechnie, divisés en cinq parties; avec un vocabulaire des termes compris dans cet ouvrage*, p. xix. This passage is quoted by Werrett, "The Finest Fireworks in the World: Chinese Pyrotechnics in Early Modern Europe.", p. 29.

[54] D'Incarville, "Manière de faire les fleures dans les feux d'artifice chinois." p. 78.

[55] Gabriel Magaillans, *Nouvelle Relation de la Chine, contenant la description des patricularitez les plus considerables de ce grand Empire* (Paris: Louis Lucas, 1689), pp. 128-129 This same quote has appeared in

D'Incarville revealed the secret of Chinese firework 'grapes': 'The material of these grapes is nothing but sulphur... with which one makes dough with flour-paste ... So that the grape should have a more violet colour, the Chinese prefer the flesh of the jujube to flour-paste…' He then described how the 'dough' is coated onto figures made of doubled iron wire: 'In this way one can make any figure that may seem appropriate…, which will last in fire as long as one might wish, in proportion to the quantity of material that has been used.[56]

He described how the dried design was provided with a fuse all along its length, and then covered with paper so that the whole would ignite at once. The result would have been an outline of the depicted object in the dull blue flame of sulfur burning in air, the flame perhaps being given a violet tinge by potassium salts present in the jujube flesh. A description of the effect was recorded by du Halde; his account of a firework display for the Chinese Emperor, witnessed by a Jesuit missionary, mentioned '…sentences wrote in large Characters of the Colour of burning Sulphur….from time to time there appeared in some Places violet, and bluish Flames in the Form of Bunches of Grapes on a Vine-Arbour, which…yielded a very agreeable Sight.'[57]

Gabriel de Magalhães had described the '*grappes*' that he had seen in 1644 as '*rouge*', whereas subsequent observers described them as 'violet' or 'bluish'. Real, so-called 'red' grapes are commonly of a dark bluish-violet colour rather than red, so it is plausible that de Magalhães was so impressed by the realistic rendering of 'red' grapes that when writing 24 years later he reported the colour of the grapes simply as 'red' rather than the bluish-violet that he actually saw. The 'chestnut' colour of the vine could easily have been rendered by burning ropes that had been soaked in oil, but the green of the leaves remains to be explained. All the materials needed to make a green alcohol flame were available in China at that time, so there is no reason to assume that such a flame could not have been used in the grapevine display. Whether or not the green alcohol flame was known to the Chinese remains to be established, but Simon Werrett has presented evidence that the effect was independently discovered by Russian pyrotechnists in the 18th century; Claude-Fortuné Ruggieri re-discovered it early in the 19th century, having heard a traveller's tale of the green 'Russian' fire.

A list of the ingredients in the Chinese firework compositions presented by d'Incarville is shown in Table 3.2:

English several times, for example *A New History of China, Containing a Description of the Most Considerable Particulars of that Vast Empire* (London: Thomas Newborough, 1688), p.104-105; Partington, *A History of Greek Fire and Gunpowder*, p. 285.

[56] D'Incarville, "Manière de faire les fleures dans les feux d'artifice chinois", p. 73. The jujube, or Chinese date, is the edible fruit of a small deciduous tree (*Ziziphus jujube*), widely cultivated in Asia.

[57] P. du Halde, *The General History of China, containing a Geographical, Historical, Chronological Political and Physical Description of the Empire of China, Chinese-Tartary, Corea and Thibet*, vol. 2 (London: John Watts, 1736), pp. 168-169.

Name	Modern English Name	Main Use in Fireworks	General and Industrial Uses
Arsenic	Arsenic	Fuel.	Silvering brass.
Camphre	Camphor	Fuel, white flame producer.	Medicine, insect repellent.
Céruse	White lead , $(PbCO_3)_2 \cdot Pb(OH)_2$	White colour agent.	White pigment.
Chair de jujube	Flesh of the jujube fruit	Making an adhesive paste that also imparts a violet tint to sulfur flames.	Food.
Charbon de saule	Willow charcoal	Fuel.	Gunpowder, metallurgy, fuel.
Cinabre mineral	Cinnabar, HgS	Supposed red colour agent.	Red pigment.
Eau de vie	Brandy (ethanol, C_2H_5OH, plus water, H_2O)	Binder activator.	Beverages, medicine, solvent.
Gomme gutte	Gamboge	Fuel.	Dying the robes of Buddhist monks.
Noir de fumée	Lampblack	Fuel, spark producer.	Ink-making.
Orpiment	Arsenic(III) sulfide, As_2S_3	Fuel, supposed yellow colour agent.	Yellow pigment.
Sable de fer	Iron sand (crushed cast iron)	Spark producer.	Purpose-made from a waste material.
Salpetre	Potassium nitrate	Oxidizer.	Gunpowder, metallurgy, preserving meat.
Soufre	Sulfur	Fuel, blue flame producer.	Gunpowder, medicine.

Table 3.2. Ingredients in the Chinese firework compositions published by d'Incarville in 1763.

The next developments in coloured fires happened in France in the late 1760s. On 14th May 1768 Antoine-Laurent de Lavoisier, then 25 years of age, deposited with the Royal Academy of Sciences a sealed envelope containing a report 'On the making of blue and yellow coloured fireworks, to which is appended some experiments on new materials that can be used in non-coloured fireworks.' [58]

Lavoisier had inherited a large fortune in his boyhood; as a young man he pursued his interests in natural philosophy, particularly geology and chemistry. Just twelve days before depositing his report on fireworks, Lavoisier had bought membership in the *Ferme générale*, a private company that collected taxes and customs duties for the King. Membership of this lucrative, but unpopular, organization would ultimately cost Lavoisier his life in the Great Terror of 1794. When he deposited his report, Lavoisier was a candidate for election to the Royal Academy of Science; he had been a candidate for some two years. His application for the position of Assistant in the Chemistry Section was not granted until May 18, 1768 – four days after he deposited his report on fireworks. At the time of his work on fireworks, then, Lavoisier was still a 'gentleman amateur' chemist.[59]

As early as 1766 Lavoisier's reputation as a chemist had led the Ruggieri brothers, renowned Italian pyrotechnists long resident in Paris, to consult him about the possibility of coloured fires. Lavoisier was optimistic. He wrote:

> If fireworks appear to have gained nothing since the discovery of Chinese fire, introduced by Father d'Incarville, it is not necessary to believe that they have been brought to the degree of perfection of which they are capable.
>
> On the contrary, there are in the hands of chemists countless substances which might be used in fires with the greatest success.[60].

Lavoisier began his report with a discussion of zinc. Long imported from China, this metal was now produced commercially in Europe, where it had attracted the attention of chemists, but not of firework-makers.[61]

Lavoisier wrote that 'Zinc, reduced to fine powder and mixed in appropriate proportions with sulphur, saltpetre and charcoal gives a fire of a beautiful blue colour, but of little depth. The great difficulty in using this semi-metal lies in reducing it to powder.' [62]

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[58] Antoine - Laurent Lavoisier, "No. 66: Pli cacheté deposé au académie royale des sciences 14 mai 1768," in *Oeuvres de Lavoisier: correspondance, recouillie et annotée* ed. Rene Fric (Paris: Editions Albin Michel, 1955), pp. 105-109 ; "No. 67: Remarques sur la Composition de quelques feux d'artifice Colorés en bleu et en jaune, dont je remets cacheteé entre les mains de l'Académie. Archives de l'Acadédmie des Sciences, 333 A," in *Oeuvres de Lavoisier: correspondance, recouillie et annotée* ed. Rene Fric (Paris: Editions Albin Michel 1955), pp. 109-113. Simon Werrett deals briefly with Lavoisier's work on coloured fireworks in Werrett, *Fireworks*, pp. 220-221.

[59] Jean-Pierre Poirier, *Lavoisier: Chemist, Biologist, Economist* (Philadelphia: University of Pennsylvania Press, 1996). See p. 28 for the date of his admission to the Academy.

[60] Lavoisier, "No. 67: Remarques sur la Composition de quelques feux d'artifice Colorés en bleu et en jaune, dont je remets cacheteé entre les mains de l'Académie", p. 109.

[61] For the history of zinc, see Mary Elvira Weeks, *Discovery of the Elements*, 6th ed. (Easton, PA: Journal of Chemical Education, 1956), pp. 141-152; W. Hommel, "The Origin of Zinc Smelting," *The Engineering and Mining Journal* 93, no. 24 (1912), pp. 1185-1187; Vijaya Deshpande, "A Note on Ancient Zinc Smelting in India and China," *Indian Journal of History of Science* 31, no. 3 (1996), pp. 275-279; Zhou, "Distilling Zinc in China: The Technology of Large-Scale Zinc Production in Chongqing During the Ming and Qing Dynasties (AD 1368-1911)."

[62] Lavoisier, "No. 66: Pli cacheté deposé au académie royale des sciences 14 mai 1768", p.105.

He mentioned that he had been led to suspect that zinc could produce a blue flame by a work by 'M. Pott', and he described several ways of powdering zinc. At this point Lavoisier ended his discussion of zinc, but the compiler of his correspondence included some previously unpublished notes that showed that Lavoisier had been studying the application of zinc in coloured fires since 1766.[63]

Lavoisier next discussed his attempts to produce yellow. It being well known to chemists (and to cooks) that sea-salt thrown into a fire gives a yellow flame, Lavoisier tested sea-salt in a saltpetre-based mixture and found that it did make a yellow flame, but also made the mixture hygroscopic. He consulted the work of French chemist Louis-Claude Bourdelin (1696-1777), who in 1755 had discussed the colours that different salts imparted to the flame of spirits of wine. Noting that all the salts of soda gave a yellow colour, Lavoisier concluded that this property lay with the base (soda), irrespective of the acid with which it was combined. He therefore tried several non-deliquescent salts of soda, but found that their introduction always inhibited the combustion. He then tried the soda salt of nitric acid (sodium nitrate, $NaNO_3$) instead of saltpetre in his firework compositions, with complete success.[64]

Sodium nitrate was not new in Lavoisier's day. German physician Johannes Bohn (1640-1718) had made some in about 1683 by boiling common salt with nitric acid; he commented on its crystals having a different form from those of ordinary saltpetre. The compound was mentioned sporadically in the early 18th century as 'cubic nitre' or 'cubic saltpetre'. [65]

Lavoisier then recorded his thoughts on some other new ingredients for 'uncoloured' fireworks. He suggested that French 'cast steel' would be better than the cast iron used by the Chinese. According to Lavoisier, this material was 'extremely charged with phlogiston' and, when reduced to coarse powder, seemed to give a better effect than cast iron. He also proposed to test iron pyrites (FeS_2) in fireworks.'[66]

He then turned to antimony (sulfide), noting that it 'is still being successfully used in fireworks; giving a white flame and imparting a very great vivacity to the pieces in which it is used…the disadvantage... is that it makes a lot of smoke.'[67]

Reviewing the available colours, Lavoisier commented 'The mixture of powdered resin [with saltpetre?] gives a soft red colour.' He commented: 'we are very close to assembling all the colours in fireworks. We have already blue and yellow and a little red.' He tried to make green by combining

[63] "No. 67: Remarques sur la Composition de quelques feux d'artifice Colorés en bleu et en jaune, dont je remets cacheteé entre les mains de l'Académie", p. 113, fn. (1).

[64] "No. 66: Pli cacheté deposé au académie royale des sciences 14 mai 1768", pp 106-107. Bourdelin's paper is Bourdelin, "Second Mémoire sur le Sel Sédatif," *Mémoires de l'Académie Royale des Sciences* (1755), pp. 397-436.

[65] For Bohn's work, see Weeks, *Discovery of the Elements*, p. 473.

[66] Lavoisier, "No. 66: Pli cacheté deposé au académie royale des sciences 14 mai 1768", p.108. The material he describes is what is now called 'white cast iron'. It contains dissolved carbon in the form of the iron carbide known as cementite, Fe_3C. Ordinary grey cast iron contains its carbon mostly as graphite (C). It is plausible that iron carbide would produce better sparks than ordinary cast iron. Iron pyrites is iron disulfide (FeS_2). It does not seem to have been found useful in fireworks; no compositions containing it were encountered during research for this project.

[67] Ibid., p.108.

zinc and sodium nitrate in the same mixture, but without success. 'The flame was always yellow on leaving the cartridge and blue at the end.'[68]

At the risk of digressing too far from the subject of materials that forms the focus of this chapter, it is interesting to note that Lavoisier was troubled by his failure to disclose full details of his results. He wrote, in a published paper in which he revealed that he had made yellow and blue fires, but had kept the details of the materials secret:

> If I keep the composition of the coloured fires secret, I hope that it will not be thought that this is from a spirit of mystery…I believed that in depositing the secret recipes in ....the Academy I would .... do my duty both to Messrs Ruggieri and to the public. To Messrs Ruggieri, by allowing them to enjoy the advantage of the novelty, to the public by ensuring that what I have done on coloured fires shall not be numbered among those mysterious recipes buried in the laboratories of the artists and lost to society. [69]

Lavoisier the savant did not approve of technical information being 'buried in the laboratories of the artists and lost to society', but he was enough of a man of the world to understand the desire of 'the artists' to keep valuable new information to themselves.

Lavoisier's introduction of sodium nitrate turned out to be of lasting value. That chemical is used in yellow fires and military illuminating flares to the present day. It is inexpensive and effective, its only shortcoming being its tendency to absorb moisture from the air. Lavoisier's reluctant secrecy was effective; the value of sodium nitrate would not be re-discovered for some 40 years, when French chemist, Joseph Louis Proust (1754-1826) reported that a mixture of five parts of nitrate of soda, one of charcoal and one of sulphur gave a reddish-yellow flame, which could 'produce some pleasant contrasts' in fireworks.[70]

Proust's note is entitled 'Sur l'utilité du nitrate du soude', indicating that any practical use for the salt was a novelty. It is remarkable that Proust, a distinguished Professor of Chemistry, was sufficiently interested in fireworks to suggest a new ingredient. In 1831 German amateur pyrotechnist Johann Martin Websky (1799-1867) published a composition for 'yellow Bengal Fire' based on sodium nitrate, commenting: 'The fire of this composition is coloured a splendid golden-yellow.' Lavoisier's choice of sodium nitrate for yellow fire had proved its worth.[71]

Lavoisier's use of zinc to produce blue was also taken up by the firework-makers. In 1802 Claude-Fortuné Ruggieri wrote that zinc 'gives a very beautiful blue colour, and produces the most beautiful effect of all the coloured fires.' Ruggieri prefaced his remarks on zinc with the observation that 'it is composed of iron and sulphur', a most peculiar comment given that Lavoisier, in 1789, had included zinc in his list of chemical elements ('substances simples'). Ruggieri's views on zinc would have surprised a contemporary chemist such as Jean-Antoine Chaptal (1756-1832), to whom Ruggieri dedicated his book in a lengthy Preface in which he emphasised the value to the pyrotechnist of a

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[68] Ibid. p. 109. Lavoisier subsequently mentioned that he had tested copper salts (well-known to colour non-pyrotechnic flames green) and found them useless. See "No. 67: Remarques sur la Composition de quelques feux d'artifice Colorés en bleu et en jaune, dont je remets cacheteé entre les mains de l'Académie", pp. 110-111.

[69] "No. 67: Remarques sur la Composition de quelques feux d'artifice Colorés en bleu et en jaune, dont je remets cacheteé entre les mains de l'Académie", pp. 112-113.

[70] Joseph Louis Proust, "Sur l'utilité du nitrate du soude'," *Journal de Physique, de Chimie, d'Histoire Naturelle et des Arts* 43 (1806), p. 69.

[71] Martin Websky, *Grundlich und fasstliche Anweisung zur Verfertigung kleiner Lustfeuerwerke, zunachst für Dilettanten der Feuerwerkskunst.* (Landeshut: W. Pfingsten, 1831), p. 35.

sound knowledge of chemistry. Despite his efforts to impress his readers with his advocacy of chemistry, Ruggieri's own knowledge of that subject was clearly very much out of date.[72]

Ruggieri's description of the blue flame of zinc as 'the most beautiful of all the coloured fires' provides an insight into the state of the art of coloured fires at the beginning of the nineteenth century. To modern eyes, this flame is a rather pale shade of greenish-blue. Although blue (or blue-green) compositions based on zinc continued to be published for many years, they were eventually superseded by much more distinct blues based on salts of copper. These new blue compositions included a new pyrotechnic chemical that had also made possible red and green firework flames of unprecedented intensity and brilliance. The story of the introduction of this new chemical, potassium chlorate ($KClO_3$), and of the colour-producing chemicals used with it, will be told in the next chapter.

With hindsight, it can be seen that Lavoisier's failure to produce a full range of coloured fires was inevitable: the necessary materials were not yet known. Before continuing with the story of the new materials that would be used in the new generation of coloured fires, it is appropriate to review the rather odd developments with one of the materials that Lavoisier discussed: antimony. Lavoisier would include this in his list of chemical elements, but for some time the name would be used interchangeably for both 'antimony regulus' (elemental antimony, Sb) and 'crude antimony' (antimony(III) sulfide, Sb_2S_3). Seventeenth century alchemists had paid much attention to these materials, attaching great significance to the star-like pattern of crystals formed on lumps of 'antimony regulus' produced by melting 'crude antimony' with iron. Heating substances with saltpetre was a common alchemical practice, which leads one to expect that the alchemists would have been well acquainted with the vigorous combustion of mixtures of antimony sulfide and saltpetre. Jean Appier mentioned antimony as an ingredient in fireworks as long ago as 1620, and in 1768 Lavoisier wrote that it was still used, and produced a white flame. It might be expected, then, the combustible properties of both varieties of antimony would have been common knowledge amongst late 18th century European chemists and firework-makers. Strangely enough, a rather simple antimony-based composition became a great novelty in late 18th century France and was successfully kept secret for some years.

Simon Werrett has shown that the British military expeditions in India in the mid 18th century found the Indians using 'blue lights' to illuminate battlefields. One witness revealed that these lights (white-burning flares) contained sulfur and antimony; he did not mention the third ingredient, saltpetre. References to 'Bengal fire', 'Indian Fire' and 'Blue Lights' soon appeared in British and French publications. "Bengal Fire' was used for flare compositions based on antimony sulfide, 'Indian Fire' for similar ones based on sulfides of arsenic. The exact formulae were kept secret. . Claude-Fortuné Ruggieri claimed that Bengal fire was introduced (presumably he meant to France) by his father, Pétroni Ruggieri. As noted by Werrett, an announcement of a Ruggieri display including 'Flammes de Bengale' is given in the Journal de Paris for 12 July 1778. One can but wonder how these 'Flammes de Bengale' differed from the antimony-based white fire that Pétroni's consultant Lavoisier had mentioned ten years earlier. [73]

According to Ruggieri his father used Bengal fire as a stage effect at the Italian theatre in Paris in 1787, to represent a house on fire. This was an important development, as Bengal Fire became widely

[72] Ruggieri, *Elémens de pyrotechnie, divisés en cinq parties; avec un vocabulaire des termes compris dans cet ouvrage*, p. 40.

[73] Werrett, "William Congreve's Rational Rockets", pp. 35-56. See p. 38 and endnote 11. Richard Owen Cambridge, *An Account of the War in India between the English and French on the Coast of Coromandel from the year 1750 to the year 1760 together with a relation of the late remarkable events on the Malabar Coast, and the Expeditions to Golconda and Surat; with the Operations of the Fleet* (London: T. Jefferys, 1761), p. 106. Ruggieri, *Elémens de pyrotechnie, divisés en cinq parties; avec un vocabulaire des termes compris dans cet ouvrage*, p. 128, pp. 314-315. For the Journal of Paris, see Werrett, "William Congreve's Rational Rockets." Endnote 11. The original is Anonymous, "Le sieur Pétroni Ruggieri..." *Journal de Paris*, Sunday 12 July 1778. p. 772. I have mentioned some of the facts in this paragraph elsewhere: Sturman, "Coloured Fire." p. 15.

used in the theatres and paved the way for the subsequent introduction of the new coloured fires as theatrical stage effects. As noted elsewhere, it is likely that the new coloured fires originated when, in an attempt to make Bengal Fire burn red, strontium nitrate was substituted for the saltpetre and potassium chlorate was added to improve the combustibility. The secret formula for Bengal fire was eventually revealed in 1800, when the French pyrotechnist A. M. Thomas Morel published the simple 3-component recipe and announced that he had bought the secret. This reveals some unexpected aspects of European pyrotechnic knowledge in the late 18th century. Practitioners were sufficiently unfamiliar with the properties of a material already known in the art that they were mystified by a simple composition based on it. That such a simple mixture could be kept secret, and that a competent pyrotechnist who had seen it in use could not work out what it was and had to purchase the formula, show that the gap between artisanal practice and chemical knowledge was greater than we might otherwise imagine. [74]

In this chapter we have seen that the introduction of new materials into firework-making up to the end of the eighteenth century was a slow and somewhat haphazard process. As expected from Rachel Forrester's insights into the sequence in which materials come into use, the earliest materials used in fireworks were naturally-occurring substances (most notably saltpetre) that were already being gathered and refined for other purposes. The Chinese use of pulverized cast iron is probably the earliest example of a material being made specifically for fireworks, albeit from a raw material that had long been produced for a completely different purpose – the manufacture of cooking utensils and the like. Not all possible materials were introduced into firework-making, even though they were available: the most conspicuous examples are the Chinese failure to use zinc (which they produced on a large scale) in fireworks and the neglect of the large deposits of antimony ore in China for any application at all. The European adoption of antimony and antimony sulfide as pyrotechnic ingredients was very slow; antimony was mentioned by Appier in the 17th century, Lavoisier discussed it, but as late as 1787 the simple antimony-based Bengal Fire introduced from India was seen as a great innovation, worthy of being kept secret. The involvement of Lavoisier in the introduction of new pyrotechnic ingredients, with the specific intent of making coloured fires, led to his introduction of zinc to make blue fires and of sodium nitrate to make yellow. The work was sponsored by commercial pyrotechnists, obliging Lavoisier to keep the details secret – an obligation that conflicted with his personal inclination, and his obligation as a public savant, to make his discoveries known to all.

That working pyrotechnists should have sought out Lavoisier to investigate coloured fires on their behalf, and that Lavoisier was able to achieve some success, was a consequence of Lavoisier's intense involvement with academic chemistry. For some decades, chemists had been engaged in intellectually-inspired projects to identify, catalogue and characterise materials. In so doing they established new experimental techniques and they developed theories that helped both to systematise their results and to suggest further experimental work. Chemists were also interested in applications of their knowledge: institutions such as the Royal Academy of Sciences promoted the value of chemical knowledge in the practical arts. In these circumstances it would have been natural for a firework-maker desirous of new effects to seek the advice of a chemist, and natural, too, for the young, ambitious chemist Lavoisier to take on the project, both for its inherent interest and for the opportunity to display his chemical skill and knowledge to the Academy and to the public at large. Lavoisier's project to make a complete range of coloured fires was ultimately unsuccessful, because some of the necessary materials were not yet known. Success would have to wait for many more decades, and would depend on the introduction of still more new materials. Meanwhile, the firework-makers continued to operate with a rather limited range of ingredients.

[74] A. M. Thomas Morel, *Traité pratique des feux d'artifice pour le spectacle et pour la guerre, avec les petits feux de table, et l'artifice à l'usage des théatres.* (Paris: Firmin Didot, 1800), p. 84; Ruggieri, *Elémens de pyrotechnie, divisés en cinq parties; avec un vocabulaire des termes compris dans cet ouvrage*, p. 42; Sturman, "Coloured Fire", pp. 66-67.

Chapter 4: Materials: Part 3. Coloured Fires from the late 18th Century to the 1880s.

The previous chapter reviewed the introduction of new materials into pyrotechny from the beginnings of the art in ancient China to the efforts of Lavoisier in the late 1760s. This chapter focuses on the new materials required for a full range of coloured fires, and also notices some additional materials that were introduced to improve the new coloured fires, both in performance and in safety. One new ingredient, potassium chlorate, was used to make a new generation of coloured fires, originally a red fire for the stage, and then a whole range of colours for fireworks, military signals, and the theatres. The recognition that a mixture of potassium chlorate and sulfur would burn with different colours depending on other chemicals added to the mixture led to searches for different colour-producing agents. In the course of this work it was discovered that calomel (mercury(I) chloride, Hg_2Cl_2), while producing no colour itself, improved the colours produced by other chemicals.

The first hint of one of the new materials that would turn out to be central to the development of the new coloured fires was given in 1787 when 'Mr Ash', an Edinburgh medical student, demonstrated to Scottish physician and chemist Thomas Charles Hope (1766 – 1844) that the solution in hydrochloric acid of a white mineral from a mine near the village of Strontian, imparted a deep red colour to a candle flame. Specimens of that mineral reached the English chemist William Cruickshank (17??–1810 or 1811), 'Chemist to the Ordnance, and Surgeon of Artillery' at the Royal Military Academy at Woolwich. Cruickshank was an assistant to Irish chemist and physician Adair Crawford (1748-1795), Professor of Chemistry at the Royal Military Academy and also Physician at St Thomas' Hospital, London. In 1790 Crawford published a paper in which he described his and Cruickshank's work on the Strontian mineral that indicated that the mineral contained a new 'earth'. The following year German physician and mineralogist Friedrich Gabriel Sulzer (1749-1830) published a paper on the Scottish mineral, which he called strontianite, presenting evidence that it contained a new 'earth'. He described 'six-sided, fairly large, and easily dissolvable crystals' deposited from a solution of the mineral in nitric acid. This is the earliest report of a chemical that was to play a central role in the transformation of fireworks. [75]

In September 1793, German apothecary and chemist Martin Heinrich Klaproth (1743-1817) described experiments on the Strontian mineral (which we now know consists of strontium carbonate, $SrCO_3$) and the similar mineral witherite (barium carbonate, $BaCO_3$) that showed that the two were indeed different. Klaproth remarked that he was led to suspect that the Scottish mineral was distinct from witherite because he had observed that a piece of paper, having been soaked in a solution of the mineral in nitric acid, dried, and then set alight, burned with a red flame. He also commented on the ability of a solution of the mineral in hydrochloric acid to impart a red colour to the alcohol flame. In November 1793 Hope reported to the Royal Society of Edinburgh that he had started work on the mineral from Strontian in 1791 and showed that it contained a new 'earth', which he called 'strontia'. [76]

[75] James Riddick Partington, "The Early History of Strontium," *Annals of Science* 5, no. 2 (1942), pp. 157-166; "The Early History of Strontium Part 2," *Annals of Science* 7, no. 1 (1951), pp. 95-100. For the red flame, see Davis, "The Early use of Potassium Chlorate in Pyrotechny: Dr Moritz Meyer's Colored Flame Compositions," pp. 95-92, on p. 78. Hope's paper is Thomas Charles Hope, "Account of a Mineral from Strontian, and of a Peculiar Species of Earth which it Contains," *Transactions of the Royal Society of Edinburgh* 4, no. 2 (1798), pp. 3-39.

[76] Partington, "The Early History of Strontium." and *"The Early History of Strontium Part 2."* Martin Henry Klaproth, "Chemische Versuche über die Strontianerde," *Chemische Annalen für die Freunde der Naturlehre, Artzengelahrtheit, Haushaltungskusts und Manufakturen: von D. Loernz von Crell* II (1793), pp. 189-202; "Chemical Researches into Strontianite compared with Witherite," in *Analytical Essays towards Promoting the Chemical Knowledge of Mineral Substances* (London: T. Cadell, Jun. and W. Davies, 1801), pp. 223-237.

The discovery of strontia (and thus of its red flame) was contingent on several unique developments in 18th century Western Europe. First, it had become fashionable for gentlemen to display in their homes 'cabinets of curiosities' containing specimens of all sorts of items, both natural and man-made, from all parts of the world. This fashion was perhaps stimulated by curiosity about the alien lands explored in the course of European trading and empire-building projects. A fine display of curiosities would demonstrate the owner's wealth and taste and show that he was in touch with the latest developments in exploration and natural history. In response to the needs of gentlemen to enrich their cabinets, enterprising individuals collected rare items and made them available for sale. Such items included unusual stones and crystals. At this same period of history, some gentlemen were involved in chemistry, both as a respectable hobby and professionally as Professors of Chemistry catering for the educational needs of medical men, apothecaries and the analysts serving the growing chemical-based manufacturing industries. Such chemists, whether amateur or professional, were keen to examine unusual mineral specimens in the hope of discovering something new, be it a new mineral or even better a new 'earth' or a new metal. A discovery would ensure the discoverer a place in the literature and would be expected to bring coveted prestige and authority. For all these reasons minerals such as strontianite, which previously would have been ignored, were noticed, collected, put on the market, and brought to the attention of people keen to examine them, discover their properties, and (most importantly) to record and publish their results.

In 1793 Hope commented on the red flame produced when a 'combustible body' was brought into contact with molten 'nitrate of strontites', consistent with Klaproth's observation in that same year of the red flame of paper that had been impregnated with that salt. The potential use of 'nitrate of strontia' in fireworks was indicated in 1801 by French chemist Antoine François, Comte de Fourcroy (1755 –1809) who wrote that nitrate of strontia 'has not yet any use. Mixed with [gun] powder, it could colour the fire of fireworks a purple-red'. It is quite difficult to make a good red firework flame with strontium nitrate and other materials available at the time. Contrary to Fourcroy's expectations, a simple mixture with gunpowder will not work.

In a book published in 1807 the German chemist Friedrich Christian Accum (1769-1838), who worked in England from 1793 to 1821, wrote, 'A beautiful red fire may also be produced by mixing one part of nitrate of strontia with two or three parts of charcoal powder, and setting fire to the mixture…' Recent tests, made at my suggestion by the American pyrotechnist Kenneth L. Kosanke, showed that this mixture ignites with difficulty and that the colour of its fire is more orange than red. This suggests that Accum had not evaluated the mixture, a suspicion that is strengthened by the vagueness of his specification of it.

A formula for an early red fire based on strontium nitrate was given by the British chemist James Marsh (1794-1846), who worked in the Royal Laboratory at Woolwich from the early 1820s. Marsh's recipe for 'Common Red Fire' is shown in Table 4.1:

Nitrate of strontian	72 parts
Sulphur	20 parts
Mealed Powder	6 parts
Coal dust	2 parts

Table 4.1. 'Common Red Fire' of the early 19th century.[77]

This composition was tested by Ken Kosanke. When burned in small quantities, it smouldered, becoming covered with white ash, but occasionally showing a red flame. In somewhat larger quantities, it burned steadily, and intermittently displayed jets of intensely-coloured red flame. These emerged at different places as the mixture burned, but each jet was soon smothered by the growing

[77] James Marsh, "On the Manufacture of Gunpowder, and on the Proportions of Ingredients Used by Various Nations; with the Modes of Preparing the Various Coloured Fires, Signal Rockets, &c. ," *The Chemist* V, volume II new series (1844), pp. 20-36, the recipe is on p. 24.

white ash, to be replaced by a new jet emerging elsewhere. It is easy to imagine that this (or some similar) mixture could account for references to red fire being used as a theatrical stage effect in the first decade of the 19th century. When it worked well, it would have been impressive, but often it would not have worked well, if at all. Strontium nitrate, unless carefully purified, absorbs moisture from the air, rendering the mixture incombustible. This could explain the remark made by a London theatre critic in 1825: 'a little red fire flickered in one corner of the stage, as if blushing to be mistaken for a conflagration'.[78]
The development of an improved red fire based on strontium nitrate would depend on the introduction of another new chemical, potassium chlorate ($KClO_3$). The story of this new ingredient is worth telling in detail, as it shows how the discovery of new materials is contingent on knowledge of other materials needed for their preparation and on some motivation to experiment with them. It also shows that the application of new materials depends on the recognition of unusual properties and an awareness of areas in the applied arts where such properties might be beneficial. Application of potassium chlorate in fireworks was delayed because authoritative accounts of its properties exaggerated the hazards of working with it, as explained elsewhere. The story of potassium chlorate begins with an academic chemist's investigation of a peculiar black mineral, to clarify the nature of a substance that had long been used in the arts but remained a mystery to savants.[79]

In 1774 German-Swedish chemist Carl Wilhelm Scheele (1742 – 1786) published investigations of the mineral pyrolusite (manganese dioxide, MnO_2). This had been used for a long time in glass-making. Added to molten glass, it removed any green or yellowish colours, leaving colourless glass. If more were added, it made violet-coloured glass. It was also used in violet glazes for pottery, and for making black pottery. Pyrolusite had been known by several different names (glass soap, black magnesia, manganese) and had been investigated by various chemists, but its nature remained obscure. In the early 1770s Scheele worked on it at the suggestion of his friend, the Swedish chemist and mineralogist Torbern Olof Bergman (1735 – 1784), who suspected that it was the 'calx' of an unknown metal.[80]

For our purposes the main interest in Scheele's project is his observations of what happened when he heated powdered pyrolusite with '*spiritus salis*'. The latter is what we now call hydrochloric acid (an aqueous solution of hydrogen chloride, HCl). This had been known for a long time, as it is easily produced by distilling a mixture of common salt and either green vitriol (iron(II) sulfate heptahydrate, $FeSO_4.7H_2O$) or oil of vitriol (sulfuric acid, H_2SO_4). Thus, neither of the substances used in Scheele's experiment was in any way new. It is also unlikely that Scheele was the first to have tried the experiment. Any of the mediaeval alchemists and their chemist successors could have heated pyrolusite and spirits of salt, been nauseated by the choking stench and resolved never to repeat the experience. Scheele, in contrast, made careful observations and followed them with systematic experiments. In his examination of this peculiar 'air', Scheele noticed that it would bleach vegetable

[78] Sturman, "Coloured Fire." For early (1807) use of a red fire on the stage, see Charles Dibdin, *Professional & Literary Memoirs of Charles Dibdin the Younger : dramatist and upward of thirty years manager of minor theatres / edited from the original manuscript by George Speaight* (London: Society for Theatre Research, 1956), pp. 90-9. Results of the tests of 'Common Red Fire' by Dr Kenneth L. Kosanke were in emails to Barry Sturman, 15-18 June, 2013. Dr Kosanke also provided videos of the burning mixtures. The composition is unusual in that it uses coal dust as one of the fuels. Compared to the more usual charcoal, this would have the advantage of providing more hydrogen, required for the formation of the red-emitting strontium monohydroxide in the flame. The beneficial effects of coal dust would have been discovered by serendipity, as there would have been no reason at the time to expect that it would help to produce a red flame. For the flickering red fire of 1825, see Q, "Theatrical Examiner," *The Examiner*, Monday October 17 1825, p. 657.

[79] Sturman, "Coloured Fire."

[80] For early knowledge of pyrolusite, see Vannoccio Biringuccio, *The Pirotechnica of Vannoccio Biringuccio*, trans. Cyril Stanly Smith and Martha Teach Gnudi (1990); the use of 'manganese' (i.e pyrolusite) in the early 16th century is discussed on p. 113, and on p. 127. For its history, see Weeks, *Discovery of the Element*, p.168.

colours: 'Blue litmus paper became almost white ; all vegetable flowers — red, blue, and yellow— became white in a short time.[81]

Scheele was able to make these observations not because he had access to any new materials, but because of a new attitude amongst chemists. They had established that the so-called 'airs' were distinct substances that could be isolated and subjected to chemical examination. A phenomenon that in earlier times might have been dismissed as nothing more than an unpleasant smell was now recognized as a new substance, worthy of further study. Scheele investigated carefully, and he made his results available by publication, so he is credited with the discovery of the gas that we now call 'chlorine' (Cl_2), even though he was almost certainly not the first to have encountered it, and its nature would not be agreed upon for decades.[82]

The recognition of chlorine as a distinct substance was the first step along the road to the application of potassium chlorate in fireworks. The road was not direct, and changed repeatedly from one that was expected to lead to the solution of an intellectual problem in chemistry to one directed towards a practical application of some new substance encountered along the way. Eleven years after Scheele's publication the French chemist Claude Louis Berthollet (1748-1822) carried out a detailed investigation of Scheele's peculiar new 'air' to test an idea that he had developed about its nature. Berthollet had adopted Lavoisier's views on chemistry, which included the notion that all acids contain oxygen. In contrast, Scheele had described the new 'air as 'dephlogisticated marine acid' – that is, marine acid [i.e. hydrochloric acid] deprived of 'phlogiston', the hypothetical substance that was believed to be lost in combustion. Pyrolusite was known to be an avid consumer of phlogiston, so the product of its reaction with marine acid was designated 'dephlogisticated marine acid'.[83]

According to Lavoisier's oxygen theory of acids, marine acid was a compound of oxygen with an unknown '*radical muriatique'*. Berthollet reasoned that Scheele's 'dephlogisticated marine acid' must be a compound of oxygen and marine acid, and he set out to find if the properties of 'dephlogisticated marine acid' supported this hypothesis. Although the work was undertaken for intellectual reasons, Berthollet was alert to practical applications. He confirmed the observations of Scheele and Bergman that the 'air' destroyed the colours of plant materials. He also found that solutions of the 'air' in water or in a solution of carbonate of potash (potassium carbonate, K_2CO_3) had this property. Observing that most vegetable dyes were bleached very rapidly, whereas to bleach the blue dye indigo required several days and much more reagent, Berthollet saw an opportunity. He wrote: 'I shall avail myself of this means of analysis … to determine the properties of colouring

[81] Carl Wilhelm Scheele, "On Manganese and its Properties," in *Alembic Club Reprints No. 13: The Early History of Chlorine* (Edinburgh: The Almebic Club 1905; reprint, 1905), p. 8.

[82]For the recognition gases as distinct substances, see William H. Brock, *The Norton History of Chemistry*, ed. Roy Porter, Norton History of Science (New York: W. W. Norton & Company, 1993), pp. 96-111. For the subsequent history of chlorine, see Chang, Hasok, and Catherine Jackson, eds. *An Element of Controversy The Life of Chlorine in Science, Medicine, Technology and War,* BSHS Monographs. London: British Society for the History of Science, 2007. For details of its early history, see Robert Siegfried, "Humphry Davy and the Elementary Nature of Chlorine," *Journal of Chemical Education* 36, no. 11 (1959), pp. 568-570. Primary sources are conveniently reprinted as Carl Wilhelm Scheele et al., *The Early History of Chlorine. Papers by Carl Wilhlem Scheele (1774). C. L. Berthollet (1785). Guyton de Morveau (1787). J. L. Gay-Lussac and L. J. Thenard (1809).* Alembic Club Reprints (Edinburgh: William F. Clay, 1897) and Humphry Davy, *The elementary nature of chlorine. Papers by Humphry Davy (1809-1818)* . Alembic Club Reprints (Edinburgh: William F. Clay, 1894).

[83]Berthollet, Claude Louis. "Observations sur Quelques Combinaisons de l'Acide Marin Déphlogistiqué, ou de l'Acide Muriatique Oxigéné." *Observations sur la Physique, sur l'Histoire Naturelle et sur les Arts* 33 (1788), pp. 217-24. For phlogiston, see Brock, *The Norton History of Chemistry*.pp 78-84. For recent discussions see Leslie V. Woodcock, "Phlogiston Theory and Chemical Revolutions," *Bulletin for the History of Chemistry* 30, no. 2 (2005), pp. 63-69; Hasok Chang, "The Hidden History of Phlogiston: How Philosophical Failure can generate Historiographical Refinement," *HYLE, the International Journal of Philosophy of Chemistry* 16, no. 2 (2010), pp. 47-79.

matters which are employed in dyeing, and I shall endeavour to make some applications, useful to the arts, of the properties of dephlogisticated marine acid.'[84]

While his original intent was to use the new bleaching agents to evaluate dyestuffs, Berthollet soon realised their value in the bleaching of textiles and went on to implement this application an industrial scale. Meanwhile, he satisfied himself that his interpretation of the nature of 'dephlogisticated marine acid' was correct, to the extent that in his next paper on the subject, he referred to 'dephlogisticated marine acid, or oxygenated muriatic acid,' thus using the old name and the new 'Methodical' name as alternatives. As in the previous paper, Berthollet began with an academic chemical problem and in the course of the work came upon something that suggested a practical application.[85]

Berthollet noticed that 'oxygenated muriatic acid', unlike other acids, did not effervesce with a cold solution of carbonate of potash, but it did lose its colour and its odour was much weakened. To explore the acidic properties of 'oxygenated muriatic acid' Berthollet, passed some of it into a solution of caustic potash (potassium hydroxide, KOH). A large quantity was absorbed, and a solid deposit was formed. This deposit consisted in part of 'earthy matter that had been held in solution by the caustic potash' (a telling comment on the purity of chemicals in those days) but also included 'some little crystals of a new shape'. Berthollet separated the deposit, evaporated the liquid and obtained a large quantity of muriate of potash (potassium chloride, KCl) and a small quantity of a 'new salt'. He found that this new salt 'detonated with charcoal', leaving a residue of ordinary muriate of potash. He concluded that the new salt was composed of 'muriatic acid combined with oxygen and potash' and he named it 'oxygenated muriate of potash.'[86]

Berthollet made a careful study of this new salt, which we now call potassium chlorate. He found that it was much more soluble in hot water than in cold, which afforded a convenient method of separating it from the 'muriate of potash' that always accompanied it; he commented on the shape of its crystals, and noted their mica-like lustre. Berthollet also tasted his new salt, finding that its taste 'much resembles that of nitre'. [87]

Having characterized the new salt, Berthollet repeated his experiments but this time with caustic soda (sodium hydroxide, NaOH) and effervescent soda (sodium carbonate, Na_2CO_3) instead of caustic potash and carbonate of potash. He observed analogous phenomena, but with a remarkable difference: 'oxygenated salt of soda' is deliquescent. 'None the less', wrote Berthollet, 'if the liquor be concentrated, and if one pours a little on hot coals, it makes a little detonation. It dissolves in spirits of wine, like all the deliquescent salts.' This is the first account of sodium chlorate ($NaClO_3$), a salt which, on account of its deliquescence, was to find little use in pyrotechnics. [88]

Potassium chlorate, in contrast, is stable in air, and Berthollet was quick to foresee an application. Noting that the new salt released pure oxygen on heating, and that it reacted with charcoal and with

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[84] Claude Louis Berthollet, "Mémoire sur l'Acide Marin Déphogistiqué," *Mémoires de l'Académie Royale des Sciences pour l'Année 1785* (1788), pp. 276-295..

[85] *Description du Blanchiment des Toiles et des Fils par l'acide muriatique oxigéné; et de quelques autres propriétés de cette liqueur, relatives aux arts* (Paris: Fuchs, 1794); *Description de l'art du blanchiment par l'acide muriatique oxigené* (Paris: Imprimerie de la Feuille du Cultivateur, 1795) ; "Observations sur Quelques Combinaisons de l'Acide Marin Déphlogistiqué, ou de l'Acide Muriatique Oxigéné," *Observations sur la Physique, sur l'Histoire Naturelle et sur les Arts* 33 (1788).

[86] "Observations sur Quelques Combinaisons de l'Acide Marin Déphlogistiqué, ou de l'Acide Muriatique Oxigéné." p. 218.

[87] Ibid. p.218.

[88] Ibid. p.222.

iron much more vigorously than did saltpetre, he wrote: 'It is probable that the [gun] powder that I propose to make with this salt will have some remarkable properties.'[89]

Berthollet must have discussed his proposal with Lavoisier, as Patrice Bret quotes Lavoisier, writing in 1788:

> 'M. Berthollet has found the way to charge ordinary sea salt with a large quantity of oxygen and, in that state, it not only detonates as well as potash nitre but it also spreads a much greater light and brilliance. It is the object of new experiments that the custodians of powder will carry out one day, but, should it turn out that M. Berthollet's oxygenated marine salt does not make a stronger powder than the powder made with ordinary saltpetre, there will at least come from this discovery a way of producing some new and unexpected effects in fireworks'[90]

Some 20 years after his efforts to make coloured fires, Lavoisier was still alert to the possibility of new firework effects. His expectation that Berthollet's new salt would be useful in fireworks would prove to be correct, but proof would not be forthcoming for many years. As shown elsewhere, the delay was a consequence of the efforts of Lavoisier and Berthollet to use potassium chlorate as a substitute for saltpetre to make a 'stronger powder' for the French Government. This 'muriated gunpowder' project has been discussed in detail in the literature; suffice it to say that the project was plagued by explosions, including some in which people were killed.[91]

Berthollet was discouraged, advising fellow chemist Louis-Bernard Guyton de Morveau (1737–1816) in June 1793: 'it is impossible to handle so hazardous a reagent…and we must, therefore, abandon our attempted project'.[92]

Despite Berthollet's advice, the project was not abandoned until the following year. The disastrous attempts to use potassium chlorate in gunpowder led to warnings of the dangers of mixing the salt with combustibles appearing in many chemistry textbooks, so much so that the material gained a reputation as being far too dangerous for use in pyrotechnics. None the less in 1805 French chemist Jean-Louis Chancel (1779-1837) used it in the first practical pyrotechnic fire-starting device. The sensitivity of mixtures of potassium chlorate and combustibles to impact and friction was exploited by Scottish clergyman Alexander John Forsyth (1768-1843), who, in 1807, patented mixtures containing potassium chlorate for discharging firearms by percussion.

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[89] Ibid. p. 223.

[90] Patrice Bret, "Une tentative d'exploitation militaire de la recherche en Chimie: Berthollet et la poudre de muriate oxygéné de potasse (1787-1794)," in *Lavoisier et la révolution chimique: actes du colloque tennu à l'occasion du bicentenaire de la publication du "Traité élémentaire de chimie" 1789* ed. Michelle Goupil (Paris: SABIX - Ecole Polytechnique, 1992), pp. 195-238. Qoute is on p.195. Bret gives the source as Lavoisier, "Sur la Détonation", *Oeuvres complètes*. Paris : Iprimerie Nationale, 1864-1893, tome V, p. 316. He says that the text is assuredly from 1788. Its early date is clear from Lavoisier's incorrect assumption that Berthollet's new salt was 'oxygenated sea salt' i.e. sodium chlorate, rather than potassium chlorate.

[91] Sturman, "Coloured Fire." For an eyewitness account of the first explosion, see Antoine - Laurent Lavoisier, "Sur l'accident d' Essonnes," in *Oeuvres de Lavoisier* (Paris: Imprimerie Nationale, 1892; reprint, Johnson Reprint Corporation, New York, 1965). For modern assessments of the project, see Bret, "Une tentative d'exploitation militaire de la recherche en Chimie: Berthollet et la poudre de muriate oxygéné de potasse (1787-1794)", pp. 195-238 and Charles Coulston Gillispie, *Science and Polity in France: The Revolutionary and Napoleonic Years.* (Princeton: Princeton University Press, 2004), pp. 350-370.

[92]Berthollet to Guyton 1 June 1793. Quoted by Gillispie, *Science and Polity in France: The Revolutionary and Napoleonic Years,* p. 367.

Potassium chlorate began to be used in coloured flame compositions in 1810 when English medical student John Forster (1793-1873) used it in a new red fire, based on strontium nitrate, for a theatrical performance at Astley's Amphitheatre in Lambeth, England. The formulation for this red fire was not published until 1820, when Michael Faraday wrote a brief note on it for the Royal Institution. In 1839, the German businessman and amateur pyrotechnist Johann Martin Websky wrote that the application of strontium nitrate in pyrotechnics was for a long time 'restricted to theatrical fire, because the way to use it was kept secret, and the substance was too rare and too costly to justify sufficient testing of it for other pyrotechnic purposes.' Websky's comment is consistent with the delay of some 10 years between the first public performance of theatrical red fire containing both strontium nitrate and potassium chlorate at Astley's Amphitheatre in London in April 1810 and the publication of its formula in July 1820.[93]

Forster's composition demonstrated the value of potassium chlorate in coloured fires. That would not be generally appreciated for some time, and the old colour effects continued to be used in firework displays. An example of the materials used in pyrotechny in the early 19th century is given in Table 3.4, which shows the materials mentioned in the final (1821) edition of Ruggieri's book as being used in firework compositions and in coloured alcohol flames.[94]

[93] Martin Websky, *Lustfeuerwerkerei für Dilettanten* (Breslau: Ferdinand Hirt, 1839), p. 83.

[94] Claude-Fortuné Ruggieri, *Principles of Pyrotechnics (translation of Élémens de pyrotechnie, 3me ed. Paris: Bachelier, 1821)* [Principles of Pyrotechnics], trans. Stuart Carlton (Buena Vista: MP Associates, Inc., 1994).

Name	Synonym	Main Use in Fireworks	General and Industrial Uses
Alcohol	Spirits of wine, brandy	Binder activator	Beverages, medicine
Amber powder	Yellow amber	Fuel	Waste product
Ammonium chloride	Sal ammoniac	Green colour enhancer	Soldering flux
Antimony(III) sulfide	Antimony crude	Fuel	Antimony ore
Camphor		Fuel	Medicine
Charcoal, wood		Fuel	Fuel, metallurgy
Coal	Pit coal, sea coal	Spark producer	Fuel
Copper filings		Spark producer	Waste product
Copper(II) acetate monohydrate	Crystallized verdigris	Green colour agent	Medicine, pigment manufacture
Copper(II) sulfate pentahydrate	Bluestone, Blue Vitriol	Green colour agent	Medicine, pigment manufacture
Gum	Gum Arabic	Binder	Adhesive
Gum benzoin	Benjamin	Perfume	Perfume, medicine
Gunpowder		Propellant	Military, sporting guns, blasting
Iron filings		Spark producer	Waste product
Iron, cast, crushed		Spark producer	Waste product
Juniper gum	Gum Sandarac	Fuel/binder	Varnish making
Lampblack		Fuel	Pigment
Linseed oil		Binder	Putty, wood preservatives
Lycopodium		Fuel	Medicine
Pitch		Fuel	Waterproofing
Potassium nitrate	Saltpetre, nitrate of potash	Oxidizer	Gunpowder, preserving meat
Sodium chloride	Common salt	Yellow colour agent	Cooking, preserving meat
Steel filings		Spark producer	Waste product
Storax	storax calamite	Perfume	Perfume, medicine
Sulfur	Brimstone	Fuel	Gunpowder, medicine
Verdigris		Green colour agent	Pigment
Yellow sand		Spark producer	Blotting ink
Zinc filings		Blue-green colour agent	Waste product

Table 3.4. Firework ingredients in 1821, showing their main uses in fireworks and in the general community. Materials in the shaded rows were used only in making green-coloured alcohol flames

Some of these ingredients were of very minor importance. Specifically, Ruggieri gives no compositions requiring the use of copper filings, nor of common salt, nor of Gum Benzoin or Storax. The last two were, as he explains, used only to produce ‘a pleasing odour, which mitigates that of gunpowder and other firework materials, the smoke of which greatly displeases some people.’ It can be seen, then, that less than a couple of dozen rather common substances were all that Ruggieri needed for his firework compositions

As late as 1821 Ruggieri was still writing enthusiastically of the green alcohol flame that had so impressed French travellers to Russia and which he had duplicated some 15 years previously. In1806

Ruggieri took a 4:2:1 mixture of crystallized verdigris (copper(II) acetate monohydrate, $Cu(CH_3COO)_2.H_2O$), bluestone (copper(II) sulfate pentahydrate, $CuSO_4.5H_2O$) and sal ammoniac (ammonium chloride, NH_4Cl) and wetted it with alcohol to make a mixture that burned with a green flame. The materials used were ancient, and, as noted in Chapter 2, this effect could well have been known to Chinese fireworkers even before its appearance in 18th century Russia. Impressive as it was at the time, Ruggieri's green flame lacked the brightness that would soon be exhibited by the new chlorate-based coloured fires. Some of the old coloured firework compositions continued to be used even after the introduction of the new chlorate-base compositions, for two good reasons. They were less costly, and their pale hues would have added interesting variety to the performance. In 1854 Chertier devoted a couple of pages to zinc-based compositions for producing a pale greenish-blue, and as late as 1867 Websky, the pioneer of chlorate-based colours, included several old recipes for coloured lances in the manuscript for the final edition of his book.[95]

Meanwhile, in the early 1820s the search for a green fire to complement the chlorate-based red fire was underway. The first known account of a chlorate-based green fire was published in London in October, 1822:

> 'Green Fire.— In a former number of this Journal we presented our pyrotechnical readers with a recipe for the red fire which has lately gained so much celebrity in the theatrical representations of conflagrations, and which forms so beautiful a change in fireworks. We now give them the component parts of a more modern invention, which has long been a desideratum in this branch of art, namely, a green fire, and which, when burned in a reflector, sheds a beautiful green light upon all surrounding objects ; it may also be employed in the changes of fireworks, alternating with red and blue fire. Take of Flowers of sulphur13 parts, Nitrate of baryta 77, Oxymuriate of potassa 5, Metallic arsenic 2, Charcoal 3.
>
> 'The nitrate of baryta should be well dried and powdered ; it should then be mixed with the other ingredients, all finely pulverized, and the whole triturated until perfectly blended together. A little calamine may be occasionally added, in order to make the compound slower of combustion; and it is above all things requisite, that both in this and the red fire the trituration of the materials should be continued until they are completely mixed.' [96]

It is likely that the new green fire was also invented by John Forster. If it was, then Forster was responsible for the first known use of a barium salt to make a green pyrotechnic flame. The

[95] For Ruggieri's enthusiasm for the green alcohol flame in 1821, see *Élémens de pyrotechnie* (1821), pp. 101-104. For its first appearance, see *Elémens de pyrotechnie*, 2 ed. (Paris: Barba, 1810). Pp. xi-xv give the circumstances of its origin, the article *Les Palmiers*, pp. 103-106 gives the manner of its use, and the formula is given as *xxve Composition*. *Feu vert pour palmier* on p. 307. For Chertier's zinc compositions, see F.-M Chertier, *Nouvelles recherches sur les feux d'artifice*, 2 ed. (Paris: chez l'auteur, 1854), pp 362-364. Websky's old colour compositions are in Julius Hutstein and Martin Websky, eds., *Martin Websky's Lustfeuerwerkkunst, Leichtfassliche, bewährte Anleitung zur Anfertigung von Lustfeuerwerken inbesondere für Dilettanten und Freunde der Lustfeuerwerkerei*, Zweite Ausgabe der siebenten Bearbeitung, nach den hinterlassenen Aenderungen des Autors ed. (Leipzig: Ferdinand Hirt & Sohn, 1878), pp 110-117.

[96] 'T.G.', "Green fire," *The Quarterly Journal of Science, Literature and the Arts*, no. 27 (1822), pp. 231-232; "oxymuriate of potassa" was an early name for potassium chlorate. The formulation also appeared in other contemporary publications: Anonymous, "Green Fire." *The New Monthly Magazine and Literary Journal IV Historical Register* (1822), p. 549; Anonymous, "Green Fire." Museum of Foreign Literature and Science 1 (1822), p. 568; "Methode Pour Faire un Feu Vert," *Bulletin général et universel des annonces et des nouvelles scientifiques dédié aux savans de tous les pays et à la librarie nationale et etrangère*, 2 (1823), p. 34; Anonymous. "Grünes Feuer." *Dinglers Polytechnisches Journal* 11 (1823), pp. 255-56.

attribution of the new green fire to John Forster is based on two pieces of evidence: the similarity of the two compositions, and the statement in Forster's obituary that 'his name will always be associated with the first practical application of the salts of strontia and baryta to theatrical purposes' Salts of strontia (i.e. strontium salts) were used in red fire, while those of baryta (i.e. barium salts) were used in green fire. [97]

The green fire recipe is of interest for several reasons. It is the second published coloured flame composition containing potassium chlorate, the first to include a barium salt, and one of the very few published European recipes for firework compositions to include 'metallic arsenic'. As noted in Chapter 2, arsenic was used in some Chinese fireworks in the 18th century but it has rarely been mentioned in the European firework literature. It is not known why Forster included arsenic in his green fire composition. The two arsenic sulfides (realgar and orpiment) had long been used in fireworks and either of them would have sufficed; furthermore, Websky later (1831) mentioned that the arsenic in this green fire composition could be replaced by antimony, a much more common and less poisonous material. Forster's use of arsenic was not of any lasting significance. In contrast, the other new ingredient in the green fire composition, barium nitrate ($Ba(NO_3)_2$) was to be of tremendous importance in pyrotechny.[98]

The story of barium nitrate began in 1774, when the salt was mentioned by Scheele in the same paper in which he gave the first description of chlorine. It was described in more detail by the English physician and naturalist William Withering (1744-1799) some ten years later in his paper on his experiments on '*terra ponderosa aërata*' from a lead mine on Alston Moor in Cumberland and on '*terra ponderosa vitriolata*' from various sources. '*Terra ponderosa aërata*' was crystalline barium carbonate, $BaCO_3$. It was subsequently (1789) named 'witherite' in Withering's honour. *Terra ponderosa vitriolata*, also known as heavy gypsum, ponderous spar, heavy spar, calk, cauk or *Marmor Metallicum*, was crystalline barium sulfate, $BaSO_4$, now called barite. Withering describes melting *Terra ponderosa vitriolata* with salt of tartar (potassium carbonate, K_2CO_3), extracting the cooled melt with water and treating the insoluble part (i.e. barium carbonate, $BaCO_3$) with nitric acid, whereupon it dissolved with effervescence. The solution 'shot readily into beautiful permanent crystals, of a rough bitterish taste.' In 1793 Thomas Hope mentioned that the newly-discovered earth 'strontia' could be distinguished from 'barytes' by, amongst other things, its solution in muriatic (i.e. hydrochloric) acid imparting a red colour to 'the flame of combustible bodies', whereas the 'muriate of barytes' gave only 'a very faint greenish hue'. Subsequent writers usually described the barium flame as yellow, no doubt because their samples were impure. The green light emitted by the molecules BaOH and BaCl is accompanied by bluish-white light from BaO and is easily obscured by red, orange or yellow emissions from such species as SrCl, SrOH, CaCl, CaOH, and Na arising from strontium, calcium or sodium impurities. It is all the more remarkable, then, that John Forster was able to develop an effective green fire based on barium nitrate. At the time, barium nitrate was a rather obscure laboratory chemical, of interest to chemists as a source of 'caustic baryta' (barium oxide, BaO), which it yields on strong heating.[99]

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[97] For its similarity to the red fire, see Davis, "The Early use of Potassium Chlorate in Pyrotechny: Dr Moritz Meyer's Colored Flame Compositions." p. 79, Sturman, "Coloured Fire." Appendix. For Forster's obituary, see "Obituary of John Forster, esq," *Proceedings of the Linnean Society for 1872-3* (1873), p. xxxii.

[98] For arsenic as a pyrotechnic fuel, see Sturman, "The Early Use of Potassium Chlorate in Pyrotechny: Part II. John Forster, Sarah Hengler and the Original Chlorate-based Green Fire", p. 71.

[99] Carl Wilhelm Scheele, "On Manganese, Manganesium, or Magnesia Vitrarorium, 1774," in *The Chemical Essays of Charles-William Scheele, Translated from the transactions of the Academy of Sciences at Stockholm, with additiions.*, ed. Thomas Beddoes (London: J. Murray, 1786; reprint, Scott, Greeenwood & Co., London. 1901, University of Toronto Libraries 2013), pp. 65, 55-76. For the early history of barium, see Thomas Thomson, *A System of Chemistry of Inorganic Bodies*, 7th ed., Two vols., vol. 1 (London: Baldwin and Craddock, 1831), p. 422. Klaproth claimed that the original source of Witherite was not Alston Moore, as stated by Withering, but Anglezarke in Lancashire. The location of the deposit was kept secret by the miners, who suspected, on account of its great density, that the stone contained some noble metal. Klaproth suggested

The story of how the new barium nitrate-based Green Fire was introduced has not previously been told. A clue to the mystery was found in a newspaper advertisement for a Gala Fete to be held at the Wellington Gardens, Vauxhall on Monday, 19 August 1822. The Fete was to conclude with 'A most superb display of magnificent and unrivalled Fire-Works, by MADAME HENGLER, Pyrotechnist to His Majesty, and Engineer for 30 Years to the London Royal Gardens'. Madame Hengler was the English pyrotechnist Sarah Hengler, née Sarah Cannon (ca. 1765-1845). Item 3 in the Order of Firing was 'The newly-invented Green Fire (unknown to any other Artist), while Item 4 was 'The Resplendent Crimson Flame, which will present every surrounding object as on fire.' It is notable that the Green Fire was said to be 'newly-invented' and 'unknown to any other artist', whereas no such claim was made for 'The Resplendent Crimson Flame'. This is consistent with my previous account of the development of these two coloured fires, which places the invention of chlorate-based Red Fire (i.e. The Resplendent Crimson Flame) early in 1810 and the first publication of its formula in 1820. The first published discussion of the Green Fire in October 1822 indicated that it had been introduced recently; Hengler was promoting a newly-invented Green Fire in August 1822. It thus seems plausible that Hengler's Green Fire was the same as that published in October 1822, which I have attributed to John Forster. Furthermore, Hengler lived and worked close to Forster's home.[100]

The new chlorate-based red and green coloured fires set a high standard for other colours. Yellow fires based on sodium nitrate (as introduced by Lavoisier) would have complemented the new fires well, as would the white Bengal and Indian fires. The zinc-based blue, on the other hand, would have looked insipid in comparison. The next generation of blue fires would be based on potassium chlorate, with copper compounds as the colour-producing agents. The discovery that copper could produce blue and purple is of particular interest, not just because it increased the range of colours but because it shows how a new material (potassium chlorate) revealed novel applications for well-known, indeed ancient, materials. So far, no information about the development of these new copper-based colours has come to light. As noted previously, copper compounds were used in the production of green alcohol flames; attempts to use them to make green colours in fireworks resulted at best in a green-edged flame, but more commonly in no green effect at all.

The green flame of copper must have been noticed by the earliest people who brought copper or copper ore into contact with fire. The occasional appearance of a deep blue flame from copper must also have been noticed long ago. It is seen, for example, when wood from shipwrecks, soaked with sea-salt and containing copper nails, is burned. A French encyclopaedia published in 1772 mentioned that the neutral, hygroscopic green crystals (hydrated copper(II) chloride, $CuCl_2.2H_2O$) formed by evaporating a solution of copper in spirits of salt are suitable for imparting a green colour to

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that 'the base interestedness of the usurious dealers in fossils' might have perpetuated the deception. See Klaproth, "Chemical Researches into Strontianite compared with Witherite", pp. 224-225. For Withering on barium nitrate, see William Withering, "Experiments and Observations on the Terra Ponderosa, &c.," *Philosophical Transactions of the Royal Society of London* 74 (1784), p. 305 and p. 311. For Hope on the faint greenish flame of muriate of barytes, see Hope, "Account of a Mineral from Strontian, and of a Peculiar Species of Earth which it Contains", p. 23. For an instance of the barium flame being described as yellow (in this case *gelblichtweißen*, i.e. yellowish-white), see Klaproth, "Chemische Versuche über die Strontianerde", p.197. For repeated statements that barium salts colour the flame yellow, see John W. Webster, *A manual of chemistry, on the basis of Professor Brande's: containing the principal facts of the science, arranged in the order in which they are discussed and illustrated in the lectures at Harvard University, N.E; the United States Military Acadamy, West Point; Brown Univerity, Amherst, and several other colleges in the United States. Compiled from the works of the most distinguished chemists* 2ed. (Boston: Richardson and Lord, 1828), pp. 308, 312, 538.

[100] A recent book made passing mention of Sarah Hengler exhibiting a newly-invented Green Fire: Gary Hicks, *The First Adman: Thomas Bish and the Birth of Modern Advertising* (Brighton: Victorian Secrets Limited, 2012), p. 160. Mr Hicks kindly provided me with the source: Anonymous, "Gala Fete," *The Bristol Mercury*, August 18, 1822, p.2. For the first publication of the crimson fire, see "Red fire," *The Quarterly Journal of Science, Literature and the Arts* 9 (1820), p. 441.

fireworks, but when the crystals are thrown into a brazier 'the flame retains, for a long time, a very lively rainbow colour.' [101]

A 'rainbow colour' implies colours in addition to green and blue, and indeed copper can also produce orange-red flames. In firework-making, this permits the production of purple fires using copper salts as the only colour agent. The ability of copper to produce a range of flame colours is a consequence of the formation of different copper-containing gases in the flame, depending on the chemical environment. The green colour that copper salts impart to alcohol flames is produced by copper monohydroxide (CuOH). In chlorate-based pyrotechnic mixtures copper salts more readily form copper monochloride, CuCl, which emits blue. The tip of the blue flame, where entrained air increases the concentration of oxygen, is coloured orange-red by emission from copper monoxide, CuO. If there is excess potassium chlorate in the composition, the oxidizing flame conditions lead to the formation of some red-emitting CuO in the body of the flame. This, combined with blue from CuCl, can produce purple. None of this detail was known in the early nineteenth century – the phenomena came long before the explanation..

Given that copper compounds were associated with green flames, it is probable that they were initially tried in the new chlorate-based compositions with the intention of making green. It must have been surprising to find that mixtures of copper compounds with potassium chlorate and sulfur burned blue or purple, depending on the proportions of the ingredients. Evidence for such compositions is difficult to find. The mention of blue firework flames, as in the note on the new green fire of 1822, is not sufficient, because zinc-based blues were already in use, and it was also common to describe the bluish-white flame of some antimony-based compositions as blue. The mention of purple is also insufficient, as the strontium flame was sometimes described as 'purple'.

Recipes for chlorate-based blue fires were published in 1831 by Martin Websky. It seems likely that copper-based blue and purple fires were already in use in England at about the same time. The evidence for this is some examples of copper-based blue and purple fires disclosed by James Marsh, who worked at the Royal Laboratory at Woolwich for some 40 years from his boyhood until his untimely death. Marsh's career is reviewed in Chapter 7. His interest in coloured fires is known from three sources, only one of which was written by him, and all of which are separated by many years from the time (the late 1820s) when the colour compositions that he quoted would have been new. These sources are the paper that Marsh wrote in 1843, a book of practical formulas published in 1845 and a book on the industrial applications of science published as late as 1881.[102]

Marsh's compositions for coloured stars containing potassium chlorate are listed in Table 4.2 Modern chemical names have been used, but Marsh's numbers are reproduced from the original.[103]

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[101] Fortunato Bartolomeo De Felice, Denis Diderot, and Jean Le Rond d' Alembert, "Cuivre," in *Encyclopédie ou Dictionnaire universel raisonné des connoissances humaines* (1772), p. 520.

[102] Marsh, "On the Manufacture of Gunpowder, and on the Proportions of Ingredients Used by Various Nations; with the Modes of Preparing the Various Coloured Fires, Signal Rockets, &c."; Arnold J Cooley, "Pyrotechny," in *A Cyclopaedia of Practical Receipts, and Collateral Information in the Arts, Manufactures, Professions, and Trades*, ed. Arnold J Cooley (1845); Watt, Alexander. "Manufacture of Fireworks", in *Scientific Industries Explained: Showing How Some of the Important Articles of Commerce are Made*. Edinburgh and London: W. & A. K. Johnston, 1881, pp. 18-26.

[103] Marsh, "On the Manufacture of Gunpowder", pp. 24-25.

	Green	Crimson	Blue	Purple	Lilac
Potassium chlorate	23.607	17.244	69	77.419	50
Sulfur (sublimed)	10.556	17.904	24	12.904	25
Barium nitrate	62.587				
Charcoal (fine)	1.625	4.138			
Arsenic sulfide	1.625				
Strontium nitrate		55.197			
Antimony sulfide		5.517			
Copper sulfate			7	9.677	
Calcium carbonate					22
Black copper oxide					3

Table 4.2. Chlorate-based colour compositions for 'pill box' stars, as presented by James Marsh.

The star compositions were to be 'driven into the smallest sized pill boxes, with very light taps with a wooden mallet and a short cylindrical stick', and primed with quick match and blue touch paper. As discussed elsewhere, the red and green star compositions in Table 4.2 are rather direct modifications of the original red and green theatrical coloured fires, suggesting that they are early. Marsh presumably obtained these recipes at Woolwich Arsenal, so it seems likely that they were developed there in the late 1820s for coloured military signal rockets, as discussed in Chapter 7. This is supported by Marsh's presentation of recipes for yellow and white stars. These recipes are not presented in Table 3.2 as they do not contain potassium chlorate, but they would have been needed for the signal rockets. These were demonstrated late in 1831, so the colour compositions used in them must have been formulated at about the same time as Websky's, if not before. [104]

Marsh did not elaborate on the 'sulphate of copper' used in the blue and purple stars. Commercial copper sulfate ('bluestone' or 'blue vitriol') is copper(II) sulfate pentahydrate, $CuSO_4.5H_2O$. It has been known since ancient times. In Marsh's day it was used for in medicine and was readily available from apothecaries and chemical merchants. In 1836 Chertier wrote that 'sulfate de cuivre' gives a 'passable blue', but must first be roasted, i.e. dehydrated. The use of anhydrous copper sulfate in coloured fires is most objectionable. It readily re-absorbs water, becoming very hot in the process, and the product is acidic. Acid and chlorates are a bad combination, producing extremely reactive substances (chloric acid ($HClO_3$) and chlorine dioxide (ClO_2)) that are explosive in their own right and readily cause combustible materials to ignite. The problem of acidity exists irrespective of whether the copper sulfate is present as the hydrate or as the dehydrated salt recommended by Chertier. Not surprisingly, Marsh remarked that a composition containing 'Sulphate of Copper' 'is very liable, in hot situations, to undergo spontaneous combustion; it is, therefore, best not to make it up until wanted.' The black copper oxide (CuO) used in another of Marsh's coloured star compositions is insoluble in water and would have been a much safer choice. It had been known for a long time as an ingredient in coloured glazes for ceramics and would have been available in Marsh's time. In the lilac composition given by Marsh, copper oxide is only a minor ingredient, the main colour agent being calcium carbonate. This would impart a red colour due to the formation of CaCl in the flame; the copper oxide provided enough blue from CuCl to make the perceived colour lilac. [105]

[104] Ibid., p. 24. For the signal rocket project, see Chapter 7, also Sturman, "Coloured Fire", pp. 50-52 and "The Early Use of Potassium Chlorate in Pyrotechny: Part III. Applications of Early Chlorate-based Coloured Flame Compositions "

[105] F.-M Chertier, *Essai sur les compositions qui donnent les plus belles couleurs dans les feux d'artifice* (Paris: Delaunay, 1836), pp 21-22. Chertier's compositions (No. 57, Blue, p. 53) are not the same as Marsh's. For Marsh's warning on spontaneous combustion, see Marsh, "On the Manufacture of Gunpowder", p. 25.

Marsh's formulations for blue and purple stars are very similar; the purple has a much higher ratio of potassium chlorate to sulfur, making the flame conditions more oxidizing and thus promoting the formation in the flame of red-emitting copper monoxide, as needed for purple stars. If the blue and purple compositions disclosed by Marsh are as early as they seem, they would be some of the first compositions to contain both potassium chlorate and a copper salt. The compositions that Marsh presented for coloured stars were probably similar to, or even identical with, those used by the British military some 12 years previously, as discussed in Chapter 7. The new ingredients introduced since Lavoisier's time were strontium nitrate, potassium chlorate and barium nitrate. The ancient materials copper sulfate, copper oxide and calcium carbonate found new applications as colour agents in blue, purple and lilac fires. The main combustible in these colour compositions was sulfur, with minor additions of the well-known combustibles charcoal, antimony sulfide and arsenic sulfide. Arsenic was a minor fuel in the original green fire.

In 1831 Johann Martin Websky published the earliest known account of the new coloured fires after the original publications of 1820 and 1822. He presented different compositions for lights, lances and stars, and introduced some new ingredients, all of which were common industrial products at the time. Websky used crystallized verdigris as a source of copper for both green and blue fires. Crystallized verdigris, as noted in Chapter 3, was an ingredient of the green alcohol flame known as Russian Fire. By including potassium chlorate in his composition, Websky made a green copper-based pyrotechnic flame – something that had been sought, but imperfectly achieved, for centuries. Potassium chlorate favours the production of blue-emitting CuCl; by keeping the amount of potassium chlorate to the minimum required to give sufficiently vigorous combustion, with saltpetre as the main oxidizer, and by adding hydrogen-containing fuels, Websky produced a mixture that yielded enough CuOH to give a clear green flame. The same copper salt, in a composition with potassium chlorate as the only oxidizer, burned blue. A tremendous amount of painstaking work must have been required to achieve these two colours from the same colour–producing chemical, especially as the cause of the colours was unknown.[106]

The other new ingredients mentioned in Websky's 1831 book included red lead (lead(II,II,IV) oxide, Pb_3O_4), soda ash (sodium carbonate, Na_2CO_3) and carbonate of strontia (strontium carbonate,$SrCO_3$). Websky used red lead as a white colour agent, which recalls the Chinese use of white lead for the same purpose, as reported by d'Incarville. Red lead has the advantage over white lead that in decomposing it yields oxygen, which enhances combustion, rather than the carbon dioxide and water released by white lead, which inhibit combustion. Sodium carbonate was used by Websky as a yellow colour agent. It is not as hygroscopic as sodium nitrate. Websky was the first to describe the use of strontium carbonate in fireworks. He did not use the naturally-occurring mineral, but prepared the pure compound himself by adding potassium carbonate solution to a solution of strontium nitrate, and used it in a composition for red stars. Strontium carbonate is insoluble in water and has the advantage over strontium nitrate of not absorbing moisture from the air.

Two years after the publication of Websky's book the Prussian military chemist Meyer published discussions of the use of potassium chlorate in coloured fires. He introduced several new colour agents. All the colour agents mentioned by Meyer, and the colours that they produced when burned with a mixture of potassium chlorate and sulfur, are shown in Table 4.3. The new ingredients are in bold type.[107]

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[106] Websky, Martin. *Grundlich und fasstliche Anweisung zur Verfertigung kleiner Lustfeuerwerke, zunachst für Dilettanten der Feuerwerkskunst.* Landeshut: W. Pfingsten, 1831. The green formulae are on p. 29, the blue is on p. 28.

[107] Meyer, Franz Eduard Moritz. "Ueber die schiesspulverartigen Mischungen zur Erzeugung bunter Flammen." *Erdmanns Journal für technische und ökonomische Chemie* 16 (1833), pp. 139-45; "Uber Schiesspulver und schiesspulverartige Mischungen zu bunten Flammen." *Pharmaceutisches Central-Blatt für 1833* 2 (1833), pp. 783-789; *Die Feurewerkerei in ihrer Anwendung auf Kunst, Wißenschaft und Gewerb*e. Leipzig: Johan Ambrosius Barth, 1833; "Bunten Flammen zur Theaterbeleuchtung." *Erdmanns Journal für technische und ökonomische Chemie* 17 (1833), pp. 380-381.

Ingredient	Chemical composition	Flame colour
Fluorspar	**Calcium fluoride, CaF_2**	Light pink, with green
Calcium chloride	**Calcium chloride, $CaCl_2$**	Pink
Gypsum	**Calcium sulfate dihydrate, $CaSO_4.2H_2O$.**	Pink-red
Carbonate of strontian.	Strontium carbonate, $SrCO_3$.	Purple-red
Chalk (carbonate of lime).	Calcium carbonate, $CaCO_3$.	Purple-red
Carbonate of soda mixed with carbonate of lime.	Calcium carbonate, $CaCO_3$, plus sodium carbonate, Na_2CO_3.	Orange
Carbonate of soda.	Sodium carbonate, Na_2CO_3.	Yellow
Nitrate of soda.	Sodium nitrate, $NaNO_3$.	Yellow
Boracic acid.	Boric acid, H_3BO_3.	Pale green
Carbonate of baryta.	**Barium carbonate, $BaCO_3$.**	Apple green
Sulphate of potash.	**Potassium sulfate, K_2SO_4.**	Pale blue
Well-burnt alum.	**Potassium sulfate, K_2SO_4 and aluminium oxide, Al_2O_3.**	Pale blue
Carbonate of copper oxide plus alum (presumably well-burnt alum, as above)	**Basic copper carbonate (could be either $Cu_2CO_3(OH)_2$. or $Cu_3(CO_3)_2(OH)_2$), plus potassium sulfate, K_2SO_4 and aluminium oxide, Al_2O_3.**	Dark blue with red sparks
2 parts ammoniated basic sulphate of copper mixed with 1 part sulphate of potash.	**2 parts tetraamminecopper(II) sulfate monohydrate, $Cu(NH_3)_4SO_4.H_2O$, and 1 part potassium sulfate, K_2SO_4.**	Blue
Well-burnt alum, or sulphate of potash, plus carbonate of lime.	Potassium sulfate, K_2SO_4, and aluminium oxide, Al_2O_3, or potassium sulfate, K_2SO_4, plus calcium carbonate, $CaCO_3$.	Violet

Table 4.3. Colour-producing materials presented by Meyer in 1833.

Most of these new ingredients are what might be categorized as 'chemicals', as distinct from the natural products and industrial wastes so prominent in lists of 18th century firework ingredients. This reflects the growing importance of chemistry, both as an academic discipline and as the basis of many industrial processes. Entrepreneurs found it worthwhile to set up businesses dedicated to the supply of chemicals for laboratories and for industrial applications, and these businesses were a source of new materials for firework-making, as discussed in Chapter 8.

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Of the new ingredients introduced by Meyer, gypsum, barium carbonate and basic copper carbonate were of lasting value as pink, green and blue colour agents respectively. They are all insoluble in water, and do not attract atmospheric moisture.

Websky and Meyer were not the only investigators working on coloured fires in the 1830s. In 1836 Chertier independently published a wide range of colour compositions, most based on potassium chlorate. Chertier introduced many new materials in this work, as shown in Table 4.4.[108]

[108] Chertier, F.-M. *Essai sur les compositions qui donnent les plus belles couleurs dans les feux d'artifice*. Paris: Delaunay, 1836.

Ingredient	Chemical composition
Arsenate of copper	Copper(II) arsenate tetrahydrate, $Cu_3(AsO_4)_2 \bullet 4H_2O$
Artificial gilding	Copper, probably with 10-12% zinc
Bicarbonate of soda	Sodium hydrogen carbonate, $NaHCO_3$
Bromate of baryta	Barium bromate, $Ba(BrO_3)_2$
Calomel	Mercury(I) chloride, Hg_2Cl_2
Carbonate of copper	Copper(II) carbonate - Copper(II) hydroxide (2/1), $(CuCO_3)_2.Cu(OH)_2$
Carbonated copper ore in blue crystals	Copper(II) carbonate - Copper(II) hydroxide (2/1), $(CuCO_3)_2.Cu(OH)_2$
Chlorate of baryta	Barium chlorate, $Ba(ClO_3)_2 .H_2O$
English blue ash	Copper(II) carbonate - Copper(II) hydroxide (2/1), $(CuCO_3)_2.Cu(OH)_2$
Litharge	Lead(II) oxide, PbO
Malachite	Copper(II) carbonate - Copper(II) hydroxide (1/1), $CuCO_3.Cu(OH)_2$
Oxalate of copper	Copper(II) oxalate hemihydrate, $CuC_2O_4 \bullet ½H_2O$
Oxalate of soda	Sodium oxalate, $Na_2C_2O_4$
Phosphate of copper.	Copper(II) phosphate hydroxide, Cu_2PO_4OH
Sulphate of copper precipitated by lime water	Copper(II) sulfate hydroxide, $CuSO_4.3Cu(OH)_2.H_2O$ mixed with calcium sulfate dihydrate $CaSO_4.2H_2O$
Tartrate of copper	Copper(II) tartrate trihydrate, $CuC_4H_4O_6 \bullet 3H_2O$
White precipitate	Mercury(II) amine chloride, $HgNH_2Cl$

Table 4.4. New pyrotechnic ingredients presented by Chertier in 1836.

The discovery of the usefulness of these materials was the result of a comprehensive program of exploratory research in which Chertier tested just about any substance that he could obtain, not just by itself but in combination with other substances. Ten of the new substances contain copper, which is indicative of the difficulty in finding one that gave a really satisfactory blue. One of the copper-containing materials mentioned by Chertier, Artificial Gilding, was a high-copper alloy in ultra-thin sheets used for gilding picture frames and the like; this was not used as a blue colour agent, but to modify the shade of red fires and to remove any yellow cast from green fires. Of the remaining copper-containing materials, copper oxalate and copper tartrate were mentioned only to note that they were not particularly good. Copper arsenate, on the other hand, was the main ingredient of some of the best blue compositions. It was available commercially, but of such inconsistent quality that Chertier made it himself, and gave detailed instructions for its preparation.[109]

Copper phosphate was available from chemical suppliers, but was so very variable in its properties from one sample to the next that Chertier abandoned it in favour of a completely different copper compound. Most of his text headed 'Phosphate of Copper' is a detailed recipe for making this substitute, to which Chertier subsequently referred as 'Sulphate of copper precipitated by lime water'.[110]

[109] I have been unable to find references from Chertier's time to any uses of copper arsenate that would account for its being available at 'chemical products factories' as stated by Chertier. It could have been one of many materials provided for chemical laboratories. Chertier gave 7 compositions containing 'arsenate of copper' in his 1836 publication.

[110] I have been unable to find any applications that would account for this chemical being commercially available; presumably it was another 'laboratory chemical'.. The recipe that Chertier gave for the substitute would produce an insoluble basic copper sulfate, most likely $4CuO.SO_3.4H_2O$ or, equivalently, $CuSO_4.3Cu(OH)_2.H_2O$, mixed with calcium sulfate dihydrate, $CaSO_4.2H_2O$ See Hubert Thomas Stanley Britton, "CCCLXXXVI.—An electrometric and a phase rule study of some basic salts of copper " *Journal of the*

Four of the materials introduced by Chertier are varieties of the two different copper carbonate-copper hydroxides. These occur as minerals: blue azurite, $(CuCO_3)_2.Cu(OH)_2$, and green malachite,$CuCO_3.Cu(OH)_2$. They can also be made synthetically. As mentioned above, Meyer used 'carbonate of copper oxide' but did not otherwise specify it. The 'copper carbonate' of commerce, made by precipitating a solution of a copper salt with a soluble carbonate, may be either blue (predominately azurite), or green (malachite). In the presence of water azurite is unstable, evolving carbon dioxide and becoming malachite. Two of the other materials introduced by Chertier ('carbonated copper ore in blue crystals' and 'English blue ash'), are also azurite. Chertier did not know that 'carbonate of copper' prepared according to his instructions, 'English blue ash' and 'carbonated copper ore in blue crystals' were the same substance. Chertier wrote that malachite 'can replace the blue crystals of carbonated copper ore. It is used in the same way and in the same proportions. I have found, however, that the blue crystals are preferable...'. For the same quantity of copper, malachite contains 50% more combined water than azurite, which may explain Chertier's preference. Water would promote the formation of green-emitting copper monohydroxide (CuOH), which would impart a greenish cast to the blue emitted by CuCl. [111]

In his search for a better blue colour agent, Chertier investigated copper chlorate, noting that it was unique among copper compounds in imparting a cornflower-blue colour to the alcohol flame. It was too deliquescent to be practical. Chertier subsequently devoted much effort to attempting to remedy this defect, with interesting results, which he presented in his 1843 book and which will be discussed later.[112]

Another promising chlorate, sodium chlorate, while less deliquescent than copper chlorate and yielding a good yellow, was considered by Chertier to be too expensive. He mentioned it only to recommend that it not be used. [113]

Chemical Society, Transactions 127 (1925), pp. 2796-2807; James M. Bell and George M. Murphy, "Basic Copper Sulfate at 100°," *Journal of the American Chemical Society* 48, no. 6 (1926), pp. 1500-1502.

[111] See B. W. Vink, "Stability Relations of Malachite and Azurite," *Mineralogical Magazine* 50 (1986), pp. 41-47. Freshly-precipitated azurite is easily converted into malachite on standing or by heat; commercial 'copper carbonate' is therefore almost always malachite. Chertier's method of preparing 'carbonate of copper' yielded the blue form, i.e. azurite. Chertier gives 12 recipes containing this blue 'carbonate of copper' in his 1836 publication.

[112] Copper chlorate was described by Vauquelin in 1815. Louis Nicolas Vauquelin, "Chlorate de cuivre," *Annales de Chimie et de Physique* 95 (1815), pp 133-134. Vauquelin commented on the magnificent *green* colour produced by the combustion of paper impregnated with a concentrated solution of copper chlorate, and this observation was subsequently repeated in various chemistry texts, to Chertier's annoyance. He wrote: 'it produces a beautiful cornflower blue flame, (not green, as certain chemists erroneously state).' Curiously, there is another instance of Vauquelin reporting a green flame where a different colour would be expected:

> A mixture of strontium nitrate, sulphur and carbon, in the same proportions in which the latter two bodies are in gunpowder, although accurate, dry, burned very slowly while throwing purplish sparks, and producing a flame of a beautiful green that licked the surface of the burning material..

"Note sur le sulfate de strontiane et les combinaisons de cette nouvelle terre, par le C.en Vauquelin," *Journal de la Société des Pharmaciens de Paris*, no. 13 (1798), p. 138. In the same publication, Vauquelin referred to the beautiful *purple* flame produced by burning a solution of strontium chloride in alcohol, and to the very beautiful purplish colour imparted to the flame of a candle by strontium nitrate. This makes the reference to a green flame from strontium nitrate all the more puzzling. Was Vauquelin colour-blind? It would be interesting to search his writings for other mentions of colours that might provide further insights into this possibility.

[113] The preparation of sodium chlorate was first reported in 1788 by Berthollet, as noted above. Further work was published in 1802 by Irish chemist Richard Chenevix (1774-1830): Richard Chenevix, "Observations and

Other yellow colour agents that Chertier investigated were bicarbonate of soda (sodium hydrogen carbonate, $NaHCO_3$) and sodium oxalate ($Na_2C_2O_4$). Both are non-hygroscopic and completely stable in air, and both decompose on heating to sodium carbonate. Sodium oxalate has the advantage of releasing combustible carbon monoxide gas when it decomposes, whereas sodium bicarbonate yields water and carbon dioxide[114]

The search for effective green colour agents led Chertier to study two chemicals that were otherwise of interest only to academic chemists. One of these was the very costly 'chlorate of baryta' (barium chlorate monohydrate, $Ba(ClO_3)_2.H_2O$). Mixed with sulfur, this gave a beautiful emerald green, but only if it were 'perfectly pure'. If it were not, it gave at best a yellowish-green and was also prone to spontaneous ignition. Chertier gave detailed instructions for its purification.[115]

The other novel green colour agent investigated by Chertier was bromate of baryta (barium bromate monohydrate, $Ba(BrO_3)_2.H_2O$. This was even more expensive than barium chlorate, and did not give as deep a green, so it was not recommended. It is worth mentioning because it shows that Chertier knew about this rare chemical, discovered only 10 years earlier; furthermore, it is the first known example of a bromine compound being used in fireworks; the green colour emitter is barium monobromide, BaBr. [116]

Experiments upon oxygenized and hyperoxygenized muriatic Acid; and upon some Combinations of the Muriatic Acid in its three States " *Philosophical Transactions of the Royal Society of London* 92 (1802), pp. 126-167, p.144-145. Chertier seems to have been the first to discuss its possible use in pyrotechny. Its costliness arose from the extreme difficulty in separating it, by repeated re-crystallization from alcohol, from the sodium chloride that was necessarily produced during its preparation.

[114] Sodium bicarbonate occurs naturally in Egypt and elsewhere as a component of the mineral Trona, but this was not characterized until as late as 1802. See Martin Heinrich Klaproth, "Chemischer Untersuchung des ägyptischen Natrum," in *Beiträge zur chemischen Kenntniss der Mineralkörpe*, ed. Martin Heinrich Klaproth (Posen: Decker und Compagnie, 1802) , pp. 80-82. It is easily prepared by passing carbon dioxide gas into a solution of sodium carbonate, and was manufactured commercially in this way in Chertier's day. See William Thomas Brande, *A manual of chemistry: containing the principal facts of the science, arranged in the order in which they are discussed and illustrated in the lectures at the Royal Institution of Great Britain* 2vols., vol. 1 (London: John Murray, 1830), p. 433. Chertier seems to have been the first to discuss its use in pyrotechny. Potassium hydrogen oxalate, KHC_2O_4, had long been known as 'salt of Sorrel' and was extracted commercially from the juice of the plant *Oxalis acetosella* (wood sorrel or common wood sorrel), especially in Switzerland. It was used for bleaching straw, for removing ink-stains and iron-mould from linen, and for cleaning metal objects. The corresponding acid, 'acid of Sorrel' was shown by Scheele in 1776 to be identical with 'acid of sugar', obtained by treating common sugar (sucrose, $C_{12}H_{22}O_{11}$) with nitric acid. See Thomas Thomson, "Of Oxalic Acid," in *A System of Chemistry. In Four Volumes* (Edinburgh: Bell & Bradfute, and E. Balfour, 1802), pp. 103-108. By 1789 the acid was known as oxalic acid (from the plant name *Oxalis*) and its salts were called oxalates. Sodium oxalate, obtained by neutralizing oxalic acid with caustic soda or sodium carbonate, was known to be only moderately soluble in water; see Antoine Francois Fourcroy, "Of the Oxalic Acidulum, or Salt of Sorrel, that is sold in commerce, and of the pure Oxalic Acid," in *Elements of Natural History and Chemistry* (London: C. Elliot and T. Kay, 1790), p. 665; also J. E. Berard, "Observations on the Alkaline Oxalates and Superoxalates, and Particularly on the Proportions of their Elements," *A Journal of Natural Philosophy, Chemistry and the Arts: Illustrated with Engravings; by William Nicholson* 31 (1812), p. 25. Again, Chertier seems to have been the first to discuss its use in pyrotechny.

[115] The preparation of this salt was first reported by Chenevix in 1802 See Chenevix, "Observations and Experiments upon oxygenized and hyperoxygenized muriatic Acid", pp. 145-147. He made it by passing chlorine gas into a solution of barium hydroxide and then removing the accompanying barium chloride with silver phosphate. Chertier seems to have been the first to discuss its use in pyrotechny. He gives one recipe (for emerald green stars, with several variations) using this chemical in his 1836 publication.

[116] Barium bromate was discovered by French chemist Antoine Jérôme Balard (1802 – 1876) only some 10 years before Chertier wrote of it. Balard mentioned that it melted and burned with a green flame when placed on

Perhaps the most important of the new materials introduced by Chertier was calomel (mercury(I) chloride, Hg_2Cl_2). This would be used in coloured fireworks until the second half of the 20th century, when its ever-increasing prices led to its being abandoned long before modern concerns about the toxicity of mercury made it unacceptable. Calomel had already been known for a long time in Chertier's day, and was used in medicine as a purgative. There was no reason to expect that it would be useful in fireworks. It is not an oxidizer, it does not burn, nor does it impart any interesting colour to the flame. Chertier's practice of testing just about any material, not just alone but in combination with others, led him to discover that calomel had a pronounced effect in coloured fires: 'mixed with the blue, it renders the colour deeper and more beautiful; it forms part of several other compositions, which it modifies and improves noticeably.' The phenomenon was not fully understood until the mid 20th century, when it was realized that calomel increases the concentration of atomic chlorine in the flame, which in turn increases the concentration of colour-emitting metal monochloride molecules. In modern coloured fires the same function is performed by less expensive materials such as chlorinated rubber or polyvinyl chloride. If ammonium perchlorate is used as the oxidizer, such additional sources of chlorine are often unnecessary. [117]

Chertier was to continue his research on fireworks for the rest of his life, and would publish his results in two editions of a rather large book. Of the materials that Chertier discussed in that book, the most important was shellac. This was not new to pyrotechny, but until Chertier studied it, its value was not appreciated. Websky mentioned it in his 1839 book, but only as one of several resinous substances of some use in pyrotechny. It was certainly not a new material, having been used in India since ancient times for wood-finishing and for making small decorative objects. Shellac is unusual among resins in being an animal product; it is exuded by female scale insects (*Kerria lacca)*. Shellac was known in Europe from the end of the 16th century and by the 18th it was being imported from India for making sealing wax and for wood finishing. It is essential for French polishing, which became popular in the 18th century. A major deterrent to its application in fireworks was its high price. In 1834 shellac was available on the London market for 21 to 25 shillings a pound, depending on the grade.[118]

The value of shellac to the pyrotechnist was first made plain by Chertier in the first (1843) edition of his book. He explained how to overcome the great difficult in powdering 'gomme laque'. He recommended melting it with saltpetre on a sand bath, pulverizing the cooled mass, and leaching out the saltpetre with water. Preferably, he suggested melting the shellac with the proper quantity of one of the other ingredients of the final composition, thus eliminating the need for leaching. Examples of Chertier's red compositions that included shellac are shown in Table 4.5.

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hot coals. Balard, "Mèmoire sur une substance particulière contenue dans l'eau de la mer (le brôme) (Extrait)," *Journal de Pharmacie et des Sciences Accessoires* 12, no. 10 (1826), pp. 518-526.

[117] For the early history of calomel, and its nomenclature, see W. R. Wahtton, "On the Origin of the Name of Calomel," *Annals of Philosophy* 2 (New Series) (1821), pp. 427-430. For a comprehensive account of calomel, including its history and its medicinal use in Chertier's day, see Jonathan Pereira, *The Elements of Materia Medica and Therapeutics*, 2nd ed., vol. 1 (London: Longman, Brown, Green, and Longmans, 1842), pp. 736-746. See also Alexander Means, "Calomel - its Chemical Characteristics and Mineral origin considered, in view of its Curative claims," *Southern Medical and Surgical Journal* 1 (New Series), no. 3 (1845), pp. 97-112. For the modern view of the sources of colour in pyrotechnic flames, see R. F. Barrow and E. F. Caldin, "Some Spectroscopic Observations on Pyrotechnic Flames," *Proceedings of the Physical Society (London)* 62B (1949), pp. 32-39.

[118]Websky, *Lustfeuerwerkerei für Dilettanten*, pp. 82- 83. Shellac was listed as an ingredient in one of several strange firework compositions published by a Scottish author in 1840 but again there was no discussion of it. See Samuel Bruce, *A New Guide to Pyrotechny : or, The Noble Art in Miniature of Making and Letting Off Fireworks of Every Kind* (Edinburgh: Nicol Bowack, 1840), pp. 30 and 41. For the production, uses and price of shellac in the 1830s, see John Ramsay McCulloch, ed. *Dictionary, Practical, Theoretical and Historical, of Commerce and Commercial Navigation*, 2 vols., vol. 2 (Philadelphia: Thomas Wardle, 1843), pp. 122-123.

Ingredient ↓ \ Composition →	**1**	**2**	**3**	**4**	**5**	**6**
Potassium chlorate	78	-	-	-	-	-
Shellac	15	24	2	9	15	9
Strontium sulphate	72	-	-	-	-	-
Mealed gunpowder	-	36	-	-	-	-
Potassium nitrate	-	12	4	-	-	-
Strontium nitrate	-	264	72	72	72	72
Sulfur	-	36	24	6	-	6
Lampblack	-	5	2	-	-	3
Calomel	-	-	-	-	-	12

Table 4.5. Examples of Chertier's red fire compositions containing shellac (1843)

Composition 1 is a versatile red fire, suitable for stars, lances and colour grains. As the colour agent is insoluble strontium sulfate, it does not absorb atmospheric moisture. Lightly dampened with spirit of wine, it can be made into pellets or granules that become quite hard on drying and do not easily break or crumble. Chertier mentioned that he had tried strontium sulfate with potassium chlorate and sulfur and obtained only a 'mediocre pink'. On replacing the sulfur with shellac, he obtained a 'sufficiently beautiful' red. This seems to be the first instance of the successful use of strontium sulfate as a red colour agent - a fine example of the application of one material (shellac) making possible the application of another (strontium sulfate), previously thought to be useless. Chertier wrote that the difference between sulfur and shellac in this application was inexplicable, because shellac does not itself burn red with potassium chlorate, but produces only a dirty white colour. Modern chemistry explains the difference with reference to chemical thermodynamics; it turns out that the shellac mixture burns at a higher temperature than the sulfur mixture, and consequently produces much more of the strontium monochloride gas that emits the red light.[119]

The rest of the compositions in Table 4.5 are remarkable examples of red fires that contain no potassium chlorate. Composition no. 2 was for red stars, said to be 'very brilliant, but not very intense'. As it contained strontium nitrate, it attracted moisture from the air and did not keep well. All the other compositions were for burning as loose powders, to illuminate the surroundings with red light. Chertier admitted that they were not as good as red fires that included potassium chlorate, but they were still useful. Chertier seems to have been particularly proud of composition no. 5. He stated that while others had unsuccessfully tried to make red fire with saltpetre instead of potassium chlorate, with this composition he had succeeded in making red fire that contained no potassium chlorate, no saltpetre and no sulfur, 'thanks to shellac, which produces a miraculous effect in this composition.' Chertier described the colour of the flame as 'nasturtium' red; whereas he called that of composition 1 'poppy' red. This difference in colour arises because composition 5, which contains no source of chlorine, produces red light from strontium monohydroxide (SrOH), rather than from SrCl, and consequently its light has the orange-red cast characteristic of SrOH, reminding Chertier of the colour of the nasturtium flower. The light from composition 1 would presumably consist of emissions from both SrOH and SrCl, the combination of the orange-red of the former with the purplish-red of the latter yielding poppy-red. Shellac thus made possible different shades of red in coloured fires.

[119] A stoichiometric mixture of potassium chlorate and sulfur can reach a maximum temperature of 2354 K on combustion, whereas a mixture of 78 parts of potassium chlorate with 15 parts of shellac (as in Chertier's composition 1 in Table 3.6) reaches a maximum of 2570 K. The addition of 72 parts of strontium sulfate (as in composition 1) reduces the temperature to 1864 K, whereas the addition of the same quantity of strontium sulfate to a stoichiometric mixture of potassium chlorate and sulfur containing the same quantity of potassium chlorate as Composition 1 produces a maximum combustion temperature of only 1618 K. At the latter temperature hardly any of the strontium sulfate is converted to gaseous $SrCl_2$, the precursor of the colour-emitting molecule SrCl. At the higher temperature produced by shellac, 15 times as much $SrCl_2$ is produced. Not only is there more $SrCl_2$, but at the higher temperature much more would be broken down to SrCl and more SrCl would be thermally excited, as required for the emission of red light.

Chertier's recognition in the early 1840s of the usefulness of shellac in red fires raises the question: what might have happened if shellac had been introduced into pyrotechny much earlier? Websky, in his 1839 book, stated in passing that one of the best of the old compositions for red lances was a mixture of 4 parts saltpetre and 1 part of shellac. This composition was mentioned by Chertier in 1843 as mediocre, but useful for pink lances and stars. It was also listed by Pacini in 1845 as suitable for a violet lance. A modern study showed that the flame has a pinkish-red core and a lilac outer region. It would be interesting to know when this composition was first discovered. Were it not for the high price of shellac, and perhaps the difficulty of powdering it, this simple composition might have been developed in the mid 18th century, when shellac was certainly being imported into in Europe. Had that happened, it would have been obvious, when the flame-colouring properties of strontium nitrate were recognized in the mid 1790s, to replace the saltpetre in the composition with strontium nitrate and thus obtain a red fire that would have been perfectly adequate for stage effects – indeed, in some respects it would have been better than the chlorate-sulfur based compositions that were eventually employed. The shellac mixture produces little smoke and only a slight, somewhat pleasant smell, and is not susceptible to spontaneous ignition. Furthermore, its orange-red flame is rather more appropriate for the representation of conflagrations on the stage than the more purplish-red of the chlorate-sulfur based mixtures. Had such a red fire been available for the theatres, there would have been no pressing need to improve it, and the value of potassium chlorate in coloured fires might not have been discovered until much later. One can even imagine that as late as 1810, when John Forster was asked to find an improved red fire, he could have tried different combustibles with strontium nitrate, found that shellac worked wonderfully, and accomplished his mission without having to use dangerous, costly potassium chlorate. Perfectly possible, but it did not happen. For whatever reason, shellac was not introduced until after potassium chlorate was already well-established. This is an instance where failure to recognize a highly useful material can be seen with hindsight as having had the paradoxical effect of advancing the development of pyrotechny.[120]

By the end of the 1840s a full range of colours was available; variations in the hue and saturation of each colour provided the pyrotechnic artist with a rich palette. Certainly there was scope for improvement, but this lay in the discovery of materials that would provide safer, more stable compositions. The ideal firework composition is effective, inexpensive and stable; in the 1840s the available ingredients often necessitated compromise in which one or two of these attributes was sacrificed. This led to a continued search for new materials.

As an example, consider Chertier's search for a blue colour agent based on copper chlorate, the only material that he knew would reliably impart a blue colour to an alcohol flame. Copper chlorate was too deliquescent and too reactive, so Chertier attempted to stabilize it. By treating it with ammonia, he made a deep blue, air-stable solid (tetraamminecopper(II) chlorate, $Cu(NH_3)_4(ClO_3)_2$). This was effective, but too expensive to be practical. Chertier then devised another ingredient, made by boiling a concentrated solution of copper sulfate and potassium chlorate. The product, 'chlorate de cuivre et de potasse' was effective and affordable, but turned out to make the compositions susceptible to spontaneous ignition. A variation of it was popularized by the English clergyman and amateur pyrotechnist 'Practicus', who named it 'Chertier's Copper'. It continued to cause accidents well into the 20th century. The chemical composition of 'Chertier's Copper' would have varied depending on the time for which the solution was boiled during its preparation, with corresponding variation in the stability of mixtures containing it. A detailed discussion has been published elsewhere.[121]

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[120] For the saltpetre-shellac composition, see Websky, *Lustfeuerwerkerei für Dilettanten*, p. 83; Chertier, *Nouvelles recherches sur les feux d'artifice*, p. 420; Vincenzo Pacini, *Il dilettante di Pirotecnia ovvero Regole da tenersi per lavorare i fuochi di artifizio e colorati* (Firenze: Tipografia Gio. Batt. Campolmi, 1845), p. 53. For a modern account, see Barry T. Sturman and Kenneth L. Kosanke, "Thermodynamic and Spectroscopic Analysis of a Simple Lilac Flame Composition," *Journal of Pyrotechnics*, no. 22 (2005), pp. 28-43.

[121]For Chertier's work, see Chertier, *Nouvelles recherches sur les feux d'artifice*, pp. 13-19. For discussion, see B. Sturman, "On Chertier's Copper," *PGI Bulletin (Bulletin of the Pyrotechnics Guild International, Inc.)*, no. 199 (2016), pp. 39-56.

Chertier commented that his best blue was produced with another ingredient, 'sulfure de cuivre'. His instructions for making it show that it was copper(I) sulfide, Cu_2S. It was effective and relatively inexpensive, but in combination with potassium chlorate it would have been susceptible to spontaneous ignition. Another blue colour agent, still in use and currently regarded as effective, inexpensive and stable is copper oxychloride ($CuCl_2.3Cu(OH)_2$). This was introduced by the French chemist and amateur pyrotechnist Paul Tessier (1816-1???) in 1859. At that time it seems not to have been an article of commerce, as Tessier gave detailed instructions for making it. It is a green powder, insoluble in water; it occurs naturally as the mineral atacamite, first noticed as green sand in the Atacama Desert and named in 1801 by the Russian diplomat and mineralogist Prince Dmitri Alexeievich Gallitzin (1728 –1803). During the 20th century copper oxychloride was produced industrially as an agricultural fungicide and thus became available at a price that made it a practical ingredient for fireworks.

Tessier introduced several other ingredients for coloured fires. There is no need to discuss them all here, but it is worth mentioning the yellow colour agent cryolite (sodium hexafluoroaluminate, Na_3AlF_6). The original yellow fires were made with sodium nitrate, which is effective and inexpensive, but has the disadvantage of being hygroscopic. Chertier introduced sodium oxalate, $Na_2C_2O_4$, and sodium hydrogen carbonate, $NaHCO_3$. These are not hygroscopic but are still water-soluble. Cryolite, one of the very few insoluble sodium salts, is also very unreactive chemically and cannot introduce any problems of chemical incompatibility when used in fireworks.

Tessier's contributions to the development of fireworks included an evaluation of a new class of coloured fires based on picric acid (trinitrophenol, $C_6H_2(NO_2)_3OH$) and its salts. Picrates will be discussed in the next chapter in the context of pyrotechnic whistles, but it is appropriate to notice their role in coloured fires. In 1868 French chemist Anselme Payen (1795-1878) presented a lengthy paper on behalf of the chemical entrepreneur Gustave Louis Gabriel Designolle (n.d.) that discussed new military explosives based on potassium picrate, the associated chemistry and the history of picric acid and the picrates. At the end of this paper three firework compositions were presented, including the original red and green picrate colours, as shown in Table 4.6. French engineer A. Jouglet (n.d.), later commented: 'Is it not to be desired that these terrible picrates should blossom in bright clouds on our festival days, rather than sowing death and terror among civilised people?'[122]

Effect→	Gold gerbe	Green fire	Red fire
Ingredient↓	Parts by Weight		
Picrate of ammonia	50	48	54
Picrate of iron	50	-	-
Nitrate of baryta	-	52	-
Nitrate of strontia	-	-	46

Table 4.6. Designolle and Casthélaz's Picrate-based firework compositions of 1868

Designolle's colleague in the commercialization of picrates, chemical manufacturer John Casthélaz (1829-1892) subsequently explained that the 'picrate of iron' made for pyrotechny was 'a mixture of picrate of iron, iron or iron oxide and picric acid that had not been completely saturated.' It burns with 'a lively brilliance, projecting sparks'. In 1869 French chemist, balloonist and editor Gaston Tissandier (1843-1899) demonstrated an indoor firework based on 'picrate of iron', commenting 'To

[122] Payen, "Arts chimiques. Note sur les nouvelles poudres ballistiques et explosives présentées au nom de M. Designolle" *Bulletin de la société d'encouragement pour l'industrie nationale* 15 (deuxième Série) (1868), pp. 714-720. For Jouglet's comment, see A Jouglet, "Les poudres Designolle," *Le Moniteur Scientifique* 11, no. 302 (1869), pp. 657-672, p. 668.

see this brilliant flame, one would not believe that such a material in certain circumstances is so dreadful, and has brought about terror, devastation and ruin.'[123]

In 1869, a French army officer, Henri Joseph Brugère (1841−1918) developed another green fire based on ammonium picrate, as shown in Table 4.7:

Ingredient	Parts by weight
Picrate of ammonia	25
Nitrate of baryta	67
Sulphur	8

Table 4.7. Brugère's Green Fire of 1869[124]

This generated little smoke, and was useful for fireworks, for theatrical illuminations and for signalling. It, and a similar composition in which barium nitrate was replaced with strontium nitrate, was used for military signalling during World War I.[125]

By 1883, Tessier had investigated the application of picrates in fireworks. He devoted two pages to picric acid and a whole chapter to the picrates, but recommended only ammonium picrate, $C_6H_2(NO_2)_3ONH_4$. This was available for 8 francs per kilogram from Casthélaz. Although costly, its use in coloured fires was justified because of the brilliance of the flame, the absence of odour and the production of very little smoke. It was not possible to make blue with ammonium picrate; the reds were somewhat orange and the greens were very pale, but the splendour and brilliance of the flame compensated for these shortcomings. Examples of Tessier's picrate-based coloured fires are shown in Tables 4.8 and 4.9. They are of technical interest in that they do not depend on chlorates or perchlorates. The red and green colours are produced by gaseous strontium monohydroxide (SrOH) and barium monohydroxide (BaOH) respectively, rather than by the corresponding monochlorides. Picrate-based coloured fires were useful as stage-effects because they produced little smoke and no objectionable odour as they burned. [126]

[123]John Casthélaz "Note sur les principaux picrates employés dans la fabrication des poudres et la pyrotechnie," *Répertoire de Pharmacie* 25 (1869), pp. 446-457. Gaston Tissandier, "Conférences du Boulevard des Capuchines: le picrate de potasse et les poudres fulminantes," *Revue des cours scientifiques de la France et de l'étranger*, no. 25 (1869), pp 395-399, the quote is on p. 399.

[124] Lieutenant Brugère, *Poudres aux picrate d'ammoniaque. Communications faite à l'Académie des Sciences le 20 Septembre 1869* (Paris: Imprimerie Gauthier Villars, 1912).

[125] Basil T Fedoroff and Oliver E. Sheffield, "Bengal Fire Powder," in *The Encyclopedia of Explosives and Related Items PATR 2700*, ed. Basil T Fedoroff and Oliver E. Sheffield (Picatinny Arsenal, New Jesey, USA: U.S. Army Research and Development Command Tacom, Ardec Warheads, Energetics and Combat Support Center, 1962).

[126] Paul Tessier, "Feux de Bengal picratés," in *Chimie pyrotechnique ou traité pratique des feux colorés*, (Paris: Librairie Militaire de L. Baudoin et Cie, 1883). "Picrates," in *Chimie pyrotechnique ou traité pratique des feux colorés* (Paris: Librairie Militaire de L. Baudoin et Cie., 1883).

. Colour →	Red	Red	Red	Green	Green	Green	Green	Aurora	Yellow	White
Ingredient↓	Parts by weight									
Picrate of ammonia	5	20	10	8	16	5	25	10	20	5
Nitrate of strontia	25	100	40	-	-	-	-	34	12	-
Lampblack	1	4	2	1	1	-	1	2	4	1
Paraffin	1	3	1	1	2	1	4	1	2	1
Nitrate of baryta	-	-	-	32	64	25	125	-	58	30
Cryolite	-	-	-	-	-	-	-	3	7	-
Antimony	-	-	-	-	-	-	-	-	-	5

Table 4.8. Tessier's picrate Bengal Fires of 1883, to be burned as loose powders.

Colour →	Red	Red	Green	Green	Green	Aurora	Yellow	Yellow	White	White
Ingredient↓	Parts by weight									
Picrate of ammonia	1	20	5	5	11	20	20	24	6	5
Nitrate of strontia	1	60	-	-	-	60	10	3	-	-
Lampblack	-	4	-	1	4	4	4	-	-	1
Paraffin	-	2	-	1	2	2	2	-	-	1
Fluoride of calcium	-	7	-	-	-	-	-	-	-	
Nitrate of baryta	-	-	6	28	36	-	60	20	4	30
Cryolite	-	-	-	-	-	7	7	4	-	-
Sulphide of antimony	-	-	-	-	-	-	-	-	3	1
Antimony	-	-	-	-	-	-	-	-	-	5

Table 4.9. Tessier's picrate Bengal Fires of 1883, to be compressed into paper cartridges.

Picrate colours were recommended well into the 20th century, but were eventually abandoned, probably because of the classification of ammonium picrate as a high explosive.[127]

Coloured fires based on ammonium picrate show that unexpected results can follow from the introduction of new materials, but they were of no lasting value. In contrast, another new material explored as an ingredient in coloured fires turned out to be extremely important. Potassium perchlorate ($KClO_4$) is currently the main oxidizer in coloured fireworks, having largely replaced potassium chlorate ($KClO_3$) for this purpose. Its great advantage is that it is much more stable; mixtures containing it are less susceptible to accidental or spontaneous ignition.[128]

Potassium perchlorate first appeared in the literature in 1816, when its preparation and composition was reported by Friedrich Graf von Stadion (1774-1821), a Canon at Bamberg Cathedral in Bavaria. That von Stadion, a clergyman, did chemical research shows that he, like many European gentlemen at the time, was an amateur chemist.[129]

[127] Davis, *The Chemistry of Powder and Explosives*, tabulates Tessier's picrate-based Bengal fires on p. 71.
[128] Joseph C. Schumacher, *Perchloric Acid and Perchlorates*, American Chemical Society Series of Monographs (New York: Reinhold Publishing Company, 1960), pp. 1-10.
[129] Friedrich Graf von Stadion, "Von der Verbindung der Chlorine mit dem Sauerstoff," *Gilbert's Annalen der Physik* 52, no. 2 (1816). pp 197-224. For a sparse biographical note on von Stadion, see Fritz Ferchl, *Chemisch-pharmazeutisches Bio- und Bibliographikon*, vol. 1 (Mittenwald (Bayern): Verlag Arthur Nemayer, 1937), p.512.

Stadion's original preparation of potassium perchlorate involved careful addition of potassium chlorate to concentrated sulfuric acid, whereupon a foul-smelling explosive yellowish-green gas (chlorine dioxide, ClO_2) was evolved. When the reaction subsided, the mixture was heated gently until it lost its yellow colour. The residue of potassium hydrogen sulfate ($KHSO_4$) and potassium perchlorate was dissolved in boiling water and allowed to cool; potassium perchlorate crystallised out and was purified by re-crystallization from hot water.

For many years potassium perchlorate was of interest only to chemists. A practical use emerged in 1831 when French chemist and military pharmacist Georges-Simon Sérullas (1774- 1832) showed that it could be converted to perchloric acid. This could be used in chemical analysis to separate potassium from other elements in solution. Also in 1831, Sérullas made potassium perchlorate by heating potassium chlorate. This method was more efficient (40 parts of chlorate yielded 17.5 parts of perchlorate) than von Stadion's method (40 parts of chlorate could yield at most 15.07 parts of perchlorate). It was also far safer, as it did not generate poisonous, corrosive and explosive chlorine dioxide gas.[130]

Another way to make potassium perchlorate was suggested in 1841 by English chemist Frederick Penny (1816-1869). He found that nitric acid reacted with potassium chlorate in a different way from sulfuric acid. Instead of chlorine dioxide, the reaction generated a mixture of chlorine and oxygen, leaving a residue of potassium nitrate and potassium perchlorate, easily separated by re-crystallisation from water. Penny pointed out that his process allowed the preparation of 'hyperchlorate of potassa' without the 'violent detonations that are so apt to occur with sulphuric acid'.[131]

Penny's process was explained in detail by one Martin Damberger (dates unknown). He wrote in 1849 that potassium perchlorate was being sold in London at 4s an ounce: '... a high price, but when we look at the danger attending its manufacture it cannot be considered exorbitant.' Damberger was interested in potassium perchlorate as a source of perchloric acid, but some of his remarks suggested that it would be useful in pyrotechnics:

> Contrary to expectations, it deflagrates with much less violence than the chlorate of the same base, in fact the nitrate almost surpasses it in this respect …it appears to be a very stable compound...[132]

The first account of the application of potassium perchlorate in pyrotechnics was published the following year by Martin Websky. In a section on the spontaneous combustion of compositions containing potassium chlorate and sulfur, Websky mentioned the desirability of replacing potassium chlorate with a less sensitive material. Potassium perchlorate (*überchlorsaure Kali*) was just such a compound. Having explained the propensity of chlorate-sulfur mixtures to ignite spontaneously with reference to the sensitivity of chlorate to sulfuric acid, which was thought to form by the slow oxidation of sulfur in air, Websky wrote that potassium perchlorate is

> very insensitive to sulphuric acid, and is decomposed by it only at a temperature of around 100 ° R. [i.e. 125 °C] whereas chlorate of potash is decomposed by sulphuric acid at any

[130] Georges-Simon Sérullas, "Emploi de l'acide oxichlorique (perchlorique) com réactif propre à distinguer et à séparer la soude de la potasse libre ou combinée à d'autres acides. - Oxichlorates," *Annales de Chimie et Physique* 46, no. 2 (1831), pp. 297-308.

[131] Frederick Penny, "On the Action of Nitric Acid on the Chlorates, Iodates and Bromates of Potassa and Soda," *Report of the Tenth Meeting of the British Association for the Advancement of Science Held at Glasgow in August 1940* (1841), pp. 79-80. For Penny's career, see "Dr Frederick Penny," *Proceedings of the Philosophical Society of Glasgow* VII (1870), pp. 364-371.

[132] Martin Damberger, "On the Preparation of Perchlorate of Potassa, with Observations on some Perchlorates," *The Chemist: a Monthly Journal of Chemical Philosophy, and of Chemistry Applied to the arts, Manufactures, Agriculture, and Medicine, and Record of Pharmacy* 1 - New Series (1849), pp. 251-253.

temperature. This property of perchlorate of potash therefore leads to the conclusion that sulphur-containing compositions prepared with it are not at risk of spontaneous combustion...

When used instead of chlorate of potash in the compositions, this salt behaves in general, much like the latter, only the flammability of compositions is slightly less and the compositions burn noticeably more slowly. The colours displayed by the colour compositions are somewhat weaker, especially with the blue and green star compositions, but this is less noticeable with the red and yellow compositions; the flame is generally smaller, the intensity, however, is noticeably greater...

The preparation of perchlorate of potash is somewhat difficult and therefore this salt is probably still too expensive at present for general use; should, however, a cheaper method of preparation be found, I would, in any event, prefer it to chlorate of potash for sulphur-containing compositions, if only for the reason that it provides a greater light intensity, and for viewing at a distance the maximum possible intensity is the main thing. Perchlorate of potash should also find useful application in those cases where it seems desirable for stars to burn as slowly as possible, for example, for stars discharged from rockets and shells, as well as for the small stars used in grain-fountains. [133]

Websky presented a set of coloured star compositions based on potassium perchlorate, as summarized in Table 4.10. Modern chemical names have been used:

Ingredient ↓ Colour →	White	Pink	Red	Yellow	Green	Blue	Violet
Potassium perchlorate	16	60	20	12	8	50	50
Sulfur	12	25	20	8	8	30	25
Lead nitrate	16	-	-	-	-	-	-
Antimony(III) sulfide	1	-	8	-	3	-	-
Potassium nitrate	-	3	-	6	-	-	-
Strontium oxalate	-	10		-	-	-	15
Gum (Arabic)	-	1	-	-	-	1	1
Strontium nitrate	-	-	40	-	-	-	-
Mastic	-	-	1	-	-	-	-
Sodium oxalate	-	-	-	3	-	-	-
Barium nitrate	-	-	-	-	16	-	-
Copper(II) carbonate - Copper(II) hydroxide (2/1) (“Mountain Blue”)	-	-	-	-		20	-
Mercury(I) chloride	-	-	-	-	-	5	15
Copper powder	-	-	-	-	-	-	15

Table 4.10. Websky’s first published pyrotechnic compositions based on potassium perchlorate.[134]

Within a year of Websky’s publication his friend and colleague Julius Hutstein, who operated a chemical manufacturing and supply business in Breslau, published a short paper describing his method of making potassium perchlorate. This was the method that Sérullas recommended in 1831:

[133] Martin Websky, *Martin Websky's Schule der Lustfeuerwerkerei. Ein Vermachtniss an die Freunde und Dilettanten dieser Kunst* (Breslau: Ferdinand Hirt's Verlag, 1850), pp 166-169.

[134] Ibid., pp 168-169.

carefully heating potassium chlorate, extracting the residue with water to remove the potassium chloride and any unreacted chlorate, and then re-crystallizing it from hot water.[135]

Hutstein's views on potassium perchlorate were quoted in a book on fireworks published in 1913:

> Every year lamentable accidents are caused by spontaneous combustion. Frequently, these endanger lives and pyrotechnic laboratories often fall victim to the explosion that follows...
>
> One cannot, therefore, fail to draw attention to the safe potassium perchlorate, the price of which is now very much more moderate and by means of which almost all spontaneous ignition can be avoided, if the salt be pure.
>
> For the chemical purity of my preparation, I can vouch. The characteristics of potassium perchlorate, as far as they have interest for the pyrotechnist, are the following: mixed with the required quantity of sulphur, it burns more slowly than potassium chlorate, but has, however, far greater intensity than the latter and is therefore of great value for fireworks thrown high and viewed from a distance. It is totally unreactive with sulphuric acid and soured sulphur and decomposes at a high temperature. The use of potassium perchlorate is not recommended for all flame and light compositions, but it is suitable in most instances and especially for star compositions. It is especially useful for grain fountains, shell candles, shells, rockets, and star mines.[136]

Hutstein was writing at some time between 1873 and 1892. The raw material for making potassium perchlorate was potassium chlorate, and the conversion was inherently inefficient. This, combined with the other costs associated with the procedure, led to potassium perchlorate costing several times as much as the already costly potassium chlorate. It is not surprising, then, that despite its great advantage in safety, and its worthwhile (if minor) advantages in the performance of the firework compositions in which it replaced potassium chlorate, potassium perchlorate received scant attention from pyrotechnists for several decades after Websky's initial work in 1850. What little notice was taken of it seems to have been restricted to German pyrotechnists, as discussed in Chapter 9.

The introduction of the new materials reviewed in this chapter essentially completed the quest to transform fireworks by providing a full range of distinct, bright colours. Ideally, these colours would be produced at affordable prices by compositions that could be handled and stored safely; in practice, compromises were made because of the high prices of potassium perchlorate and shellac, ingredients that permitted the elimination of the hazardous combination of potassium chlorate with sulfur or sulfides. As discussed in Chapter 9, accidents resulting from such mixtures would continue for many decades.

A particularly noteworthy aspect of the introduction of the new materials for coloured fires is the dominant role played by the amateurs Forster, Websky, Chertier and Tessier. The reasons why amateurs were so prominent will be explored in Chapter 6. The introduction of colours did not complete the 19th century transformation of fireworks. The second half of the century saw the introduction of still more new materials that led to the production of some novel visual effects: flashes, silver sparks, and flames so bright that landscapes could be illuminated in white or coloured light. There were also novel sound effects: explosions far sharper and louder than the familiar thud of gunpowder, and shrill, shrieking whistles. These were all the result of the application of materials that had long been known to science but which were too costly for use in fireworks until the materials

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[135] Julius Hutstein, 'Ueber beireitung und Anwendung des überchlorsauren Kalis', *Archive der Pharmacie*, 1, 1851, pp. 159-160; Julius Hutstein, Beireitung des überchlorsauren Kalis für die Pyrotechnik', *Dingler's Polytechnisches Journal*, 20, 1851, p. 394.

[136] Gelingsheim, Karl. *Die moderne Kunstfeuerwerkerei: Eine Anleitung für Dilletanten*. Stuttgart: Strecker & Schröder, 1913, pp. 36-37.

were produced on an industrial sale for other applications. Amateur pyrotechnists are not as prominent in the introduction of these new materials, probably because the materials became affordable after the manufacture of fireworks had become more strictly controlled. As a consequence, amateurs had to be careful about drawing attention to their activities and would have been most unwise to disseminate the results of their work in open publication.

Chapter 5: Materials: Part Three. The Second Half of the 19th Century.

The preceding chapter showed how a range of new materials was introduced into pyrotechny during the 19th century in the search for effective, affordable and stable colour-producing compositions. This chapter presents case studies of three new materials introduced into firework-making in the second half of the 19th century. These materials, magnesium, aluminium and potassium picrate, were not primarily associated with the production of colours, although magnesium and aluminium were later used to good effect in colour compositions. They were all introduced into fireworks after having been applied in related fields: photographic flash powders in the case of magnesium and aluminium, military signals in the case of magnesium and military explosives in the case of potassium picrate. All three were known to chemists for decades before they became available at prices affordable for practical applications. Prices were reduced when entrepreneurial chemists saw potential applications that would become money-making opportunities for any supplier who could provide the material at a price that would permit both supplier and user to profit.

Magnesium was recognized as a potentially valuable light source for photography, aluminium as a strong, light, corrosion-resistant structural metal, and potassium picrate was investigated as a military explosive when the price of its precursor, picric acid, was reduced as a consequence of its being produced in bulk as a yellow dye. While knowledge of these new materials was to some extent disseminated by the writings of amateur firework-makers, and there is reason to suspect that the application of potassium picrate in fireworks was discovered by the amateur who first discussed it in print, there is good evidence that magnesium and aluminium were in use by commercial firework-makers for some time before they were discussed by amateurs. In the case of magnesium, this could be because it was too expensive to be used by amateurs. Aluminium and potassium picrate became practical ingredients at a time when amateur pyrotechny was increasingly inhibited by new, more stringently enforced regulations and amateurs had to be more circumspect in publicising their work. This may explain why it has not been possible to establish whether the amateur who first discussed potassium picrate whistles actually discovered the phenomenon and invented the compositions. As we shall see, initial disclosure of some of the novel compositions containing aluminium certainly took place through patents, showing that the mixtures had been developed in the context of commercial manufacture of fireworks.

Each of the ingredients will be discussed in sufficient detail to show how it became known, how its price came to be reduced and, as far as possible, how the material came to be used in pyrotechny. The novel effects will be described, showing how each material contributed to the transformation of fireworks in the 19th century.

5.1 Magnesium

From about 1866 the use of the metal magnesium in fireworks brought some remarkable additions to the art: intensely white flames and sparks, brighter colours and sharp, very loud bangs, accompanied by flashes of light. The early history of magnesium is well documented and need not be recited here. The preparation of the reasonably pure metal was reported in early 1831 by French chemist Antoine Alexandre Brutus Bussy (1794-1882) who obtained it by the action of potassium on magnesium chloride ($MgCl_2$). Magnesium appeared as shiny, silvery-white globules that 'burned with scintillations like iron in oxygen'. German chemist Justus Freiherr von Liebig (1803-1873) repeated the experiment and commented on the 'most lively brilliance' of the combustion. Similar comments were made by Faraday in 1833.[137]

[137] For the early history of magnesium, see Weeks, *Discovery of the Elements*. pp. 521-528. Bussy, "Mémoire sur le radical métallique de la magnésie," *Annales de Chimie et de Physique* 46 (1831), pp. 434-437; Justus Liebig, "Sur le radical métallique de la magnésie," ibid., pp. 437-439. For the French view of its discovery, see Henri Étienne Sainte-Claire Deville and Henri Caron, "Chimie minérale - de magnésium, sa préparation et de sa volatilisation," *Comptes rendus hebdomadaires des séances de l'Académie des Sciences* 44 (1857), pp. 394-396 and "Du magnésium," *Annales de Chimie et de Physique* 67 (3 ser.) (1863), pp. 340-349.

Knowledge of the spectacular combustion of magnesium was thus available in the scientific literature from 1831, yet magnesium would not be used in pyrotechnics for another third of a century. It was far too expensive. The process of extracting it was difficult, dangerous and inefficient, and required an expensive reagent, potassium metal. Consequently magnesium was made only in small batches for chemical research and education. As late as 1860 it was being sold in Vienna for the equivalent of $US 1.50 per gram, when the price of gold was $US 0.66 per gram. Seven years later, the price of magnesium had fallen to around $US0.09 per gram, in response to a sudden demand for it when photography enthusiasts discovered its value as a light source. An English printer and bookseller decided to turn his hand to chemical metallurgy and applied the discoveries of a pair of French chemists to the production of magnesium on a commercial scale. The story of the commercialization of magnesium illustrates several aspects of 19th century life that favoured the transfer of knowledge from the savant's laboratory to the public at large and to technological entrepreneurs, and is worth telling in some detail.

In 1833 Faraday, attempting to establish the laws of electrochemistry, passed an electric current through molten magnesium chloride and made globules of molten magnesium. Some 19 years later German chemist Robert Wilhelm Eberhard Bunsen (1811-1899) prepared magnesium in this way as part of a program to prepare pure metals. A few years afterwards a young British student, Augustus Matthiessen (1831-1870) came to Bunsen's laboratory and improved the process. Later, in the laboratory of physicist Gustav Kirchhoff (1824-1887,) Matthiessen took on the task of measuring the electrical conductivities of a range of metals. He devised a process for making magnesium wire for these experiments by extruding the metal through a hole in a heated steel die in a powerful press. The availability of magnesium wire was to prove important in the transformation of magnesium from a chemical curiosity to a commercial product.[138]

Bunsen, like previous investigators, had noted the remarkable brilliance of the combustion of magnesium. Some seven years later, he returned to the subject in a paper on the research into photochemistry that he and a British student, Henry Enfield Roscoe (1833-1915), had begun in 1852. Bunsen and Roscoe wrote: 'The application of this metal as a source of light may even become of technical importance'. They explained how magnesium wire was made, and speculated that rolls of wire might be incorporated in a lamp. The two savants had magnesium wire at their disposal because another scholar in their institution (Matthiessen) had developed a procedure for making it so that he could measure its electrical conductivity. [139]

Later in 1859, and again in 1860 a German Professor, A. Schmidt (n.d), pointed out that Bunsen and Roscoe's suggested application of magnesium as a light source was precluded by the high price of the metal – with one exception. The magnesium flame would 'be useful in photographing by night or in any dark or subterranean locality...' Photographic use of magnesium would require it to be burned only 'for exceedingly short intervals of time', so magnesium could be used by photographers, despite its high price. The possibility of using burning magnesium for photographic illumination was also raised by English scientist William Crookes (1832-1919), who wrote in 1859: 'a brilliant light, but a terribly expensive one, can be obtained by burning the new metal, magnesium…' Steps towards less

[138] Bence Jones, *The Life and Letters of Faraday*, 2 vols., vol. 2 (London: Longmans, Green & Co, 1870), p. 26; Gustav Kirchhoff, "Ueber die Leitungsfähigkeit für Elektrictät von Kalium, Natrium, Lithium, Magnesium, Calcium und Strontium," *Annalen der Physik und Chemie von J. C. Poggendorff* 10, no. 2 (1857), pp. 177-193; Robert Bunsen, "Darstellung des Magnesiums auf electrolytischen Wege," *Annalen der Chemie und Pharmacie* 82, no. 2 (1852). "Préparation du magnésium par voie de décomposition galvanique," , pp. 137-145; *Annales de Chimie et de Physique* 36 (3 ser.) (1852), pp. 107-112; A. Matthiessen, "IX.-On the preparation of strontium and magnesium," *Quarterly Journal of the Chemical Society of London* 8, no. 2 (1856), pp. 107-108.

[139] Bunsen, "Préparation du magnésium par voie de décomposition galvanique"; "Darstellung des Magnesiums auf electrolytischen Wege"; Robert Bunsen and Henry Enfield Roscoe, "Photo-Chemical Researches. Part IV," *Philosophical Transactions of the Royal Society of London* 149 (1859), pp. 879-926. The discussion of the possible technical application of magnesium is on page 923.

expensive magnesium had already been taken in France, where in 1857 two chemists, Henri Étienne Sainte-Claire Deville (1818-1881) and Henri Caron (1823-1876) presented a paper on their method for producing magnesium with sodium instead of potassium. Some six years later they published a more comprehensive account, with an illustration of the apparatus for purifying magnesium by distillation. [140]

Early in 1861 an English printer and bookseller Edward Sonstadt (1829-1908) began working on a project for making magnesium commercially. By 8th November 1862 Sonstadt had secured a British patent for 'the manufacture of the metal magnesium by acting by means of sodium on a material obtained by heating to redness a mixture in solution of chloride of magnesium with chloride of sodium…'. By the following June he was producing magnesium 'by the pound' and was 'ready to manufacture it by the hundredweight or ton.' As outlined by British metallurgist A. S. Darling, Sonstadt went into partnership in 1863 with a Samuel Mellor(1831-1909), 'an enthusiastic amateur chemist' who, as a part-time student at Owens College 'worked under Roscoe and had established close personal contact with him.' [141]

Roscoe, whom we last saw working with Bunsen in Heidelberg, had become Professor of Chemistry at Owens College in Manchester in 1857 at the early age of 24. He would certainly have endorsed any enthusiasm that Mellor might have expressed for the commercial production of magnesium. Roscoe and Bunsen had already suggested that it would be useful for the metal to be made more widely available because of its value in photo-chemical measurements and possibly as a light source. They had not explicitly stated that it be used in photography, but Roscoe would later claim that they had exactly that application in mind when they wrote about the possibility of the magnesium light becoming 'of technical importance'. He was presumably rather peeved when Schmidt and Crookes had the temerity to point out the photographic applications; if so, Roscoe had only himself and his Heidelberg mentor to blame for being so vague in their original paper. According to Darling, Mellor introduced Sonstadt to a pharmaceutical chemist, William White, who had developed a new process for extracting sodium. This was of immediate relevance, as sodium was required for the extraction of magnesium and was far and away the most costly raw material for the new enterprise.[142]

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[140] Schmidt's views were reported (without acknowledgement) in "The Magnesian Light," *The Photographic News: A Weekly Record of the Progress of Photography* 4, no. 92 (1860). p. 70 and, with proper citation, in "Magnesium as a Source of Light," *The Edinburgh New Philosophical Journal Exhibiting a View of the Progressive Discoveries and Improvements in the Sciences and the Arts* 13 (New Series) (1861), p. 334. For Crookes' comments, see "Artificial Light for Photographic Purposes," *The Photographic News: A Weekly Record of the Progress of Photography* 3, no. 58 (1859). p. 71.

[141] T. E. Thorpe, "Edward Sonstadt. Born November 25th, 1829; Died July 5th, 1908.," *Journal of the Chemical Society, Transactions* 95 (1909), pp. 2209-2213. For Rousseau's magnesium, see "Paris Exhibition of 1867. Gallery V. Class 44: Chemical and Pharmaceutical Products " *The Chemical News and Journal of Physical Science* 15 (1867), pp. 256-257; William White, "Manufacture of Magnesium," ibid.8 (1863), pp. 10-11. It has not so far been possible to find primary sources to confirm the information given in Darling, A. S. "Non-Ferrous Metals", in *An Encyclopaedia of the History of Technology*, edited by Ian McNeil. London and New York: Routledge, 1990, pp. 113-121, which did not cite any sources. Alan Sydney Darling was an engineer and metallurgist, and sometime head of Metallurgical Research at Johnson Matthey and Co. That company had absorbed the Magnesium Metal Company in 1870 and it is plausible that its archives held material not available elsewhere, and that Darling used this in compiling his article. This is inconsistent with a statement in the company history that its archives were destroyed in the bombing of its works in the blitz of 1940. See Tom C. B. Elliott et al., "Johnson Matthey PLC," *International Directory of Company Histories* 128 (2012), p. 300. For Mellor's chemical interests, see A. S. Darling, "Non-Ferrous Metals", p. 113-114.

[142] Little could be found about William White, who was presumably the same person who had defended Sonstadt's reputation and his patent in The Chemical News. He was born in Oldham in 1832, the son of a chemist and druggist, and followed his father in that calling, probably as his apprentice. Well after the initial involvement with Mellor and Sonstadt he took out patents on the production of magnesium, potassium and sodium. He must have been financially successful because by the 1881 Census he was a 'retired chemist' at the

Roscoe was a willing participant in the promotion of magnesium. On February 9, 1864, at a regular meeting of the Manchester Literary and Philosophical Society he praised Sonstadt for his efforts in the metallurgy of magnesium and predicted that the metal would find important applications in photography. This was supported by photographers present, including Alfred Brothers (1826-1912). Brothers was given a small lump of magnesium, which he subsequently hammered into thin sheet and cut into strips. The results of his experiments with it were reported in the printed account of Roscoe's lecture. Brothers thus had the honour of being the first to demonstrate the use of magnesium in photography. On 22 February Brothers took the first portrait by magnesium light; the sitter was Professor Henry Enfield Roscoe. [143]

In a few years in the early 1860s magnesium was transformed from a costly chemical curiosity to a well-publicized, affordable (but still expensive) material. In 1867 magnesium was being sold at a retail price of $US 40 per pound – a little under 9 cents per gram, compared to $1.50 per gram that was being charged only seven years previously. The first pyrotechnic mixture containing magnesium seems to have been made for the same purpose for which the pure metal was already being used: photographic illumination. In April 1865 British astronomer and pyramid enthusiast Charles Piazzi Smyth (1819-1900) tried to light up the King's Chamber in the Great Pyramid with a mixture of gunpowder and magnesium filings. He considered the experiment a failure.[144]

In November 1865 Scottish photographer John Traill Taylor (1827-1895) demonstrated a flash-light mixture (Table 5.1) to the South London Photographic Society.

Ingredient	Parts by weight
Magnesium filings	1
Chlorate of potash	4
Sulphide of antimony	2
Sulphur	1

Table 5.1 John Traill Taylor's photographic flash powder of 1865[145]

The brief flash produced by this dangerous mixture would not have been suitable for the slow photographic emulsions of the day. For the next 22 years magnesium light for photography was provided by burning magnesium ribbon or by passing a stream of powder through the flame of a lamp. In 1887 German photographers Adolf Miethe (1862-1927) and Johannes Gädicke (1835-1916)

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age of only 49. He was in exactly the same situation for the next two censuses, but he seems to have disappeared from the record after the census of 1901. No record could be found of his death.

[143]"Ordinary Meeting, February 9th, 1864," *Proceedings of the Literary and Philosophical Society of Manchester* 3, no. 12 (1864), pp. 233-235. For Brothers, see Steven R. Joseph, "Alfred Brothers (1826-1912) and his role in photographic publishing," *History of Photography* 11, no. 1 (1987), pp. 63-76. Brother's own account of his role in the development of magnesium light is in Alfred Brothers, *Photography: Its History, Processes, Apparatus and Materials. Comprising Details of all the More Important Methods*, 2nd revised ed. (London: Charles Griffin and Company, Limited, 1899), pp. 59 - 62. For magnesium ribbon, see Chris Howes, *To Photograph Darkness: The History of Underground and Flash Photography* (Gloucester: Alan Sutton Publishing, 1990), p. 23; the inventor's remarks on the subject are in Brothers, *Photography*, pp. 61-62. The portraits of Roscoe and of Faraday can be seen in Michael Hallett, "Early magnesium light portraits," *History of Photography* 10, no. 4 (1986), pp. 209-301, p. 300. This paper erroneously gives the date of Roscoe's lecture as 1862. For the celebrity portraits, see "Magnesium and its Light," *The Telegraphic Journal* 2, no. 42 (1864), pp. 181-182, p. 181 col. 2.

[144] Howes, *To Photograph Darkness*, p.103.

[145] Ibid., p. 104.

patented pyrotechnic flash powders for photography, quite similar to Taylor's original but with more magnesium. The improved photographic emulsions of the day required far shorter exposures, so flash powders became widely used; they became obsolete for routine photographic purposes during the first half of the 20th century with the development of electrically-initiated 'flash bulbs' in which metal foil or wire was burned in oxygen in a glass envelope.[146]

Magnesium was soon introduced into other areas of pyrotechnics. Its use by the military is discussed in Chapter 7; its introduction into fireworks seems to have followed naturally from its well-publicised application in photography, which led to magnesium becoming an amusing scientific novelty. The use of magnesium wire or ribbon as a 'firework' can be inferred from a comment made in 1865 about alloys of magnesium and zinc: 'In the shape of wire, they form a simple and efficient fire-work, cheaper, if less dazzling, than magnesium alone, and quite worthy of Guy Fawkes's day.' Magnesium-zinc alloys in the form of powder were said to 'supply a brilliant ingredient for rockets'. No record of their use has yet come to light in any firework books; it may well be that the details were kept secret and have since been lost[147]

The main technical problem with using magnesium in pyrotechnics is its susceptibility to corrosion, but this problem is readily solved by coating it. An article in an engineering magazine published in March 1867 noted:

> Magnesium has recently been applied with the greatest success in pyrotechny. The powdered metal, when covered with paraffin ... can safely be employed in the manufacture of fireworks. If only from two to five percent of magnesium be mixed with the ordinary rocket [star] powder the light is greatly intensified; and the effect was seen to great advantage in the recent pyrotechnical displays at the Crystal Palace. In rockets the dense white smoke produced by magnesium is an advantage rather than a loss, for the canopy then seen floating like a network of snow-white gauze over each burning star not only adds by its appearance to the beauty of the display, but reflects downwards an additional amount of light. [148]

Another article from 1867 mentioned that balloons carrying 'rockets' (i.e. fireworks) charged with a mixture of magnesium powder and potassium chlorate had been sent up at the Crystal Palace, as shown in Figure 5.1:

[146]Romyn Hitchcock, "Flash-light Powders," *The International Annual of Anthony's Photographic Bulletin and American Process Year-book* 10 (1897), pp. 17-21. M. Andresen, "Magnesium Flashlight," *Wilson's Photographic Magazine* 49 (1912) , pp. 200-208. For flash bulbs, see Howes, *To Photograph Darkness*, pp 234-235.

[147]"Magnesium and its Light", p. 181 col. 2; W. White, "Recent Applications of Magnesium," *Journal of the Photographic Society of London* 9, no. 161 (1865), pp. 145-148.

[148] "Magnesium and Sodium," *The Engineer* 23 (1867), p. 225.

Figure 5.1 A balloon carrying a firework charged with magnesium and potassium chlorate. The towering spiral of white smoke adds to the spectacle.[149]

The appearance of magnesium in fireworks at the Crystal Palace shows that the metal was being used by the commercial pyrotechnists William Edwin Jonathan Brock (1813-1869) and his son Charles Thomas Brock (1843-1881), some years before it was mentioned by amateur pyrotechnists. The magnesium 'rockets' carried by the balloons would 'illuminate the Palace and the surrounding country with a radiance between sunshine and moonshine, and display the countenances and dresses of the gazing crowd, and the flowers and foliage of the garden, in the tints of daylight.' They first appeared at the Crystal Palace in 1866. [150]

Magnesium had an unexpected disadvantage: firework makers complained that 'its very excellence is an objection, for those who see it once demand it always, to the prejudice of the commoner and less costly articles.' The case might have been better stated: 'to the prejudice of the more profitable articles.', but the point is well-made. However excellent an ingredient may be, its cost remains an important factor limiting its practical application.[151]

In 1872 English clergyman Denis Times Moore (1836-1897) published the first discussion of magnesium by an amateur pyrotechnist:

> 'Magnesium filings are used in Pyrotechny only when expense is of no consequence. Their effect is quite inimitable. When mixed with suitable compositions, they can be employed for stars, or for lights. The magnificent effect of the balloons which carry a magnesium light, and of the shells filled with magnesium stars, is well known to all who have witnessed the grand displays furnished by Mr Brock to the Crystal Palace Company.' [152]

[149] John Henry Pepper, *Cyclopædic Science Simplified* (London: Frederick Warne and Company, 1869), p. 627.

[150] For Brock and the Crystal Palace, see Brock, *A History of Fireworks*, pp.86-91. The appearance of the magnesium lights at the Crystal Palace is in "Magnesium and Sodium", p. 225, col. 1.

[151] "The Manufacture and Uses of the Metal Magnesium," *The Mechanics' Magazine and Journal of Engineering, Agricultural Machinery, Manufactures, and Shipbuilding* 18 (new series) (1867), pp. 140-141..

[152] Denis Times Moore ('Practicus'), *A Manual of Pyrotechny* (London and Wolverhampton: Bolton & Co and William Bailey & Son, 1872; repr., BiblioLife, Charleston, 2009), pp. 37-38.

Moore gave the price of magnesium filings as 6 shillings per ounce. Presumably assuming that this would be beyond the reach of his readers, Moore did not give any compositions containing magnesium.[153]

The following year English surgeon, chemist and amateur pyrotechnist William Henry Browne (1840-1891) drew attention to the high cost of magnesium, but unlike Moore he explained how it could be used. Magnesium filings were mixed with a white fire composition and loaded into thin paper tubes, 0.25 inches in diameter and 0.5 inches long, to make 'pill box' stars for rockets. The ratio of magnesium to white fire mixture could be adjusted as required.[154]

The resulting compositions are shown in Table 5.2:

Composition →	1	2	3
Ingredient ↓	Parts by weight		
Magnesium filings	-	11	100
Saltpetre	32	32	32
Sulphur, washed	4	4	4
Antimony	7	7	7
Realgar	4	4	4
Red lead	2	2	2
Shellac	1	1	1

Table 5.2. White flame compositions for rocket stars, from Browne, 1873 (re-calculated). Composition 1 is the base white fire mixture, composition 2 has the minimum recommended amount of magnesium, 3 gives the optimum effect, but is the most expensive.

Brown mentioned a costly but effective way of using magnesium in firework displays. A special magnesium ribbon was made with a groove along its length to contain a pyrotechnic mixture to ensure reliable ignition of the ribbon and keep it burning. The ribbon was formed into a coil, attached to a parachute, and placed in the head of a rocket. When the rocket reached its maximum height, the ribbon would be ignited and thrown into the air, suspended from the parachute. This, Browne wrote, 'is one of the grandest effects that science can produce. The pure brilliant white light, the duration of the effect, and marvellous appearance of the surrounding scenery, is a sight once seen never to be forgotten.' The shortcoming was the cost: the magnesium coil alone cost from 28 to 30 shillings.[155]

In 1878 the English schoolmaster, book-keeper and amateur pyrotechnist Thomas Kentish (1810-1894) published recipes for coloured stars containing magnesium, as shown in Table 5.3.[156]

[153] Ibid., pp. 33-34.

[154] W. H. Browne, *The Art of Pyrotechny, being Comprehensive and Practical Instructions for the Manufacture of Fireworks, Specially Designed for the Use of Amateurs* (London: The Bazaar, 1873), p. 45.

[155] Ibid., pp. 45-46.

[156] Thomas Kentish, *The Pyrotechnist's Treasury: The Complete Art of Making Fireworks* (London: Chatto & Windus, 1878), p.197. For Kentish's career, see B. Sturman, "Thomas Kentish: A Victorian Amateur Pyrotechnist," *Fireworks*, no. 69 (2016), pp. 31-33.

Colour →	Crimson	Scarlet	Green	Blue	Yellow	White
Ingredient↓	Parts by weight					
Magnesium filings	2	3	2	2	1	2
Nitrate of strontian	8	6	-	-	-	-
Chlorate of barytes	-	-	12	-	-	-
Oxychloride of copper	-	-	-	2	-	-
Oxalate of soda	-	-	-	-	2	-
Sulphuret of antimony	-	-	-	-	-	1
Chlorate of potash	2	4	-	5	4	-
Saltpetre	-	-	-	-	-	12
Sulphur	2	2	1	2	-	4
Charcoal	1	-	-	-	-	-
Shellac	-	2	3	1	1	-
Calomel	-	4	-	2	1	1

Table 5.3. Coloured firework stars containing magnesium, from Kentish, 1878.

In these compositions magnesium is present in relatively small amounts to enhance the brightness of the flame. The reason for this parsimonious use is presumably the high price of magnesium, which Kentish gave as 7s. per ounce. At such a price any use of magnesium was an extravagance. Using it in large quantities would have been out of the question in all but the most lavish public displays, where extravagance would to some extent be expected and admired. Wider application of magnesium in fireworks would have to wait until its price was reduced. That was not long in coming, with the marriage of a resurrected technology for making magnesium to new developments in electrical engineering.[157]

By the 1880s progress in electricity generation made electrochemical production of metals economically feasible. The work that Bunsen and Matthieson had published a quarter of a century ago became of intense interest to entrepreneurial German chemists eager to exploit the mineral carnallite ($KMgCl_3.6H_2O$), which occurs abundantly in the vast salt deposits of Stassfurt, as a source of magnesium. In 1882 German chemist Heinrich August Wilhelm Ferdinand Fischer (1842-1916) described the production of magnesium by the electrolysis of a molten mixture of magnesium chloride and potassium chloride, obtained by dehydrating carnallite. In April 1885 Aluminium und Magnesiumfabrik Hemelingen was set up to exploit the method commercially, beginning production in 1886. Magnesium was sold at a much lower price than previously possible, with the result that the old sodium reduction process became uncompetitive.[158]

Magnesium was still more expensive than other pyrotechnic chemicals, which is probably why firework-makers were slow to use it. As late as 1899 the section on magnesium in a German book on pyrotechnic materials stated that its property of burning with an intense light made it a useful addition to firework mixtures and coloured fires. Some 14 years later the versatility of magnesium was

[157] For the price in 1878, see Kentish, *The Pyrotechnist's Treasury*, p. 172.

[158] Darling, "Non-Ferrous Metals", p.114, says that the price was 1s.6d. ($US 0.36) *per pound* in 1890, but that seems to be a mistake. A price of 1s 6d per *troy ounce* ($US 5.32 per pound) is consistent with data from other sources for the prices in 1888 and 1914. According to E.G. Brown, "The Magnesium Metal Company of Salford and Patrimore," in *Golden Jubilee Miscellany of Past Lectures* (Eccles: Eccles & District History Society, 2006), p. 15, magnesium was sold by the troy ounce until 1911.

demonstrated by the range of compositions shown in a book for amateur firework-makers. The effects produced would have been most impressive: silver sparks, lightning-like explosions, and brilliant white and multi-coloured stars.[159]

For many years magnesium had been extremely costly, because of the high cost of the potassium used to extract it. The fall in the price of magnesium in the mid 1860s was brought about by the commercial extraction of the metal in response to a demand for it as a light source for photography. Once magnesium became available in sufficient quantity, it began to find applications as an illuminant in other areas and, despite its high price, was soon being used in military signals and in fireworks. It was used by professional pyrotechnists before it was discussed in books written by and for amateurs. In this, it resembles the second important metal introduced into pyrotechny in the 19th century: aluminium.

5.2 Aluminium

Like magnesium, aluminium was known from an early date to burn in a pyrotechnically interesting fashion, and, also like magnesium, it was too expensive to be used in practice. Unlike magnesium, aluminium is resistant to corrosion, so its original application beyond the chemical laboratory was as a decorative structural metal. Originally a precious or semi-precious metal, aluminium would have been recycled, not 'wasted' in fireworks. It did not become affordable for pyrotechnic use until the last decade of the nineteenth century. Aluminium is an important ingredient in modern fireworks, producing some unique effects. It is the only practical source of the beautiful 'glitter' phenomenon, in which initially rather dim orange-red sparks suddenly explode with brilliant flashes of light. It is widely used in 'flash powder' to produce a loud bang accompanied by a lightning-like flash. It can produce sparks having colours ranging from golden-yellow to silvery-white, and can also enhance the brightness of coloured flames. Furthermore, it is a component of the very popular 'electric sparkler'. Aluminium was isolated in an impure form as early as 1827, and its ability to burn with brilliant sparks was commented on in the first published accounts of its properties. When aluminium eventually became available at a price that made its use in pyrotechnics practical, it was used as a substitute for magnesium in photographic flash powders. This development was made by amateur photographers and was quite widely discussed, even in the popular press. The application of aluminium in fireworks happened a few years later, and seems to have been initiated by commercial manufacturers, who either kept their formulas secret or attempted to protect them by patents. The first presentation of aluminium-based firework compositions in a book was in a Spanish volume published in 1909; further details were given in a German book published in 1913. Both of these books were intended for amateur firework makers.[160]

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[159] Alfons Bujard, *Leitfaden der Pyrotechnik: Einführung in die Chemie der wichtigsten Rohmaterialien und Sprengstoffe der Kunstfeuerwerkerei nebst Besprechung der einschlägigen Polizei- und Eisenbahnverkehrsverordnungen* (Stuttgart: Arnold Bergsträsser Verlgbuchshandlung, 1899), p. 96; Karl Gelingsheim, *Die moderne Kunstfeuerwerkerei: Eine Anleitung für Dilletanten* (Stuttgart: Strecker & Schröder, 1913), pp. 41-42, 75-78, 86, 89-90, 98-99.

[160] The history of aluminium has attracted sufficient interest to justify the existence of a dedicated "Institut pour l'histoire d'aluminium" established in 1986. (http://www.histalu.org/accueil.php Accessed 8th March, 2017) This issues its own journal, *Cahiers d'Histoire de l'Aluminium* (https://www.cairn.info/en-savoir-plus.php?ID_REVUE=CHA Accessed 8th March 2017). The early history of aluminium is dealt with in great detail in Joseph W. Richards, *Aluminium: Its History, Occurrence, Properties, Metallurgy and Applications, including its Alloys* (Philadelphia: Henry Carey Baird & Co., 1890). For recent treatments, see Muriel LeRoux, "From Science to Industry: The Sites of Aluminium in France from the Nineteenth to the Twentieth Century," *Ambix* 62, no. 2 (2014), pp. 114-137 and Fathi Habashi, "Movement of Scientists and the Production of Aluminum," *International Committee for the Study of Bauxite and Alumina Newsletter [ICSOBA}* 13 (2015), pp. 9-13.

The early history of aluminium and its commercial production is well recorded, so it need not be told in detail here. Like magnesium, aluminium was originally extracted with the aid of potassium and subsequently sodium, and was thus very costly. After 1888, with the introduction of the Castner process and then the Hall-Heroult process, the price was below $5/lb. and falling, so wider application became practical. Aluminium was soon being used in cooking utensils, in parts of bicycles, tricycles and carriages, in luggage and in components of precision instruments, and, foreshadowing its future extensive application in architecture, as a roofing material.[161]

A minor application of aluminium that proved extremely important for its subsequent use in pyrotechnics was in aluminium pigments for 'silver paint'. These were made by subjecting aluminium to the mechanical process developed in the early 1840s by English inventor Sir Henry Bessemer (1813-1898) for converting copper and some of its alloys into microscopic flakes for use as pigments. The art of making such pigments by hand was known to the ancient Chinese and by the early 1840s it had become a specialty of German craftsmen, who kept the details secret. The powders, sold under the name of 'bronze powders', were used to make 'gold paint'. When Bessemer wanted some bronze powder for an artistic project he was astonished to find that it cost seven shillings an ounce, and that it contained only brass. The fact that the powder sold at £5/12/- per pound, while the brass from which it was made cost no more than 6d, suggested to Bessemer that he had stumbled upon an opportunity to make a fortune. The story of how he succeeded in doing so is told in his autobiography. His ingenious use of heavy machinery of his own invention, operated in absolute secrecy for some 40 years, allowed him to make a vast amount of money that he used to fund his subsequent ventures, which also proved lucrative. Bessemer is best known for the steel-refining process that bears his name.[162]

Bessemer's bronze-powder process was kept secret until the early 1880s. By 1888 German manufacturers were applying it to aluminium, producing a silver-coloured pigment known as 'aluminium bronze powder'. The name referred to 'bronze powder' made from aluminium, not to a powdered form of any of the aluminium-copper alloys called 'aluminium bronze'.[163]

The availability of aluminium as a fine powder at an affordable price opened the door to pyrotechnic applications. In 1892 French author and amateur photographer Frédéric Dillaye (1848-1905) claimed to have suggested aluminium as a replacement for magnesium in photographic flash powder. He mentioned that the use of aluminium for photographic illumination seems to have been first announced by 'M. Putz', who presented his work to the Vienna Photographic Society. [164]

Max Putz (n.d.) reported his work on photography by the light of burning aluminium to the Vienna Photographic Society on 3rd March 1891. A mixture of 10 parts of chlorate of potash, 4 parts of aluminium powder, and 1 part of sugar gave a most intense light, but the mixture is explosive and

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[161] For early applications of aluminium in architecture, see James Ashby, "The Aluminium Legacy: The History of the Metal and its Role in Architecture," *Construction History* 15 (1999), pp. 79-90

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[162] Henry Bessemer, "The Manufacture of Bronze Powder," in *Sir Henry Bessemer, F.R.S. An Autobiography with a Concluding Chapter* (London: Offices of "Engineering", 1905).

[163] For aluminium bronze powder in 1888, see "Aluminium powder - not free of duty as bronze powder," in *Synopsis of Decisions of the Treasury Department on the Construction of the Tarriff, Navigation and Other Laws, for the Year Ended December 31, 1888* ed. Charles S. Fairfield (Washington: Government Printing Office, 1889) pp. 483-484. See also Aluminum Company of America, *Aluminum and Aluminum Alloys in the Form of Ingots, Castings, Bars, Plates, Sheets, Tubes, Wire and All Forms of Structural Shapes* (Philadelphia: Myers and Shinkle Company, 1897), p.9; Junius David Edwards and Robert I. Wray, *Aluminum Paint and Powder*, 3rd ed. (New York: Reinhold Publishing Corporation, 1955), p. 2

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[164] Frédèric Dillaye, "Le mouvement scientifique: les nouveautés photographiques," *La Science Illustrée* 9 (1892), pp. 203-204.

dangerous. Alternatively, thin leaves of aluminium could be sandwiched between sheets of paper made from nitrated cotton and impregnated with potassium chlorate. Putz's work was widely reported in the photographic periodicals and even in the popular press.[165]

Aluminium flash powders were discussed by French chemist A.–Mathieu Villon (1867-1895) in 1892; examples are shown in table 5.4: [166]

Composition →	1	2	3
Ingredient↓	Parts by weight		
Aluminium powder	4	10	10
Chlorate of potash	10	25	25
Sugar	1	-	2
Nitrate of potash	-	5	-
Sulphide of antimony	-	4	-
Yellow cyanide (potassium hexacyanoferrate(II) trihydrate, $K_4Fe(CN)_6.3H_2O$)	-	-	3

Table 5.4. Aluminium-based photographic flash powders of 1892.

Composition 1 is Putz's; all are explosive and dangerous. Each could be placed in a metal cup and ignited with a piece of cotton wick coated with gunpowder, or, it could be wrapped in nitrated paper as proposed by French photographer and medical researcher Albert Londe (1858-1917) for magnesium flash powders.[167]

By 1894 aluminium was being used in display fireworks at the Crystal Palace. Figure 5.2 shows an advertisement for the 1894 season; the wording is consistent with the common description by firework-makers of the effects produced by aluminium as 'electric'. [168]

CRYSTAL PALACE.

GRAND ILLUMINATED GARDEN FÊTE.

Bands of 2nd Life Guards, Royal Engineers, 2nd Batt. Norfolk Regiment (by permission of Officers commanding), and the Crystal Palace Military Band.—Conductors, Mr. Leonard Barker, Mr. J. Sommer, Mr. E. Elford, and Mr. Charles Godfrey, Junr.

CRYSTAL PALACE FIREWORKS.

Magnificent Display every Thursday at 9 0 by the Unrivalled and World-Renowned Crystal Palace Pyrotechnists, Messrs. C. T. BROCK & CO. Electricity outdone in brilliance by new and dazzling effects, introduced this season for the first time.

Wet or fine, the Crystal Palace displays are always given ; they can be witnessed by tens of thousands without extra payment.

Figure 5.2. Advertisement for displays for the 1894 season at the Crystal Palace.

[165]. "Photography in Austria," *The Photographic News: A Weekly Record of the Progress of Photography* 34 (1891), p. 363; "Aluminium Flash-Light," *The Photographic News: A Weekly Record of the Progress of Photography* 35 (1891), p. 173; "Snapshots," *Los Angeles Herald*, 6 September 1891, p. 11.

[166] A.-M. Villon, "Éclairage à l'aluminium," *Bulletin de la Société Française de Photographie* 8 (2 ser.) (1892), pp. 133-136.

[167] Ibid. p.135. For Londe's method, invented in 1889, see Albert Londe, *La photographie à la lumière artificielle* ed. A. Seyewetz, Encyclopedie scientifique (Paris: Octave Doin et fils, 1914), pp. 60-61.

[168] For aluminium in firework displays, see Brock, *A History of Fireworks*, p.164. The advertisement is "Crystal Palace," *The Saturday Review of Politics, Literature, Science and Art* 78 (1894), p. 85.

Aluminium was also being used in ‘garden’ fireworks, including a novelty that would become the most widely used of all fireworks – the wire-cored ‘electric sparkler’.[169]

The origin of the ‘electric sparkler’ can be inferred by reference to a British patent issued in 1893 to one Gustav Gillischewski of Berlin, disclosing a composition (shown in Table 5.5) remarkably similar to those subsequently used for wire-cored sparklers:

Ingredient	Parts by weight
Barium nitrate	33
Iron or steel filings	15
Aluminium bronze powder	5 to 10
Stearin	1
Dextrin	3
Milk sugar	3

Table 5.5. Spark-producing composition containing aluminium, 1893.

Part of the novelty of the invention lay “in the application of aluminium powder for pyrotechnical purposes ... for the production of brilliant sparks”. This is the first time that a novel application of a material in fireworks was disclosed by a patent, indicating that at this period of time innovation in fireworks was coming from commercially-focused organizations rather than from the amateurs who had dominated in previous decades.[170]

A different approach to making firework sparks with aluminium was patented by English pyrotechnist Frederick James Bishop (1861-1957) in 1901. The invention was ‘for producing a new kind of sparkling fire, to be used in the art of pyrotechny.’ The formula is shown in Table 5.6.[171]

Ingredient	Parts by weight
Gunpowder	12 to 20
Black sulphuret of antimony (Sb_2S_3)	3 to 9
Sulphur	2 to 6
Aluminium	0.5 to 3 "

Table 5.6. Sparkling fire (glitter) composition containing aluminium, 1901.

This could well be the earliest disclosure of the beautiful firework effect now known as ‘glitter’.[172]

The first mention of aluminium in a book on firework-making seems to have been in a Spanish work published in 1909 by pyrotechnist and industrial chemist Juan Bautista Ferré y Vallvé (no dates) for the instruction of those wishing to make fireworks at home ‘to liven up a private party’. He specified

[169] The use of aluminium in shop fireworks in 1894 can be inferred from "'Remember, Remember, the Fifth of November!' Are Fireworks Going Out of Fashion?," *The Westminster Gazette*, 3 November 1894, p. 3, col. 2. This includes a reference to such ‘popular and novel’ items as the electric sparkler, the electric wheel and the fountain of silver, all suggestive of aluminium-based compositions.

[170] Gustav Gillischewski. Improvements in Pyrotechnical Compositions or Fireworks. Great Britain Patent 11,073, filed 6 June 1893, and issued 8 July 1893.

[171] Frederick James Bishop. Improvements in Sparkling Fireworks Great Britain Patent 1508 of 1901, filed 23 January 1901, and issued 18 January 1902.

[172] John Wraige, "The Search for the Glitter Phenomenon," *Journal of Pyrotechnics* 24 (2006), pp. 40-49.

two grades of aluminium 'la purpurina de aluminio' and 'aluminio granular N°. 2'. The former was almost certainly pigment-grade aluminium, the latter a coarser powder.[173]

Table 5.7 shows some aluminium compositions from this book:[174]

Composition →	1	2	3
Ingredient↓	Parts by weight		
Fine aluminium powder	3	14	8
Granular aluminium N°. 2	1	10	5
Roll sulphur	1	3	4
Chlorate of potash	3	30	-
Nitrate of baryta	3	-	4
Mealed gunpowder	10	-	8

Table 5.7. Spanish firework compositions containing aluminium, 1909.

The use of each composition was as follows:
1. Volador roncador eléctrico N°. 4 – electric flying croaker – a small sky rocket..
2. Ramilletes eléctricos – electric bouquets – a garden firework.
3. Surtidores eléctricos – electric jets – another garden firework.

Aluminium was the last of the transformational materials introduced into 19th century pyrotechny. A few years earlier, a remarkable new effect had appeared in firework displays in France: the pyrotechnic whistle. This depended on a new material that had its origin not in inorganic chemistry or chemical metallurgy, but in organic chemistry – the chemistry of carbon compounds. The new material was potassium picrate ($C_6H_2(NO_2)_3OK$). This had been known in chemical laboratories for many decades. When its parent, picric acid (2,4,6-trinitrophenol,$C_6H_2(NO_2)_3OH$) began to be produced on a large scale as a yellow dye in the1860s, potassium picrate attracted attention for use in military explosives. The circumstances of its introduction into pyrotechny as the key ingredient in pyrotechnic whistles are not documented, but there is some evidence that a French amateur pyrotechnist was responsible. If so, this would be the last contribution of 19th century amateurs to the transformation of fireworks.

5.3 Potassium Picrate and the Pyrotechnic Whistle

The loud screeching of the picrate whistle was the most bizarre firework effect introduced in the 19th century. The circumstances of its introduction are not known, but the history of picric acid and the picrates has been well-covered by 19th century authors. The formation of a yellow dye by the action of nitric acid on indigo was recorded in 1791; in 1799 French chemist Jean-Joseph Welter (1763–1852) prepared what we now know was potassium picrate from the products of the treatment of silk with nitric acid. Finding that the material exploded like gunpowder when heated, he suggested that it could be effective in a fire-arm. [175]

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[173] Juan Bautista Ferré y Vallvé, *La pirotecnia moderna. Tratado general de fuegos artiflciales y manera práctica de prepararlos con fórmulas nuevas comprobadas experimentalmente, por Juan Bautista Ferré y Vallvé, industrial pirotécnico y químico. Con un prólogo y anotaciones técnicas del Dr. D. Francisco Perpiñá García, farmacéutico.* (Barcelona: Sucesores de Manuel Soler 1909). p. 15. Michael S. Swisher kindly drew my attention to this book. The term 'purpurina de aluminio' translates as 'Aluminium glitter', but here 'glitter" refers to the appearance of the powder, not to the firework effect that would later bear that name.

[174] Ibid. pp. 103, 130, 132.

[175] Jean-Joseph Welter, "Notice sur quelques matières particulières, trouvées dans les substances animals, traitées par l'acide nitrique," *Annales de Chimie* 29 (1799), pp. 301-305.

By the early 1840s picric acid and its salts had been investigated by several chemists. In 1841 French chemist Auguste Laurent (1808–1853) showed that picric acid was phenol (C_6H_5OH) in which three equivalents of hydrogen had been replaced by nitro (NO_2) groups; it could be produced from phenol, which was easily obtained from coal tar. In July 1847 a chemist and dyer of Lyon, Philibert Nicolas Guinon (1807-1885), began making picric acid from coal tar for use as a yellow dye. His results were reviewed by French chemist Jean Pierre Louis Girardin (1803-1884), who mentioned that in 1851 picric acid was available in Paris for 25 francs (£1) per kilogram, or just over 9 shillings per pound.[176]

Attempts to find new uses for picric acid continued, presumably in expectation of profit as the scale of production increased. One application was in explosives. In 1861 Parisian chemical manufacturer Aristide-Pierre Fontaine (n.d.) wrote to the Inspector-General of Artillery for the Navy, suggesting the use of picrates in military explosives. Fontaine was summoned to Toulon where, after a series of experiments made with the collaboration of Colonel Virgile, Director of the School of Pyrotechnics, the so-called 'Fontaine Powder' was made suitable for use in firearms. Its composition was not disclosed. On 25 March 1863 General Ildephonse Favé (1812-1894, aide-de-camp to Napoléon III (1808-1873, reigned 1852-1870)) presented His Majesty with a sample of Fontaine's powder; a commission was appointed, and, on 6 July 1865, the Minister of the Navy received 400 kilograms of the powder at Toulon for filling the torpedoes invented by Vice-Admiral Octave Pierre Antoine Henri de Chabannes-Curton (1803- 1889). Chabannes' torpedoes received much publicity, and it was not long before the composition of the explosive used in them was revealed. According to Fontaine, it was disclosed by 'Captain Vergnaud', in a book published in 1865. Amand Denis Vergnaud (1791-1885), was an artillery colonel associated with the pyrotechnic school at Toulon, and a prolific writer of technical books. Fontaine's powder was a mixture of equal parts of potassium picrate and potassium chlorate.[177]

In 1867 French chemical entrepreneurs Paul Gustave Louis Gabriel Designolle (n.d.) and John Casthélaz (1829-1892) applied for a patent for the use of picrate of potash, other picrates and of picric acid itself in explosive and fulminating powders. Casthélaz had so improved the process for manufacturing picric acid that he could sell potassium picrate at 7 francs per kilogram. Designolle and Casthélaz disclosed a range of explosives, including a mixture of about 55 parts of potassium picrate and 45 parts of saltpetre; this, subsequently known as 'Poudre Designolle', was recommended as a mining powder and for filling explosive projectiles. Years later, almost identical mixtures would be used in pyrotechnic whistles. [178]

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[176] J. Dumas, "Sur la nature de l'indigo et sur la véritable composition de quelques produits auxquels il donne naissance," *Annales de Chimie et de Physique* 63 (1836), pp. 265-272; Jons Jacob Berzelius, "Acide nitropicrique," in *Traité de chimie* (Bruxelles: Société Typographique Belge, Adolphe Wahlen et cie 1839), pp. 212-214; Auguste Laurent, "Mémoire sur le phényle et ses dérivés," *Annales de Chimie et de Physique* 3 (3 ser.) (1841), pp. 195-228; R. F. Marchand, "XLVIII. Ueber die Pikrinsalpetersäure," *Journal für Praktische Chemie* 23 (1841), pp. 363-375; Guinon, "La préparation de l'acid picrique et son application à la teinture en jaune," *Annales des sciences physiques et naturelles, d'agriculture et d'industrie, publiés par la société nationale d'agriculture, etc., de Lyon* 1 (deuxième série) (1849), pp. 178-174; J. Girardin, "Note sur l'acide picrique considéré comme matière colorante jaune," *Journal de pharmacie et de chimie, troisième série.* 21 (1852), pp. 30-35; "On Picric Acid Considered as Yellow Coloring Matter," *The Chemist* 3 (new series) (1852), pp. 271-273.

[177] Anonymous, "Arts chimiques. Note relative a une réclamatlon de priorité présentée au sujet de la fabrication de la poudre de guerre à base de picrate de potasse, par M. Fontaine," *Bulletin de la société d'encouragement pour l'industrie nationale* 16 (deuxième série) (1869), p. 123. For Vergnaud, see Philip, *A Bibliography of Firework Books: works on recreative fireworks from the sixteenth to the twentieth century*. pp. 154-150; vide infra, Chapter 7. For the composition of 'Poudre Fontaine', see Lt-colonel Hennebert, "Sciences militaires: la mélinite," *La science illustrée* 1 (1888), pp. 21-23.

[178] Anonymous, "Brevets d'invention," *Le Moniteur Scientifique* 10 (1868), p. 711; John Casthélaz "Acides picriques du commerce. Moyen d'en renconnaitre la pureté." *Le Moniteur Scientifique* 8 (1866), pp. 984-987. Jouglet, "Les poudres Designolle." For the British patent, see Vaughan, "Patents. Communicated by Mr Vaughan, F. C.S., Patent Agent, 54, Chancery Lance, W. C. Grants of Provisional Protection for Six Months,"

As discussed in Chapter 4, in 1883 Paul Tessier investigated picrates for use in fireworks and presented a range of coloured fires based on ammonium picrate. He also tried potassium picrate in coloured fires, but abandoned it because of the 'peculiar and irritating crackling that always accompanied the burning....' Had he tried a 'crackling' composition in a thick-walled tube, Tessier might well have discovered the pyrotechnic whistle. It is easy to see why he did not do so: a flame is at its best when it is not obscured by surrounding cardboard, so there would have been no point in burning a flame composition in a thick-walled tube.[179]

At some unknown time in the mid 1880s it was discovered that a thick-walled cardboard tube filled with compressed potassium picrate produces a loud screeching whistle when ignited. This was discussed in print in 1888 by French photographer, graphic artist and amateur pyrotechnist Amedée Denisse (1827-1???). The circumstances in which the effect was discovered remain a mystery, but the discovery can be placed between the publication of Tessier's work in 1883 and 1888, when the new effect was being exhibited at French displays and Denisse's book was published. The initial reception of pyrotechnic whistles was unfavourable; spectators at a display at Le Havre in July 1888 were annoyed by the shrill noise and, believing it to be a prank played by youngsters, shouted: 'Remove the whistlers!' 'Throw the whistlers in the water!' When they realized that the fireworks were whistling, they laughed at their mistake. In Britain at least, the public must have come to appreciate pyrotechnic whistles, as Brock referred to 'the always popular whistling rocket' in which whistles replaced the usual stars at the apex of the rocket's flight. Denisse's whistling rocket had a single whistle attached to the rocket and ignited at the same time, so the rocket whistled as it ascended.[180]

Denisse is yet another example of an amateur pyrotechnist disseminating knowledge of a novel pyrotechnic effect produced by a material new to the art. Whether he was the discoverer of the effect is not known, but there is evidence that he invented at least one of the whistling compositions mentioned in his book. Although pure potassium picrate will whistle, it is dangerous to handle because it is easily ignited by shock or friction. Denisse recommended a mixture of 15 parts of picrate with 1 part of Bitumen of Judea, which he somewhat optimistically claimed could be ground 'with no more danger than any other preparation employed in pyrotechny.' The choice of Bitumen of Judea as a desensitising agent is indirect evidence that the whistling composition was invented by Denisse. Bitumen of Judea was used in photoengraving. Denisse, as a professional photographer and illustrator, would have used it, or at least known of its use, for that purpose and could well have had some to hand. He specified 'true' Bitumen of Judea; this is not something that would have been in the workshop of an ordinary French pyrotechnist. Neither Chertier nor Tessier mentioned it, and the Vergnauds specifically stated that asphalt or bitumen, 'present in almost all former incendiary compositions', was no longer used in fireworks. The use of a photo-engraving material in pyrotechny points to the inventor being both a photo-engraver and a pyrotechnist, as was Denisse. If this is correct, the use of potassium picrate in pyrotechnic whistles provides yet another example of the contribution of amateur pyrotechnists to the transformation of fireworks in the 19th century.[181]

The Chemical News 17, no. 425 (1868), p. 50. The American patent is Designoble(sic), G., and John Casthelaz "Improvement in Explosive-Powders." United States of America Patent 76,173, dated March 31, 1868.

[179] Paul Tessier, "Picrates," in *Chimie pyrotechnique ou traité pratique des feux colorés* (Paris: Librairie Militaire de L. Baudoin et Cie., 1883), pp. 226-241. The comment about the crackling sound is on page 229.

[180] Amédée Denisse, *Feux d'artifice sifflants* (Paris: Poulenc frères, 1888). The reaction of the spectators is given in "Sifflets chimiques," *La Nature* 7 (1888), pp. 226-227. This also quotes from Denisse's book and reproduces one of his Figures. For Brock's comment, see Brock, *A History of Fireworks*, page 205.

[181] A. D. Vergnaud and P. Vergnaud, *Nouveau manuel complet de l'artificier. Seconde partie: pyrotechnie civile* (Paris: Roret, 1865), p. 20. For the use of bitumen in photoengraving in 1888, see W. T. Wilkinson and Edward L Wilson, "Printing on Zinc in Bitumen," in *Photo-engraving, photo-etching, and photo-lithography in line and half-tone; also, collotype and heliotype* (New York: Edward L. Wilson, 1888), pp. 48-50.

Denisse also presented several other mixtures, notably a mixture of potassium picrate and saltpetre. This, familiar since 1868 as the explosive 'Poudre Designolle' has the advantages of being much less costly and somewhat less prone to explode than pure potassium picrate. English pyrotechnist Ronald Lancaster, writing in the early 1970s, stated that one manufacturer still made small quantities of potassium picrate for the firework trade - an example of a material being specifically made for fireworks long after it had otherwise become obsolete. In current practice potassium picrate seems to have been replaced by a range of somewhat less dangerous whistling compositions developed during the 20th century. [182]

The application of picrates in fireworks follows the familiar trajectory of materials originating in the laboratories of academic chemists becoming items of commerce as a result of practical applications being found and laboratory methods of production being implemented on an industrial scale. In this case, when a means of making picric acid more economically was discovered in the course of chemical research, entrepreneurs began to make it on a large scale as a yellow dye. Entrepreneurs and chemical manufacturers then sought new uses for it and its derivatives. Potassium picrate was already known to be explosive, so its application in military explosives was an obvious field of research. During this work the picrate-based coloured fires were discovered, as discussed in Chapter 4. Firework-makers began experimenting with picrates, and someone, probably Amedée Denisse, stumbled across the completely novel pyrotechnic whistle.

5.4 Concluding Remarks

This project began with the question: 'Why were new materials introduced into firework-making in Europe in the 19th century, and not in some other place, at some other time?' Each of the three new materials reviewed in this chapter shows that at least part of the answer is that the material was discovered and characterised in Europe in the 19th century, so it could not have been introduced earlier anywhere else. The reason that the materials became known in that place and at that time is because the science of chemistry was sufficiently advanced, for reasons that are the province of historians of science and will not be discussed here. The chain of explanation has to stop somewhere.

It is still necessary to explain why these materials became available at a price and in quantities that made them useful in fireworks. This was not inevitable: they could conceivably have remained indefinitely as costly arcana of interest only to savants. They did not, because they found practical applications that made it profitable to produce them in quantity. Those applications differed greatly from one material to another: as ingredients in explosives in the case of potassium picrate, as a photographic light source in the case of magnesium, and as a light, strong structural material in the case of aluminium. The existence of these applications needs to be explained, too. The explanations lie in the social conditions of 19th century Europe: militarism and international conflict and suspicion led to interest in novel explosives, increased wealth and leisure time were favourable to the growth of amateur photography, and general material prosperity prompted the introduction of new structural materials. Even under these circumstances, availability of the materials at an affordable price was contingent on the existence of appropriate forms of production and on the development of the necessary technology. Electrochemical production of magnesium and aluminium, for example, had been demonstrated long before cheap electric power made the processes economically feasible. Developments were interactive and mutually reinforcing, as previously inaccessible materials became

[182] For the early history of the picrate whistle, see Michael S. Swisher, "Brisantly Explosive Pyrotechnic Compositions: A Survey of Their History and Use," *Pyrotechnica*, no. 16 (1995), pp. 57-63; George A. Mannie. Pyrotechnic Signal. United States Patent 385,562, filed May 10 1888, and issued July 3 1888; Antonio Del Grande. Preparing Pyrotechnic Compounds. United States Patent 411,714, filed January 5 1889, and issued September 24 1889. For 20th century developments, see Ronald Lancaster, *Fireworks Principles and Practice* (New York: Chemical Publishing Co., Inc., 1972), p.120; Takeo Shimizu, "Manufacturing Process of Firework Composition. Japanese Fireworks.", in *Fireworks Priciples and Practice*, ed. Ronald Lancaster (New York: Chemical Publishing Co. Inc., 1972), pp. 234-235; Selçuk Öztap, "The Pyrotechnic Whistle and its Applications," *Pyrotechnica*, no. XI (1987), pp.. 49-54.

available and in turn facilitated improvement of technology. Long-range transmission of electricity, for example, was facilitated by strong, light and highly conductive aluminium cables, which were feasible only because of cheap aluminium, produced by electricity. To go further would take us too far from the subject, but it is clear that the developments discussed here fit well with our knowledge of the broad social circumstances of 19th century Europe.

The last four chapters have shown how and why the materials needed for the transformation of fireworks came to be known and how they became available in the requisite quantities at affordable prices. That has explained how the transformation of fireworks became possible in 19th century Europe; the next chapters will explain why that possibility became reality. To do that, it is necessary to understand who wanted to transform fireworks, and why.

Chapter 6: The Role of Amateurs in the Transformation of Fireworks in the 19th Century.

Perhaps the most interesting discovery of this project is that many of the new materials fundamental to the transformation of fireworks in the 19th century were introduced by amateur pyrotechnists. Furthermore, knowledge of how those materials could be used was spread mainly in books written by or for amateurs. The best records that we have of the technical development of fireworks in 19th century Europe were written by Meyer, an officer in the Prussian war ministry; Websky, a Prussian linen-merchant; Chertier, a retired French artillery officer, and a trio of Englishmen: Moore, a clergyman, Browne, a physician and surgeon and chemist, and Kentish, a schoolmaster and accountant. Each of these authors wrote specifically for amateur firework-makers, as did the French polymath and publisher Louis-Eustache Audot (1783-1870). Audot's *l'art de faire a peu de frais les feux de'artifice* first appeared in 1818 and re-appeaered in six revised editions over the course of the century, the final version being published as late as 1891. The French amateur pyrotechnists Paul Tessier and Amédée Denisse addressed their books to both amateur and professional firework-makers.

The word 'amateur' is used here in the original sense of a person who engages in an activity primarily for non-pecuniary reasons, while 'professional' refers to one who makes a living by it. When using terms such as 'professional' and 'amateur' we take care not to project our current understanding of these terms onto the past. In current usage 'professional' carries connotations of advanced skill and high standards, often authenticated by the State, while 'amateur' can imply an incompetent dabbler. These implications are not intended here; most amateurs mentioned were at the forefront of the art. The people described here as 'amateurs' either specifically stated that they engaged in firework making in their spare time, or they actually referred to themselves as 'amateurs'. The word seems to have had two connotations: the person was what we might call an 'enthusiast' – the work was a source of pleasure and personal satisfaction – and that he (all the amateurs discussed here were men) did not rely on the work as a source of income. In reality, a pyrotechnist would probably lie somewhere on a continuum between a 'professional' who worked with fireworks to make money, and a true amateur who worked with them even though it cost him time and money to do so. A practitioner's status could also change over time. The American shoemaker Edmund Soper Hunt (1827-1909) turned firework-making from a hobby to a lifetime career; the English journalist and amateur pyrotechnist William Platt Ball (1844-1917) temporarily turned professional for 15 months in the early 1870s when his friend Charles Thomas Brock assigned him to set up a firework factory in Turkey.[183]

As with most categories applied to historical actors, shades of grey are much more to be expected than black or white. None the less, the distinction between amateurs and professionals is useful because of the likely differences in their attitudes to dissemination of knowledge. Self-proclaimed amateurs tend to be open to passing knowledge to others, whereas professionals have an understandable desire to keep knowledge to themselves. This goes a long way towards explaining why amateurs played such a large part in the introduction of new materials into firework-making. To show the significance of their role, it is useful to examine some figures.

A survey of 23 publications on fireworks, dating from 1766 to 1972, revealed that of 35 ingredients introduced in the 19th century, and that were still being used in the 20th century, 26 were introduced by amateurs. Of the remaining 9, one (strontium nitrate) had been introduced as an ingredient in theatrical red fires by around 1807, but it has not been possible to find any details. Another

[183] For Hunt, see Edmund Soper Hunt, *Weymouth Ways and Weymouth People. Reminiscences by Edmund Soper Hunt* (Boston: Privately Printed, 1907). For William Platt Ball, see Brock, *A History of Fireworks*, pp. 90-91.

(aluminium) was introduced by a commercial manufacturer of matches and fireworks in 1893. The remaining 7 had been introduced by men associated with the military, as discussed in Chapter 7. [184]

The 26 useful ingredients introduced during the 19th century by amateurs (Table 6.3) give an insight into the extent to which 19th century amateurs contributed to the transformation of fireworks by introducing new materials. The word 'introducing' is used here for either an author first recording use of the material, or definitely asserting that he had discovered the value of the material in fireworks. Much effort has been spent in searching for records of earlier 'introduction', without success. For most of the materials, the attribution was straightforward, but a couple deserve comment. Chertier's specific advocacy of antimony (as opposed to the sulfide, confusingly also called 'antimony' by early writers) is a rather marginal contribution and could well be omitted. Shellac is much more important, and its attribution is difficult. If mentioning it, and giving a recipe including it with no further comment is taken as its introduction, then the honour goes to Websky (1839). If being the first to discuss it in detail, point out its special advantages, and include it in a range of recipes, is the criterion, then Chertier (1843) is to be credited. Both were amateurs, so the attribution is irrelevant to the point being made.

The ingredients in Table 6.3 are not of equal importance – indeed, it was surprising to find some of them still listed in 20th century books. Several others are now obsolete. The removal of all of these would not affect the point being made: a remarkable number of essential ingredients in modern fireworks were introduced in the 19th century by amateurs. This is shown in Table 6.3 by indicating in bold type the ingredients listed in two recent books on fireworks.[185]

[184] Robert Jones, *Artificial Fireworks, Improved to the Modern Practice*, 2nd ed. (London: J. Millan, 1766); Ruggieri, *Elémens de pyrotechnie*, (1802); Websky, *Grundlich und fasstliche Anweisung zur Verfertigung kleiner Lustfeuerwerke* (1831); Chertier, *Essai sur les compositions qui donnent les plus belles couleurs dans les feux d'artifice* (1836); Bruce, *A New Guide to Pyrotechny* (1840); Chertier, *Nouvelles recherches sur les feux d'artifice* (1843, 1854); Tessier, *Chimie pyrotechnique* (1859) ; Moore ('Practicus'), *A Manual of Pyrotechny* (1871) ; Browne, *The Art of Pyrotechny* (c. 1873) ; Hutstein and Websky, *Martin Websky's Lustfeuerwerkkunst* (1878); Kentish, *The Pyrotechnist's Treasury(*1878); Denisse, *Traité pratique complet des feux d'artifice*(1882); Paul Tessier, *Chimie pyrotechnique ou traité pratique des feux colorés* (Paris: Librairie Militaire de L. Baudoin et Cie, 1883); W. H. Browne, *Firework Making for Amateurs* (London: L. Upcott Gill, 1888); Bujard, *Leitfaden der Pyrotechnik* (1909): Ferré y Vallvé, *La pirotecnia moderna* (1909); Gelingsheim, *Die moderne Kunstfeuerwerkerei* (1913) Brock, *A History of Fireworks*(1949) ; Lancaster, *Fireworks Principles and Practice* (1972).

[185] Takeo Shimizu, *Fireworks: The Art, Science and Technique* (Tokyo Maruzen Co. Ltd, 1981). Ronald Lancaster, *Fireworks Principles and Practice*, 4th ed. (New York: Chemical Publishing Co., Inc., 2006).

Ingredient	Synonyms	Main use in fireworks	Introduced by, year
potassium chlorate	Chlorate of potash	Oxidizer	Forster, 1810
barium nitrate	Nitrate of baryta	Green colour agent	Forster, 1822
copper(II) oxide	Black copper oxide	Blue colour agent	Websky, 1831
strontium carbonate	Carbonate of strontia	Red colour agent	Websky, 1831
lead(II,II,IV) oxide	Red lead	White colour agent	Websky, 1831
sodium carbonate	Soda ash	Yellow colour agent	Websky, 1831
copper(II) sulfate—copper(II) hydroxide (1/3) monohydrate	Basic sulfate of copper	Blue colour agent	Chertier, 1836
mercury(I) chloride	Calomel	Colour enhancer	Chertier, 1836
barium chlorate monohydrate	Chlorate of baryta	Green colour agent	Chertier, 1836
sodium oxalate	Oxalate of soda	Yellow colour agent	Chertier, 1836
sodium hydrogen carbonate	Bicarbonate of soda	Yellow colour agent	Chertier, 1836
shellac	Gum lac	Fuel	Websky 1839
strontium chlorate	Chlorate of strontia	Red colour agent	Bruce, 1840
dextrin		Binder	Chertier, 1843
copper(I) sulfide	Sulphide of copper	Blue colour agent	Chertier, 1843
antimony	**antimony regulus**	**Fuel**	**Chertier, 1843**
strontium sulfate	Sulphate of strontia	Red colour agent	Chertier, 1843
lead(II) oxide	Litharge	Spark producer	Chertier, 1843
lead(II) nitrate	Nitrate of lead	White colour agent	Chertier, 1843
sodium chlorate	Chlorate of soda	Yellow colour agent	Chertier, 1843
potassium perchlorate	Perchlorate of potash	Oxidizer	Websky, 1850
copper(II) chloride—copper(II) hydroxide (1/3)	copper oxychloride	Blue colour agent	Tessier, 1859
lead(II) chloride	Chloride of lead	Colour enhancer	Tessier, 1859
lactose monohydrate	Milk sugar	Fuel	Websky,1865
strontium oxalate monohydrate	Oxalate of strontia	Red colour agent	Tessier,1883
sodium hexafluoro-aluminate	Cryolite	Yellow colour agent	Tessier,1883

Table 6.3. Pyrotechnic ingredients introduced by amateurs in the 19th century and still mentioned as useful in 20th century publications.

We must now explain why amateur firework-makers existed at all in the 19th century. In the early 19th century fireworks were a well-established part of European life, just as they had been for the previous four or five centuries. The 19th century was different from previous centuries in that many more people had the time and money to pursue interests in non-essential activities. Some of these activities included participation in fields such as natural history, chemistry, photography and even firework-making. People would use shared interests in such fields to facilitate social interactions; expertise in a

chosen field would enhance a person's esteem in the eyes of like-minded friends and in the community at large.

Fireworks were much more prominent during the 19th century than in previous centuries because they had become commercialized in the late 18th century. In these circumstances it is to be expected that at least a few people would become sufficiently fascinated by fireworks to take up firework-making. While some might well have hoped that this would lead to financial gain, the more usual reward would have been the admiration and respect of fellow enthusiasts. This explains the propensity of some successful amateurs to write books to make their knowledge available to fellow enthusiasts, as happened with Websky in Germany; Audot, Chertier, Tessier and Denisse in France and Moore, Browne and Kentish in England.[186]

Several circumstances were favourable to amateur firework-makers making new contributions to the art. The necessary materials were available to anyone who could afford them: as discussed in Chapter 8, some materials were quite costly, but there were no other restrictions on obtaining them. Furthermore, even though rules prohibiting the unauthorized making or use of fireworks existed, they were not strictly enforced for most of the century. Knowledge needed to contribute to pyrotechny did not have to be acquired through formal training. On the contrary, at the beginning of the development of the new coloured fires formal training in either chemistry or pyrotechnics would have been a disadvantage. As discussed elsewhere, chemists taught that potassium chlorate, the key to success, was too dangerous to use, and pyrotechnists taught that fiercely-burning mixtures were ineffective for producing colour. This explains why the first of the new generation of coloured fires was invented by a 16 year old medical student, rather than by an experienced chemist or pyrotechnist.

As explained in Chapter 3, by the time John Forster developed the new red and green fires it was already known that yellow fire could be made with sodium nitrate. White was easily produced with Bengal Fire, Indian Fire, or a simple mixture of saltpetre, sulfur and a small amount of gunpowder, but there was no satisfactory blue. That changed in 1831, thanks to Johann Martin Websky.[187]

This pioneer of modern fireworks was born on 12 March 1799 at Breslau, Dolnoslaskie and died on 14 January 1867 at Wüstegiersdorf, Kreis Waldenburg. In those days that part of Europe was called Silesia and was part of the Kingdom of Prussia. Since 1945 it has been part of Poland. Breslau is now Wroclaw, Wüstegiersdorf is Głuszyca. Websky's parents (Friedrich August Websky (1769–1823) and Friederike Eleonore Henriette Schmige (n.d.)) were successful business people. Young Websky became a wholesale linen merchant and owner of a textile mill. Like his father, he earned the honorific title of Commerzienrath (commercial councillor); his obituary notes his generosity and his willingness to use his wealth to benefit others. Websky was a family man, having married Friederika

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[186] Websky, *Grundlich und fasstliche Anweisung zur Verfertigung kleiner Lustfeuerwerke*; *Praktisches Handbuch der Lustfeuerwerkkunst* (Breslau: August Schulz und Comp., 1834); *Lustfeuerwerkerei für Dilettanten*; *Lustfeurwerkkunst; oder, Leicht fassliche und bewahrte Anweisung zur Verfertigung von Lustfeuerwerken*, 4th ed. (Breslau: Ferdinand Hirt, 1842); *Martin Websky's Lustfeuerwerkerei insbesondere Dilettanten und Freunde dieser Kunst. Nebst einem Doppel-Anhang: (I) Die Stoffe und Substanzen der Lustfeuerwerkerei in ihrem chemischen und physikalischen Verhalten theoretisch betrachtet von Ernst Schnell; (II) Auszug des Neuen und Beachtenswerthen aus F. M. Chertier's Lustfeuerwerkerei nach dem Französischen mit Anmerkungen von Martin Websky.*, 5 ed. (Breslau: Ferdinand Hirt's Verlag, 1846); *Martin Websky's Schule der Lustfeuerwerkerei. Ein Vermachtniss an die Freunde und Dilettanten dieser Kunst*; Hutstein and Websky, *Martin Websky's Lustfeuerwerkkunst, Leichtfassliche, bewährte Anleitung zur Anfertigung von Lustfeuerwerken inbesondere für Dilettanten und Freunde der Lustfeuerwerkerei*; Chertier, *Essai sur les compositions qui donnent les plus belles couleurs dans les feux d'artifice*; *Nouvelles recherches sur les feux d'artifice*; *Nouvelles recherches sur les feux d'artifice*; Tessier, *Chimie pyrotechnique ou traité pratique des feux colorés*; *Chimie pyrotechnique ou traité pratique des feux colorés*; Denisse, *Traité pratique complet des feux d'artifice*; *Feux d'artifice sifflants.*

[187] Sturman, "Coloured Fire." "The Early Use of Potassium Chlorate in Pyrotechny: Part I. John Forster and the First Chlorate-based Colored Fire."

Karolina Kramsta (1801-1872) in 1822; they were to have six children. He was active in music, mechanics, physics and chemistry, as well as being an authority on fireworks. At the time of his death one of his firework books had already appeared in six editions; he has also written two other books on fireworks.[188]

Some time before 1831 Websky set out to find exactly what colours could be produced in fireworks. He added compounds of all the common metals to a test mixture of potassium chlorate, sulfur and mastic. Most of the results were disappointing, but copper oxide produced a beautiful blue flame. He published the results in a little book on amateur pyrotechny. Websky could do this work because he was sufficiently wealthy to indulge in a science-based hobby and could get hold of the necessary chemicals – by the early 19th century suppliers of chemicals had established themselves to supply not just educational institutions and commercial users, but amateur scientists and experimenters as well.[189]

In 1836 Chertier published his first work on coloured fires. Chertier's birth year can be estimated from a portrait of him (Figure 1) by Denisse, included in Denisse's 1882 book:

[188] "The Early Use of Potassium Chlorate in Pyrotechny. Part IV. Martin Websky's Colored Flame Compositions of 1831". Philip, *A Bibliography of Firework Books: Works on recreative fireworks from the sixteenth to the twentieth century*, pp. 157-160.

[189] Websky, *Grundlich und fasstliche Anweisung zur Verfertigung kleiner Lustfeuerwerke.* The tests and their results are on p. 38; the corresponding test mix for copper oxide appears on p. 37 as 'Composition for light balls. No. 3. Blue'. For chemical suppliers, see e.g. Fredrick Accum, "A Descriptive Catalogue of the Apparatus and Instruments employed in Experimental and Operative Chemistry, in Analytical Mineralogy and in the Pursuits of the Recent Discoveries of Voltaic Electricity," (London: Fredrick Accum, 1817); Kersaint, "L'usine de Vauquelin et Fourcroy", pp. 35-30;. Sur la fabrique de produits chimiques établie par Fourcroy et Vauquelin 23, rue de Colombier, à Paris." *Comptes rendus hebdomadaires des séances de l'Académie des Sciences* (28 Juillet 1958), pp. 461-64.

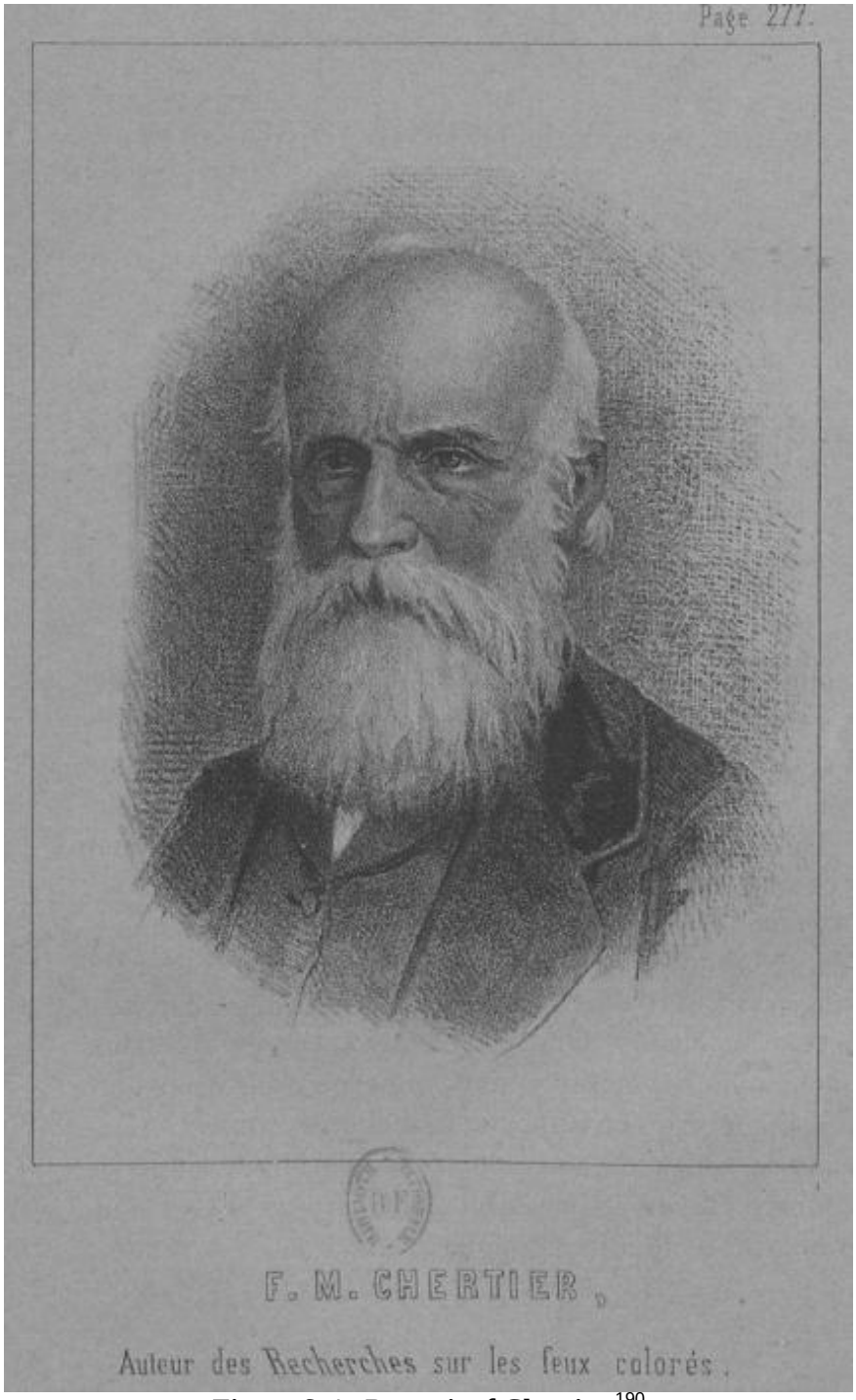

Figure 6. 1. Portrait of Chertier.[190]

Michael Swisher has commented that as the portrait depicts a man probably over seventy years of age, and if it was made around the time of the publication of the second issue of his book (1854), Chertier would have been born before 1785. His death record shows that François Chertier, formerly of the 1st Arrondissement, died on March 12, 1855.[191]

[190] Denisse, *Traité pratique complet des feux d'artifice*. Facing p. 277.

[191] Chertier, *Essai sur les compositions qui donnent les plus belles couleurs dans les feux d'artifice*. Michael S. Swisher, "Chertier," in *PyrotechnicsMailing List (PML)* (2008). Note: this is a members-only mailing list. The death record was found in the Paris archives by Professor David Garrioch, to whom I am most grateful.

British pyrotechnist Thomas Kentish (1810-1894) wroter:

> ‘To Chertier belongs the great improvement in colours. He was, as I was informed by the late Mr Southby, who knew him personally, and who derived much information from him while in Paris, a retired French Artillery Officer, who made colours “his study and theme’ [192]

At the time of his first publication (1836), Chertier would have been over 50 years of age. Nothing could be found about his family, nor about his personal circumstances in 1836. Clues about his later life are in his addresses, given his two self-published books. In 1843 he was living at No. 40, rue St Thomas du Louvre. This was the address of the Hôtel de Lille et d’Albion, established around 1824. It was centrally located, near the Palais Royale, the Louvre and the Tuileries Gardens, and said to be ‘well known to English visitors’. Chertier must have been reasonably prosperous to have afforded such accommodation. In 1847 the Hôtel de Lille et d’Albion was re-located to No. 323, rue St Honoré, ‘nearly opposite the Church of St Roch’. This is a short distance from the previous address. According to a contemporary advertisement, the re-location provided ‘more commodious and centrally situated premises, containing numerous spacious apartments for large families, replete with every convenience.’ In Chertier’s 1854 book his address is given as 323, rue St Honoré. This is in the 1st Arrondissement, consistent with Chertier’s death record. We can conclude that when the Hôtel de Lille et d’Albion moved to that address in 1847, Chertier went with it.[193]

Chertier not only lived in a rather fine hotel, but, according to Denisse, he carried out his pyrotechnic researches there. Denisse’s book includes the following illustration of Chertier at work (Figure 6.2):

[192] Kentish, *The Pyrotechnist’s Treasury: The Complete Art of Making Fireworks*. p. vi.

[193] B. Sturman, "The Early Use of Potassium Chlorate in Pyrotechny. Part VII. F. – M. Chertier and the Development of Chlorate-based Coloured Fires in France.," *PGI Bulletin (Bulletin of the Pyrotechnics Guild International, Inc.)*, no. 193 (2015).

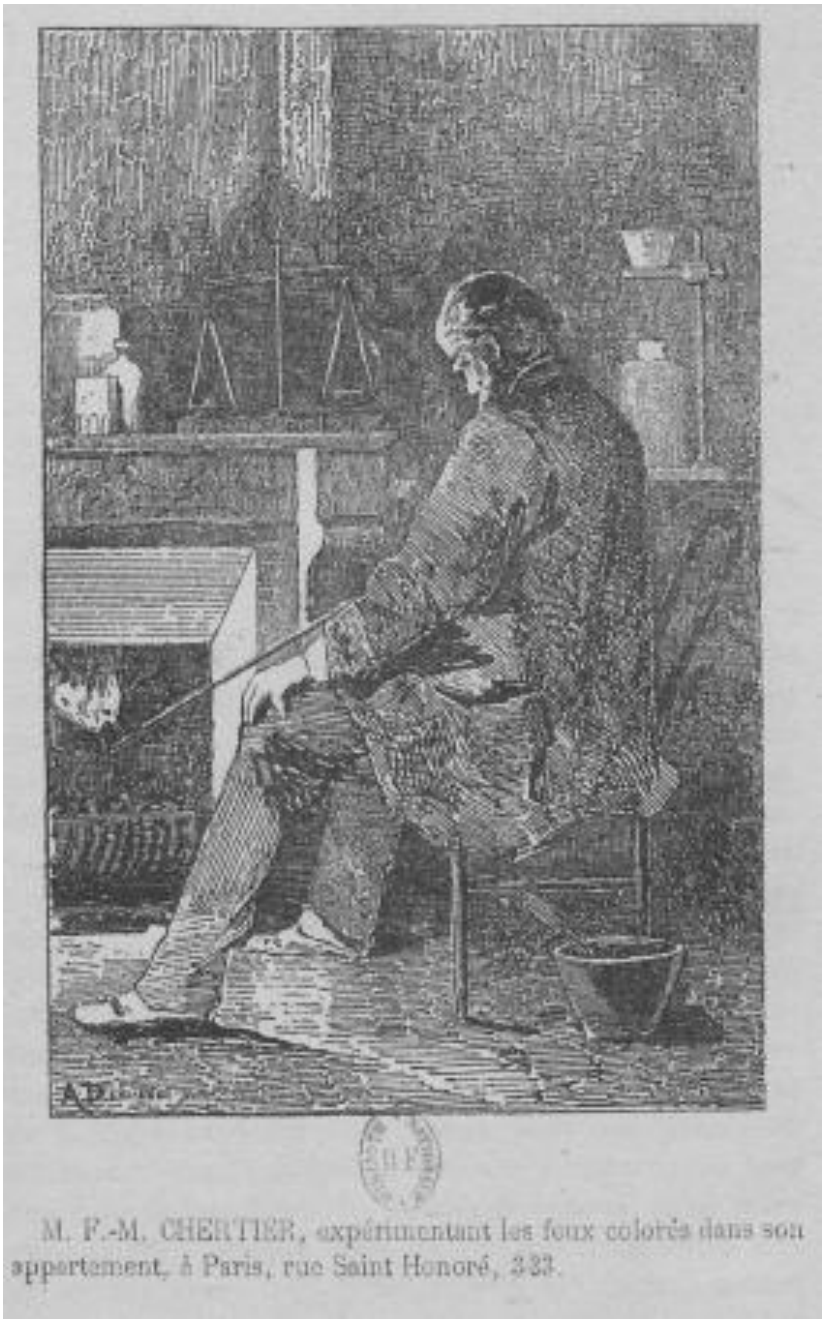

Figure 6.2. Chertier at work.[194]

The picture was published some 35 years after Chertier moved to 323, rue St Honoré and 27 years after his death. It is likely that Denisse had visited Chertier and witnessed the scene shown in the picture. The two seem to have been acquaintances; Denisse's portrait of Chertier (Figure 6.1) was presumably drawn from life and Denisse's book contains previously unpublished recipes for coloured fires identified as 'the last researches of M. Chertier'.[195]

The pieces of apparatus shown in Figure 6.2 are what one would expect to see in the laboratory of a pyrotechnic experimenter of the day. A balance is on the mantle piece, filtration apparatus for

[194] Denisse, *Traité pratique complet des feux d'artifice*. Frontispiece.

[195] Ibid., p. 280.

separating solids from liquids is on a shelf to the right of the picture, and a large mortar and pestle is on the floor in the right foreground. Chertier seems to be using a long metal rod, with a ring at the end, to hold a burning coloured fire under the chimney flue in the fireplace.

Chertier's use of his hotel room for pyrotechnic experiments confirms that he was not a professional firework-maker; a professional would have had a workshop. He presented himself as an amateur writing for his fellow amateurs. The value of his work is shown by following extract from the reminiscences of Edmund Soper Hunt, who began as an amateur firework-maker but became a successful professional, shows the value of Chertier's work. Writing of his early experiences with fireworks, in 1856, Hunt stated:

> Though a beginner, the work of Chertier placed me far in advance of the old pyrotechnists who had learned their trade by rule of thumb. The book not only told me what chemicals to use, but how to make each kind, and their nature. In boyhood I had made rockets and Roman candles, and had had many mysterious fires from spontaneous combustion. This book explained all such things and why they occurred, and how to avoid these dangers[196]

Unlike Websky, Chertier did not restrict his tests to individual chemicals, but tested combinations of them. This led him to discover that calomel (mercury(I) chloride, Hg_2Cl_2, long used as a laxative) could enhance the beauty of red, green, blue and purple flames although by itself it imparted no colour. The reason for this was not understood until the 20th century, and could not have been predicted by the chemists of the day. As discussed in Chapter 9, some 15 years after Chertier's discovery a German chemistry professor published a paper on coloured fires in which he criticised firework-makers for including such a useless material as calomel in their mixtures. Useless according to the chemical theory of the day, calomel was anything but useless in practice.[197]

In 1834 Chertiers' research was set back by some two years by a phenomenon that was to plague firework-makers for decades to come: mixtures containing potassium chlorate or barium chlorate would spontaneously burst into flame. A fire broke out in Chertier's rooms, consuming all his notes. He had to start again. As we shall see in Chapter 9, the problem was caused by the use of sulfur in combination with a chlorate. Sulfur had been the fuel of choice since the introduction of potassium chlorate into the art in 1810, but Chertier searched for alternatives and found that shellac, a material that had long been imported from India to make sealing wax and for polishing wood, was an excellent substitute and removed the problem of spontaneous combustion. Unfortunately it was also much more expensive than sulfur, which inhibited its adoption by commercial manufacturers of fireworks.[198]

Some four years after Chertier's death another French amateur pyrotechnist, Paul Tessier, published a book entitled '*Chimie pyrotechnique ou traité pratique des feux colorés'*, a classic in the literature of coloured fires. Little could be found about Tessier. Philip gave his birth year as 1816. Tessier's book is dedicated to Jules Pelouse (1807-1867), Professor of Chemistry at the École polytechnique and the Collège de France; Tessier might well have studied chemistry under Pelouze. His book reveals him as well-educated in chemistry. He made no statement about his occupation, but Denisse, who knew him, specifically referred to Tessier as 'this chemist'.[199]

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[196] Hunt, *Weymouth Ways and Weymouth People. Reminiscences by Edmund Soper Hunt*, p. 133.

[197] Chertier, *Essai sur les compositions qui donnent les plus belles couleurs dans les feux d'artifice*, Preface, and p. 7, For the reason for calomel's colour-enhancing properties, see Barrow and Caldin, "Some Spectroscopic Observations on Pyrotechnic Flames". For the German chemist, see Winkelblech, "Ueber Farbige Feuer," *Dingler's Polytechnisches Journal* 19, no. 4 (1851) 208-217; 294-302; vide infra, Chapter 9.

[198] For the fire, see Denisse, *Traité pratique complet des feux d'artifice*, p. xi. For Chertier on spontaneous combustion, see Chertier, *Nouvelles recherches sur les feux d'artifice*, (1854), pp. 400-401.

[199] Tessier, *Chimie pyrotechnique ou traité pratique des feux colorés*. Denisse, *Traité pratique complet des feux d'artifice,* p.13.

In his Preface Tessier admitted to having for ‘long years’ spent the better part of his leisure hours on pyrotechny, and claimed to have been making fireworks successfully since the discovery of coloured fires. This is credible, as he would have been about 20 years old when Chertier’s first pamphlet was published. Tessier wrote that as far as he knew, Chertier was the first to explore this ‘new path in pyrotechny’. Although we know next to nothing about Tessier’s life, there is a portrait of him (Figure 6.3), made by his younger contemporary and admirer, Amédée Denisse.

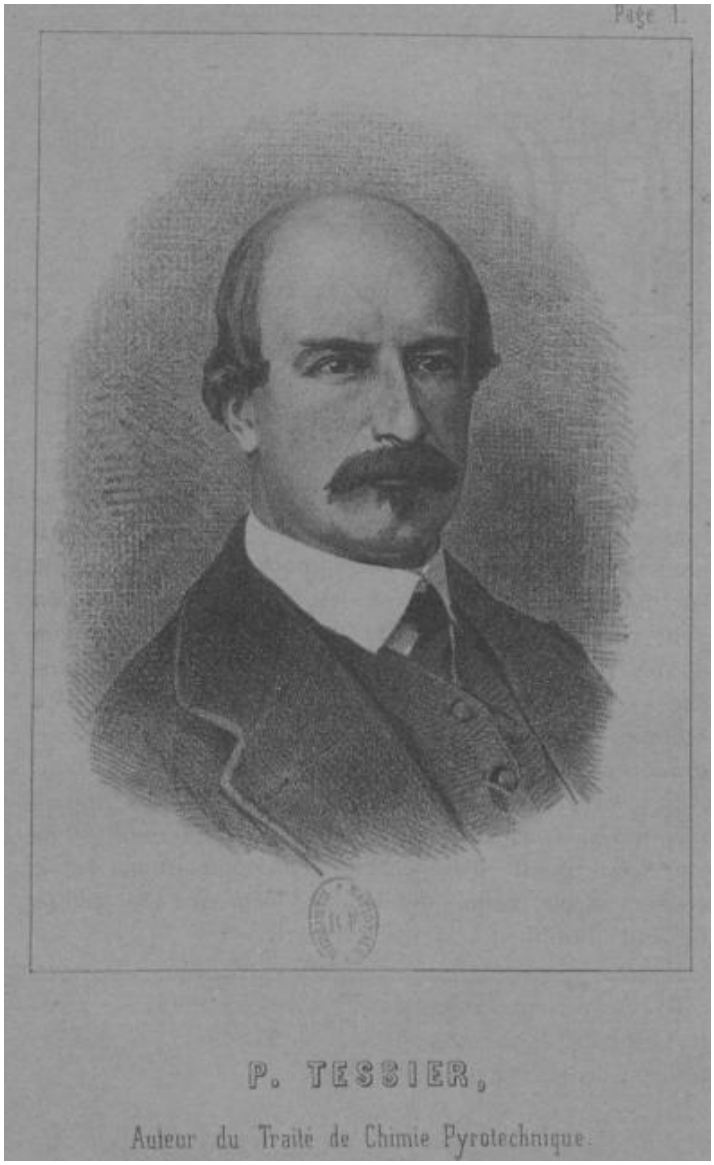

Figure 6.3. Portrait of Tessier by Denisse

The first 15 pages of Tessier’s book are devoted to an exposition of chemistry and chemical equivalents. This would have been useful to those wishing to understand Tessier’s instructions for making ingredients, but had no direct relevance to formulating firework compositions. This might have disappointed those who bought Tessier’s book on the strength of its title. While the theoretical section is of only limited relevance, the opposite is true of the bulk of the book, which could be categorized as descriptive chemistry. There are 291 pages of detailed information on a huge range of materials of possible interest to firework-makers. Tessier discussed not only materials that his research had shown to be valuable, but those that he deemed useless or dangerous. He included the latter, he wrote, so that pyrotechnists would not waste their time on them. Tessier included the cost of each material, considering economy to be second only to the beauty of the results. The next section, of

84 pages, gave instructions for making coloured stars, lances and Bengal lights. It included 113 compositions, with the price of each. The final section (34 pages) is devoted to pinwheels, for which he shared Chertier's enthusiasm. Here, too, the price was carefully calculated. In 1883 Tessier published a second, enlarged edition, notable for its discussion of picrates, as outlined in Chapter 4. Among the new materials that Tessier introduced are the yellow colour agent cryolite, the red colour agent strontium oxalate and the blue colour agent copper oxychloride. All of these have the advantage of being insoluble in water and being compatible with potassium chlorate. He also introduced lead chloride ($PbCl_2$) as a less costly alternative to calomel as a colour enhancer.

The artist responsible for the portraits of Chertier and Tessier reproduced here was the amateur pyrotechnist Amédée Denisse, who we have already encountered in Chapter 4 as the first to disclose the picrate whistle. Denisse was a professional illustrator and photographer. His enduring claim to fame is that he was the first to invent a way of taking aerial photographs with a camera carried aloft by a rocket and returned by parachute. This achievement is mentioned in many works on the history of rockets and of photography, but despite this it has not been possible to find the date of Denisse's death. He was born in 1827, so he was some 11 years younger than Tessier and substantially younger than Chertier.

Denisse' comprehensive treatise on firework-making, self-published in 1882, begins with a warning to the reader not to turn first to the chapter on compositions, and even venture to test some, without having read the preceding sections. To do so would risk mediocre results. He gave this warning, he wrote, because he recalled finding a second-hand book on pyrotechny in which the pages of formulae were blackened with use, but the remaining pages had not even been cut. Denisse stated that he had written his book 'to be useful to the friends of pyrotechny... to offer them the results of long years of observation of the progress of an art that we have always loved.' An amateur in the original sense of the word! He paid tribute to Chertier (who he believed to have been the first to publish 'truly coloured fires'), but criticised him for having published some dangerous compositions 'of which he was among the first victims' (referring to the fire in Chertier's rooms in 1834). He praised Tessier for his contributions to reducing the danger of spontaneous combustion.

Denisse's book is a comprehensive textbook of fireworks, extremely detailed and beautifully illustrated. The colour compositions that he presented were selected from Chertier and Tessier, and include some unpublished recipes described as being 'the result of M. Chertier's final researches'. They are somewhat puzzling, as many of them contain both potassium chlorate and sulfur, a combination that Chertier warned against in the second edition of his book because of its propensity to spontaneous combustion, as discussed in Chapter 9. Denisse presented a comprehensive table of ingredients and their costs, but did not introduce any new ingredients; his contribution in that regard was the disclosure of the picrate whistle some seven years later, as discussed in Chapter 5.[200]

Figure 6.5 shows a detail from the cover of Denisse's booklet on whistles, drawn by Denisse.

[200] *Traité pratique complet des feux d'artifice*. The comment about 'M. Chertier's final researches' is on p. 280.

Fig. 6.5. Detail from the cover of Denisse's booklet on pyrotechnic whistles, 1889. [201]

This fantasy artwork represents one aspect of Denisse's ability to use his artistic skills to promote pyrotechny; another is shown in the technical illustrations that adorn his book; an example is shown in Figure 6.6.

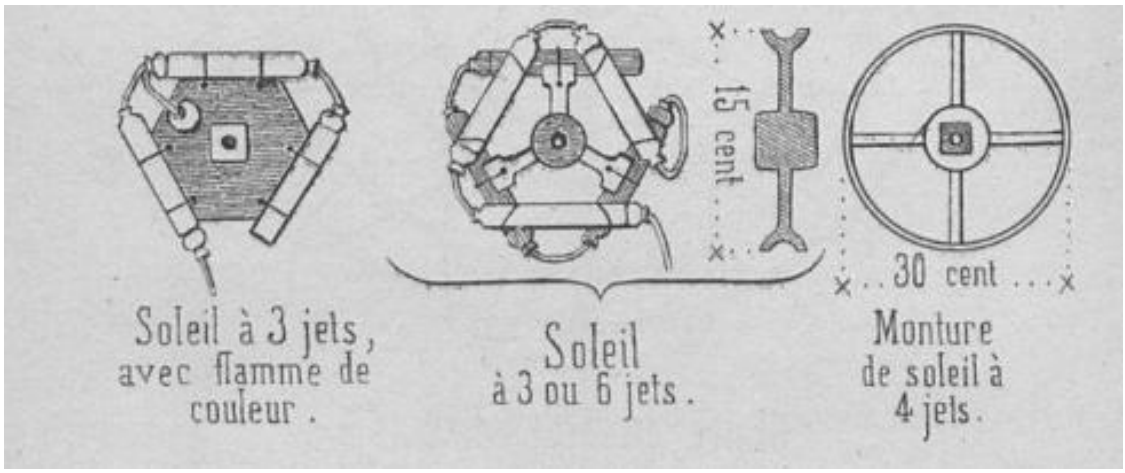

Fig. 6.6. Detail from a technical plate in Denisse's firework book, 1882[202]

Dennise exemplifies the highly effective role played by amateurs not only in invention, but in the dissemination of pyrotechnic knowledge in the 19th century. This aspect of the contribution of amateurs is worth examining in more detail, as it was not always as positive as the examples given so far would suggest.

[201] *Feux d'artifice sifflants*. Portion of cover.

[202] *Traité pratique complet des feux d'artifice*, p. 302.

The Role of Amateurs in the Dissemination of Knowledge.

The early Continental pioneers Chertier and Websky published their results in books presenting knowledge of new materials in the context of practical instructions for firework-making for amateurs. Even though the earliest work on coloured fires had been done in England, and the earliest recipes published there, there was no published British work equivalent to that of Websky and Chertier. Some four years after the publication of Chertier's Essay in Paris, a short work on fireworks was published in Edinburgh. The contrast between the two booklets could hardly be greater. Chertier's work stands as a classic; the Scottish one leaves the modern reader puzzled and sometimes appalled. The author was one Samuel Bruce, who identified himself as 'Aforetime Schoolmaster in the Westport, Edinburgh: Friend and Pupil of the late Rev. Eglington Thologus, B.D., quondam Pyrotechist in ordinary at the Courts of St Petersburg, Vienna, Paris and Berlin.' No record could be found of either Bruce or Thologus. It is odd, to say the least, that one man could have served as Pyrotechnist to four of the great European courts, and odder still that he somehow escaped notice.[203]

Bruce claimed to possess Thologus's 'fifty thousand experiments in manuscript', a resource from which he stated that he may 'hereafter enlarge this Treatise considerably' – a promise that he never kept. Bruce claimed that his intention was to ensure that people living at a distance from large towns (and thus presumably unable to get hold of fireworks) should be able to make some themselves to celebrate the forthcoming Royal Wedding. He particularly directed his work to youngsters, stating that the compositions 'will be both easily understood, and within the reach of even the most juvenile aspirant.' Bruce's booklet makes strange reading. His descriptions of the ingredients give the impression that he has worked with them, but his firework compositions convey quite the opposite, as do some of his descriptions of the construction of fireworks. Some of his recipes could be guaranteed not to work as described, others not to work at all, and others again to ignite spontaneously or even to explode in the face of the would-be pyrotechnist. The work is dedicated to 'The Queen's Most Excellent Majesty', and written in a most pompous style. Bruce's list of ingredients is of interest as it gives the price of each material, a matter that will be taken up in Chapter 8.

Bruce's work is mentioned in the interests of balance, to show that even though the best works on pyrotechny in the 19th century were written by and for amateurs, one cannot conclude that every such work was valuable. Many years after the publication of Bruce's booklet knowledge of the new materials introduced by Continental researchers was disseminated in England by three amateur pyrotechnists: an Anglican clergyman (Denis Times Moore, who wrote under the name 'Practicus'), a London schoolmaster (Thomas Kentish) and a Yorkshire doctor and analytical chemist (William Henry Browne). In complete contrast to Bruce's work, the books written by these men remain useful to this day.[204]

According to the late Chris Philip, there was 'considerable activity by amateur firework-makers...in England during the first three quarters of the 19th century, but the coming of the Explosives Act of 1875 put an end to much of this activity because all manufacturing became strictly controlled and subject to licensing'. Despite this, enough amateur firework-making persisted to justify the publication of books by Kentish and Browne long after the Explosives Act came into force. It seems that the new Act was widely ignored, just as the 1685 prohibition of fireworks had been ignored in the earlier decades of the 19th century.[205]

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[203] Bruce, *A New Guide to Pyrotechny*.

[204] 'Practicus', *Pyrotechny, or, the Art of Making Fireworks, at little cost, and with complete safety and cleanliness* (London: Ward, Lock and Tyler, ca. 1871); Moore ('Practicus'), *A Manual of Pyrotechny*; Browne, *The Art of Pyrotechny*; Kentish, *The Pyrotechnist's Treasury*; Browne, *Firework Making for Amateurs*.

[205] Chris Philip, "The Manuscripts of William Allen Hanbury," *Pyrotechnica*, no. XII (1988), pp. 36-42. Books published after the Act of 1875 include several editions of Kentish, *The Pyrotechnist's Treasury.* A second,

Philip's remarks were made in an article about a manuscript by English amateur pyrotechnist William Allen Hanbury (1823-1898). Although Hanbury left no published works, he is worth noticing as an example of the interactions between professional and amateur pyrotechnists in England in the second half of the 19th century. Hanbury (Figure 6.7) was a wealthy man, thanks to his family's ownership of the Allen and Hanbury pharmaceutical business. Census records describe his occupation as either 'Annuitant' or 'Gentleman'.

William Allen Hanbury.

Figure 6.7. William Allen Hanbury, Amateur Pyrotechnist.[206]

revised edition was published in 1887, and subsequent editions appeared in 1899 and 1905, all from the original London publisher, Chatto & Windus. It is telling that the next reprint (1975) was issued in the United States; by that time, the Explosives Act of 1875 was being very strictly enforced in the United Kingdom, and the market for such books was now predominantly in the United States. Another British book published well after the passage of the 1875 Act was Browne, *Firework Making for Amateurs* (1888).

[206] A. Audrey Locke, "William Allen Hanbury," in *The Hanbury Family*, ed. A. Audrey Locke (London: Arthur L. Humphries, 1916), facing page 303.

Hanbury became interested in pyrotechny at an early age: one of his comments suggests that he began making fireworks before the age of 10. The pharmacy on the ground floor of the family residence (Figure 6.8) would have provided him with easy, if unauthorized, access to the necessary chemicals.

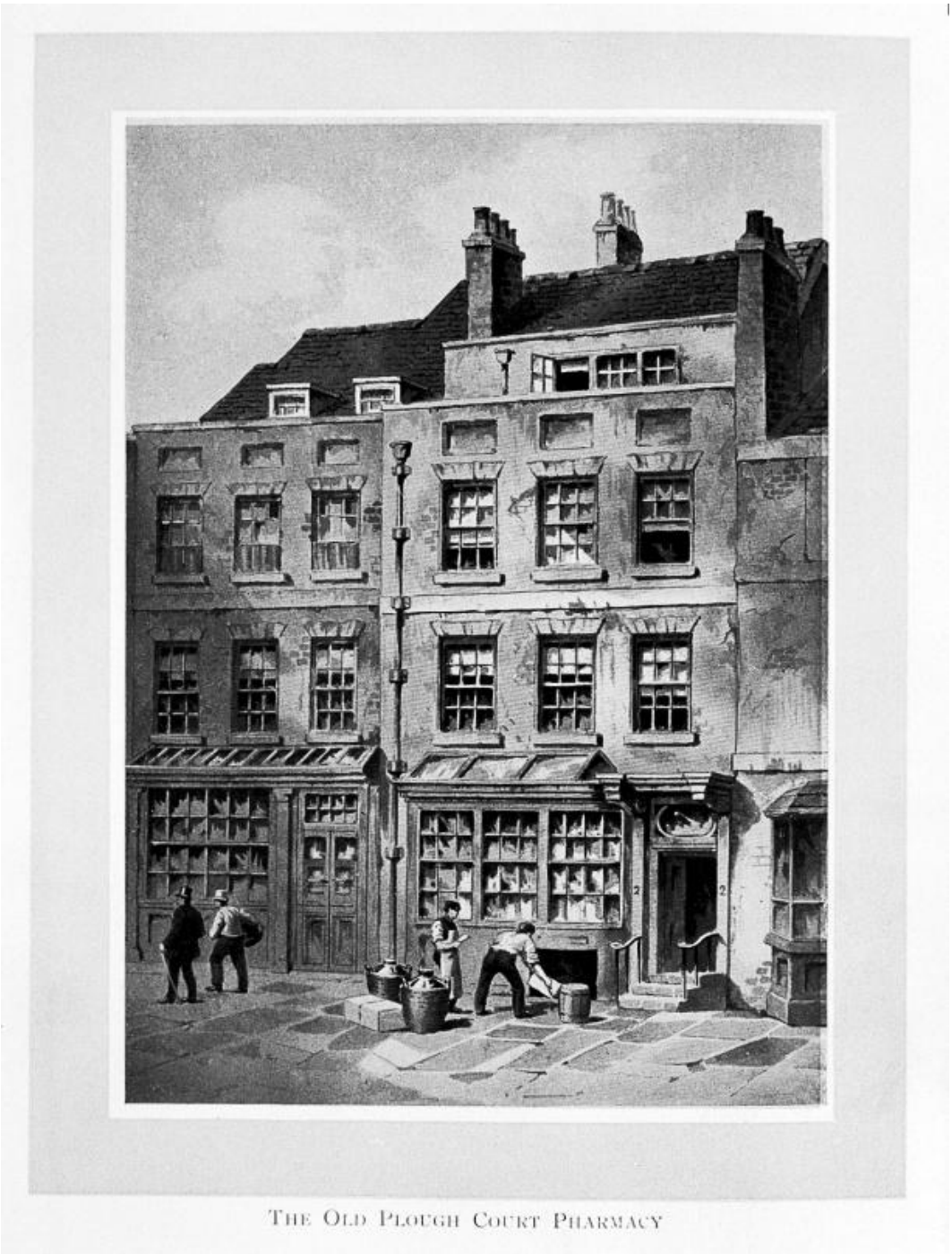

Figure 6.8. The Old Plough Court Pharmacy, Boyhood Home of William Allen Hanbury.[207]

By the mid 1850s, when he was in his 30s, Hanbury had free access to the Royal Laboratory at Woolwich and for many years went there every morning. He was there for the peace displays of 1856. Following his marriage in 1861 to an aristocratic German woman he spent much time on the

[207] Ernest C. Cripps, *Plough Court The Story of a Notable Pharmacy 1715 - 1927* (London: Allen and Hanburys Limited, 1927),, frontispiece.

Continent but occasionally returned to England. He knew the professional pyrotechnist William Brock (1813-1869) and Brock's sons and successors Charles Thomas Brock (1843-1881) and Arthur Brock (1858-1938). He also knew the professionals Joseph Southby and his son George, as well as the amateur Kentish. In the early 1880s Hanbury was friendly with a young pyrotechnist named John George Craig (1860-1949), who worked at James Pain and Sons' firework factory at Mitcham in Surrey and provided Hanbury with much useful information. Hanbury's circle of pyrotechnic acquaintances thus included men from the military, professional and amateur fields. Such interactions must have facilitated the dissemination of knowledge between firework-makers. Hanbury seems to have taken the Explosives Act of 1875 to heart, writing at some time after 1881: 'Amateurs cannot now work in England because of the Explosives Act. I have not a single tool of any kind here, all my Receipts, Manuscripts, Tools etc are abroad...' [208]

This chapter has focussed on the role of amateurs in creating and disseminating pyrotechnic knowledge in the 19th century. Before concluding, it is instructive to look at a counter example, in which useful pyrotechnic knowledge was created purely for the prospect of monetary gain, and kept secret, even from the Patent Office. This happened in the United States, and relates to utilitarian pyrotechnics rather than to fireworks, but as it involves coloured fires it is appropriately included here

Secrecy and Entrepreneurship: A Contrast to the Openness of Amateurs in the Dissemination of Pyrotechnic Knowledge

In the 1840s an American naval officer Benjamin Franklin Coston (1821-1848), working at the Naval Yard in Washington, D.C, commenced a project for sending signals at night, using pyrotechnic flares displaying up to three colours in succession. A code book related the number and sequence of colours to a numeral, which corresponded to a message. A dispute over intellectual property rights to a percussion primer that he had developed led Coston to quit the Navy without completing the signalling project. He went to work for the Boston Gas Company, where his health deteriorated rapidly. After Coston's death in 1848 his widow Martha (née Martha Jane Hunt, 1826-1904) took up the signals project in a desperate attempt to find a source of income for her family. Years later, she wrote a book giving an account of her quest and its outcome. Figure 6.9 shows Coston in her more prosperous years.[209]

[208] Philip, "The Manuscripts of William Allen Hanbury", p.36.

[209] Martha J. Coston, *A Signal Success, The Work and Travels of Mrs. Martha J. Coston: An Autobiography* (Philadelphia: J. B. Lippincott Company, 1886).

Figure 6.9. Martha Coston.[210]

While the concept of the transmission of codes with coloured flares had been fully developed by Benjamin Franklin Coston, the practical implementation had not; Martha Coston spent almost 10 years bringing it to perfection. The original intention had been to make the three colours red, white and blue, for patriotic reasons. Coston claimed that she eventually produced satisfactory white and red, but not blue, but she did not disclose any of her compositions.

On the evening of 17th August 1858 Coston saw a firework display in New York, celebrating the first use of the transatlantic telegraph cable, and was impressed by the brilliant colours. It occurred to her that a New York pyrotechnist might provide her with the blue flame composition for the signal flares. Fearing that a woman would not be taken seriously she wrote to several pyrotechnists, pretending to

[210] Mark Weaver, "Martha Coston," http://www.americancivilwarstory.com/martha-coston.html, accessed 9th March, 2017.

be a man, asking for an intense blue composition, failing that, a green one. One pyrotechnist replied 'intelligently', claiming that he had made a 'pure blue' some years before but had abandoned it as too expensive. He sent Coston samples of blue and green, and she tested them by having a friend fire them from a mountain, some five miles away. The green was perfectly satisfactory, so B. F. Coston's signalling system now seemed entirely practical.

Problems still remained, so Coston revealed her identity to the pyrotechnist, and worked with him at his house for some weeks. They then consulted the pyrotechnist's brother-in-law, who Coston described as 'a much more skilful chemist', and soon the signals were ready to be demonstrated to the U.S. Navy. Coston, who flaunted the names of high-ranking naval officers in her book, never once mentioned the name of the pyrotechnist, nor that of his skilful brother-in-law; she seems to have regarded them as her social inferiors. She did mention that the pyrotechnist had insisted that he and Coston should each take out patents on aspects of the new flares. Records of the United States Patent Office, followed by genealogical research, reveal that the pyrotechnist was Gustavus Augustus Lilliendahl (1829 -1907); his brother-in-law was Jacob Johan Detwiller (1834-1910). Both of these men were professional pyrotechnists. Detwiller for many years operated the Detwiller and Street Fireworks Company of New York. It is puzzling that Coston took almost 10 years to hit upon the idea of consulting a pyrotechnist for advice on coloured fires. Perhaps the explanation lies in her evident reluctance to deal with those beneath her in the social scale; if so, we have an unexpected example of social prejudice delaying the progress of pyrotechnics. In this context it is relevant to mention again that Coston showed no reluctance in dealing with naval officers and Government officials, and took care to mention them by name in her book. This shows that her difficulty lay in interacting with those she considered her social inferiors, rather than in any general reluctance to interact with men. On her own testimony she was initially fearful of not being taken seriously by the pyrotechnists because she was a woman, but that does not explain why she remained aloof from them, and refrained from naming them, even after they had, on her own testimony, worked together for some weeks.[211]

The new flares, named The Coston Telegraphic Night Signals, were successfully demonstrated and in February, 1859 an official report recommended their adoption by the United States Navy. They were used to great effect during the Civil War. Most of Coston's book is devoted to her trials and tribulations as she struggled to obtain payment for the invention and to persuade the navies of other nations to take it up. She was successful with the navies of France, Italy, Denmark and Holland; but not with that of Great Britain. Coston did not explain why the British were not interested; perhaps the reason was that they already had a satisfactory percussion-ignited flare, patented by Woolwich pyrotechnist and ammunition maker Thomas Robson (1819-1???) in 1852.[212]

The question of secrecy that led to Coston's exploits being recounted here arises from her assertion that her flares were not subject to spontaneous ignition, and that this had been proved both by chemical analysis and by tests involving prolonged exposure of the flares to extreme heat. Her claim is further supported by the existence, after some 150 years, of specimens of the flares, in apparently excellent condition, in museum collections of material associated with the Civil War, as shown in Figure 6.10.

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[211] Gustavus A. Lilliendahl. Pyrotechnic Signal. United States Patent 23,529, issued April 5, 1859. In his fictionalized adaptation of Coston's book, Tom Lonergan replaced Lilliendahl with the imaginary 'Edmund Hibbert'. Tom Lonergan, *Martha Coston and the Box of Light* (Bloomington: iUniverse, 2013), e.g., pp. 64-66. Lilliendahl is identified in Lisa A. Marovich, ""Let Her Have Brains Too": Commercial Networks, Public Relations, and the Business of Invention," *Business and Economic History* 27, no. 1 (1998), pp. 140-161, p. 146. Marovich cites Coston, *A Signal Success*, p. 54, but must have done her own research to find the pyrotechnist's name.

[212] Thomas Robson. "Improvements in apparatus for igniting signal and other lights." Great Britain Patent 140 of 1852, issued 1st October 1852. For a description and illustration of the flare, see Robert Postans, "Night Signals at Sea," *Colburn's United Service Magazine and Naval and Military Journal* 1856 Part III (1856), pp. 27-38, p. 35.

Figure 6.10. Museum Specimens of Coston's Signals.[213]

Not one of the patents relating to Coston signals discusses the compositions. Chemical analysis of one of those museum-pieces could provide useful insights into mid-nineteenth century pyrotechnic chemistry. One intriguing possibility is that the compositions were based on potassium perchlorate (discussed in Chapter 5), rather than potassium chlorate. This would account for their stability. As noted in Chapter 4, potassium perchlorate was not widely used in those days because of its high cost; Coston did mention that a fire in the factory producing her signals destroyed 'a large store of expensive chemicals.' Perhaps potassium perchlorate was one of them.[214]

Martha Coston took out the original patent in her deceased husband's name, to comply with the law that a United States Patent can be granted only to 'the true and first inventor'. She subsequently was granted a patent in her own name for a different invention: means of firing a flare by friction. She founded the Coston Signal Company, Inc. of New York, for the manufacture and distribution of

[213] "Image Courtesy of SCA (1860-1865) Digital Collection, www.civilwarsignals.org, accessed 2 March 2017.

[214] For the tests, see Coston, *A Signal Success*. p. 309. Coston noted that the analysis was done by 'Professor Doremus of New York', presumably Robert Ogden Doremus (1824-1906). For the store of expensive chemicals, see ibid., p. 141.

marine night signals. Coston has attracted the attention of feminist writers; it is not appropriate to review that here, but it should be said that she does not need to be given credit, as she often is, for something that she did not do, namely 'invent the signal flare'. Furthermore, it should not be assumed that she made the invention disclosed in the original patent and falsely attributed it to her deceased husband to give it credibility as the invention of a man. Had she done so, the patent would have been invalid. Nor should it be assumed that Coston was always at a disadvantage because she was a woman. On her own evidence she was treated courteously by British naval officers because she was a woman. In contrast, the male American inventor Jacob Snider (1811-1866) was summarily sent on his way.[215]

Coston's story has a place in this narrative not just to show the contrast between the secrecy of a commercially-motivated inventor and the openness of most amateurs. She provides an example of interactions between the military and people from other fields in the development of pyrotechnics. In this instance the driver of change was Coston, whose motivation, on her own admission, was to make money. She called upon professional pyrotechnists to solve the technical problems, and the result was a worthwhile improvement in signalling technology. The evidence suggests that the coloured fire compositions used by Coston were a major advance, in view of their freedom from spontaneous combustion and their stability even after prolonged exposure to heat, but as their chemical constituents were never disclosed we do not yet know how that advance was achieved.

Concluding Remarks

There were no rigid boundaries between professionals and amateurs in early 19th century pyrotechny. None the less, it is useful to notice the self-assessed status of practitioners as amateurs or professionals, because amateurs can be expected to be more open to passing their knowledge to others, whereas professionals tend to keep knowledge to themselves. There are, as always, exceptions. Claude-Fortuné Ruggieri was from a family of professional firework makers, yet he claimed to scorn those who, for reasons of greed or insecurity, jealously guarded their secrets. Perhaps most professionals were simply too busy earning a living to write books. As noted by Brock, Ruggieri wrote his first book when the opportunities to engage in his business had all but disappeared in the aftermath of the Revolution. Later, he became official pyrotechnist to Napoleon and then to the restored monarchy. Assured of work and income, he could afford to release further editions of his book, asserting his claim to pre-eminence without fear that any disclosed information would put him at a commercial disadvantage. Werrett has pointed out that Ruggieri used his book to associate himself (and pyrotechny) with chemistry, presumably in the expectation of gaining prestige and credibility.[216]

It has well been said that absence of evidence is not evidence of absence. We must be open to the possibility that some of the new materials that the evidence indicates were introduced by amateurs were introduced by professionals, and kept secret. If that is what happened, then those professionals traded the credit that posterity might have granted them for their discoveries for the immediate advantages of keeping the discoveries secret. The professional pyrotechnists Liliendahl and Detwiller, who developed the highly stable (and highly secret) coloured flares for Martha Coston, could well be a case in point.

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[215] The first patent is B. Franklin Coston. Pyrotechnic Night Signals. United States Patent 23,536, issued April 5, 1859. The second is Martha J. Coston. Improvement in Pyrotechnic Night Signals. United States Patent 115,935, issued June 13, 1871. For a feminist interpretation of Coston's career, see Denise E. Pilato, "Martha Coston: A Woman, a War, and a Signal to the World," *International Journal of Naval History* 1, no. 1 (2002), http://www.ijnhonline.org/issues/volume-1-2002/apr-2002-vol-1-issue-1/ , accessed 9 March 2017. For the courtesy extended to Coston, and the lack of courtesy to Snider, see Coston, *A Signal Success*. pp. 74-75.

[216] Brock, *A History of Fireworks*. p. 220; Werrett, *Fireworks*. pp. 226-229.

There are good reasons for expecting that professional firework-makers would not often have been the first to introduce new materials. Many years ago Davis drew attention to the highly conservative nature of pyrotechny. Two aspects are relevant. First, professional firework-makers were proud practitioners of an old craft with strong traditions. Some presumably had the attitude (still found in some quarters) that everything worth knowing is written down in grandfather's notebooks. More rationally, it is likely that professionals would have been concerned about the dangers of introducing new materials. Part of the credibility of a professional was the ability to provide products and services without mishap. As this required an intimate knowledge of all the materials used, the introduction of unfamiliar materials was to be avoided.[217]

Amateurs, in contrast, had much to gain and little to lose by being adventurous in seeking out new materials, discovering their applications and spreading the knowledge. They would achieve the personal satisfaction of having advanced the art, and earn the admiration of their fellow enthusiasts. The attitude of a prominent amateur can be seen in Chertier's closing remarks in the Preface of this last book:

> I hope that this work will allow amateurs to produce any fireworks that their imaginations might suggest. If I have achieved this goal, I will be rewarded for my efforts to popularise an art that I have always greatly loved...[218]

If an amateur's researches were unsuccessful, he would have wasted time and money, but would have been compensated by the pleasure of the quest, undertaken as a freely-chosen hobby.

Amateurs discovered many useful new materials and wrote books disclosing how to obtain them, along with recipes which used them to best advantage. Professionals soon adopted the discoveries of their amateur colleagues, and fireworks were transformed. This happened when and where it did for several reasons. In 19th century Europe fireworks were far more important than they had previously been; the new materials required for their transformation were available at affordable prices as a result of the industrial applications of chemistry, and amateur firework makers could afford to spend time and effort to discover applications of the new materials in fireworks, to develop the necessary mixtures, and to write books to spread the knowledge.

[217] Davis, "The Early use of Potassium Chlorate in Pyrotechny", p. 91.

[218] Chertier, *Nouvelles recherches sur les feux d'artifice* (1854), p. vii.

Chapter 7: The Role of the Military in the Transformation of Fireworks.

The introduction of new materials was fundamental to the transformation of fireworks from the mid 18th century to the end of the 19th century. This chapter will show that people in the armed forces, usually working with civilian experts, played a central role in introducing some of those new materials. At this period of history the categories of 'military' and 'civilian' were the extremes of a continuum – at the 'military' end were people who spent their entire careers in the armed forces, at the 'civilian' end were those who never interacted with them. In between were people who, at some time in their careers, to different degrees and in different capacities, had some involvement with the army or navy. This social continuum was important in the transfer of knowledge of new technical developments between the military and the broader community. Technical knowledge created or acquired in a military context could be disseminated by people whose duties, or life choices, gave them access to the military without their being constrained by obligations of military secrecy. The transfer also went in the other direction; the armed forces, being less sensitive to cost than civilian customers, presented an attractive opportunity to entrepreneurs who developed goods or information of possible use to the military. Another aspect of great relevance to the creation and transmission of technical knowledge was that the armed forces possessed facilities for training people in fields of technology seen as having military relevance. One such field was pyrotechnics. As a result of the activities of people associated with the military, some useful new materials were introduced into pyrotechny in the19th century, as shown in Table 7.1.

Ingredient	**Synonyms**	**Main use in fireworks**	**Introduced by, year**
boric acid	boracic acid	Green colour agent	Cutbush,1825
copper(II) carbonate—copper(II) hydroxide (2/1)	azurite, English blue ash, mountain blue	Blue colour agent	Meyer, 1833
barium carbonate	carbonate of baryta	Green colour agent	Meyer, 1833
potassium sulfate	sulphate of potash	Pale blue colour agent	Meyer, 1833
calcium sulfate dihydrate	gypsum, plaster	Pink-red colour agent	Meyer, 1833
calcium carbonate	precipitated chalk	Red colour agent	Meyer, 1833
magnesium		Fuel	Colomb and Bolton, 1865

Table 7.1. Firework ingredients, still in use in the 20th century, introduced in the 19th century by people associated with the military.

That military people should have contributed to the improvement of fireworks seems surprising today, when the armed forces are not in the least involved with artistic and entertaining applications of pyrotechnics, but for many centuries the management of fireworks in Europe was primarily in the hands of the military. As masters of the use of gunpowder, artillerymen were expected to know how to make and display fireworks to celebrate triumphs and to salute dignitaries. Well into the 19th century artillerymen were taught how to make and display fireworks as part of their education in military pyrotechnics. An example of military men preparing a firework display in the early 19th century is show in Figure 7.1.

The reason for this apparently irrelevant training was usually given as 'completeness' – all aspects of pyrotechnics were to be covered. It may also be relevant that at that period of history display fireworks were the most complicated of all pyrotechnics; a team of soldiers capable of making, setting up and firing a good firework display had proved its mastery of the pyrotechnic art, and could be expected to have no difficulty in managing the pyrotechnic devices used in warfare. This explains why the military had an interest in fireworks, but not why they might have wanted to improve them.

An important reason for military people taking an interest in, and encouraging, new developments in fireworks was that they used fireworks for signalling; this will be discussed later.[219]

Figure 7.1. British soldiers setting up fireworks for the display fired in London in 1814. The result is shown in Figure 1.1. [220]

Military training also played a vital part in the propagation of knowledge about fireworks, mainly because certain individuals who had become interested in fireworks during their military training published papers and even books on the subject. In 1820s and 1830s military men contributed to the introduction of new coloured flame compositions. Their contributions included the development of new coloured fires at Woolwich Arsenal near London, a French artilleryman's modification of English theatrical red fire to make red fireworks, and an attempt by a German military chemist to apply chemical theory to the formulation of coloured flame compositions. One of the outstanding

[219] For discussion of the early association of the military with fireworks, see Brock, *A History of Fireworks*, Chapter 3, esp. p.31; Davis, *The Chemistry of Powder and Explosives*, Chapters 2 and 3; Werrett, *Fireworks*, Chapter 1. For an example of recreational fireworks being treated as part of the gunner's repertoire, see Casimir Simienowicz, *The Great Art of Artillery*, trans. George Shelvocke (London: J. Tonson, 1729), especially p.333-381. For an early 19th century comment, see James Cutbush, *A System of Pyrotechny* (Philadelphia: Clara F. Cutbush, 1825), pp. xxxix-xl. For the inclusion of recreational fireworks in the training of students at the French École Centrale de Pyrotechnie Militaire at Metz in 1828, see Munier, "Extrait d'une note sur le feu d'artifice tire à Metz le 4 September 1828, par M. Munier, Capitaine d'Artillerie,"*Memoires de l'academie royal de Metz. Lettres, sciences, arts, agriculture* 1828-1829 (1829), pp. 180-188.. See also Jocelyn, "The connection of the Ordnance Department with National & Royal fire-works, including some account of Sir Martin Beckman, Colonel Henry John Hopkey, & Sir William Congreve (2nd Baronet.)."

[220] http://historicalromanceuk.blogspot.com.au/2014/07/peace-breaks-out-1814.html. Accessed 25 February 2017.

contributors to the development of coloured fires (F.-M. Chertier, whose work has already been discussed in Chapter 4), had been an artillery officer. It can be presumed that all these pioneers of pyrotechny received their technical education during their military training.

As exemplified by the career of James Marsh (1794-1846), a young person who joined the military and demonstrated appropriate talent and interest could receive technical training that might otherwise have been inaccessible. Marsh began working at Woolwich Arsenal in 1806, at the age of 12, in some unknown, but lowly, capacity. He would remain at the Arsenal for the rest of his life.

In the early 1820s Marsh assisted the mathematician, physicist and engineer Peter Barlow (1776-1862) with work on electromagnetism. Barlow taught mathematics at the Royal Military Academy, part of the Woolwich Arsenal complex; this presumably explains why he could obtain Marsh's assistance. Marsh was at that time working at the Royal Laboratory as a wheelwright. While assisting Barlow, Marsh designed and built improved equipment to demonstrate the laws of electromagnetism. In 1823 the Society of Arts awarded Marsh its large silver medal and the sum of 30 guineas for this work, which seems to have attracted the attention of his employers. According to Hogg, Marsh left the Royal Laboratory on 29 January 1824, and 'studied chemistry with great success.' This was presumably at the Royal Military Academy. On 28 February 1824, while he was still a student, the Board of Ordnance appointed Marsh Surgeryman and Dispenser of Medicines at Woolwich Arsenal His pay was increased to £63 18s per year; his duties were to assist the resident medical officer, and to dispense medicines. Contrary to some statements in the secondary literature, Marsh never held the position of Ordnance Chemist, which was abolished in 1825.

James Marsh's interest in military applications of pyrotechnics is first documented in records of his work in the early 1830s to improve percussion tubes used to fire cannon. Percussion tubes were an important advance in artillery, particularly in naval warfare. Traditionally, cannon had been fired by applying a light to the touchhole, and there was a slight delay before the cannon discharged. At sea, especially in heavy weather, this delay could mean the difference between striking the enemy ship or missing it, as the ships moved up and down with the waves. The problem was solved by the percussion tube - a metal tube containing a pyrotechnic mixture that exploded instantly when struck a heavy blow. Inserted into the touch hole of a cannon, a percussion tube provided practically instantaneous discharge of the weapon. Early percussion tubes required the gunner to strike the tube with a hammer, but this was very dangerous. The cannon recoiled violently on firing and it was unsafe for anyone to be standing nearby. In recognition of this, mechanisms called 'percussion locks' were developed, which allowed the percussion tube to be initiated by pulling on a lanyard, so the gunner could stand at a safer distance, but flying fragments of metal from the exploding percussion tube still presented a risk of injury. To address this problem, Marsh developed a percussion tube made from the quill of a crow's feather, instead of a metal tube. The need for such an improvement was brought home when, in a demonstration of the old and new tubes on board the training ship HMS Excellent at Portsmouth, the chairman of the evaluating committee was struck in the face by fragments of one of the conventional tubes. In 1832 Marsh received a bonus of £30 from the Board of Ordnance for the crow's quill percussion tube.

The following year, Marsh was drawn into a very different area of applied chemistry, in which he was to earn international renown. In 1833 Faraday was asked to carry out some tests for arsenic to assist investigations of a suspected murder. He delegated the task to Marsh, who duly carried out the appropriate tests, found them unsatisfactory and invented a better one. On April 9, 1836 Marsh presented his new test for arsenic to the Chemical Committee of the Society of Arts of London, and on June 7 he received the Large Gold Medal of the Society of Arts. Marsh's test was subsequently used in several prominent murder investigations and his name became widely known, both at home and abroad. The attention given to the arsenic test seems to have prompted the Society of Arts to review his other achievements. In 1837 the Society belatedly awarded Marsh its Silver Medal and a purse of 30 guineas for the crow's quill percussion tube that he had invented some 5 years earlier.

Despite his discoveries and awards, Marsh was never promoted from the humble position to which he was appointed in 1824. His employers rightly described him as 'a very clever chemist', but that was the limit of their recognition of the achievements of the former child labourer and wheelwrght. Fame and achievement were not sufficient to overcome the stigma of humble origins. Although contemporary accounts refer to him as 'Mr Marsh, the Woolwich chemist', he modestly described himself in his will as by his official title: 'dispenser of medicines'.

Marsh's career shows how specialized technical training provided by the military permitted a person of humble background to participate in scientific and technical societies and to publish in respectable journals. Such publications, along with records kept by men employed by the military to work with fireworks, led to the survival of information that helps to explain how and why the introduction of new materials transformed fireworks from the middle of the 18th century to the close of the 19th. Military technical training was usually conducted in special military academies, such as the Royal Military Academy at Woolwich, the United States Military Academy at West Point, near Washington D.C. and the École Centrale de Pyrotechnie Militaire at Metz. In Germany a promising young officer could even be sent to University for specialist training. For example one such officer, Franz Eduard Moritz Meyer, was sent to the University of Breslau for 5 years to study chemistry. Subsequently, he was appointed to the Prussian War Ministry where he made important contributions to the development of coloured fireworks. There are also examples of the military employing civilian experts to teach in the military academies; some of those experts, such as Dr John MacCulloch (1773-1835) in Britain and James Cutbush (1788-1823) in the United States, published information about fireworks that helped spread pyrotechnic knowledge beyond the military.

Another example of the role of the military in the chemical transformation of fireworks was that some new materials that had been developed for military use found applications in fireworks. For example, as discussed in Chapter 5, potassium picrate was used as a military explosive long before it was introduced into fireworks as the essential ingredient in the first pyrotechnic whistles; likewise, investigations of picrates as military explosives led to the discovery of coloured fires based on ammonium picrate. A major reason for these developments was that costs of materials were far less important to the military than they were to civilians, who had to turn a profit. For the military, the advantages expected by the use of new materials were more important than minimizing expenditure. Chemical manufacturers thus had an incentive to explore applications of their products that might be of interest to the military. Picric acid, for example, was first produced on an industrial scale as a dyestuff and later applied in explosives and pyrotechnics, as explained in Chapter 5. Another example of the insensitivity of the military to the cost of materials can be found in the 1860s, when military men applied the barely-affordable metal magnesium for signalling and for illuminating the battlefield, some time before the price of the metal became sufficiently low to permit its wide use in fireworks. This application of magnesium was the latest development in a long tradition in the military of using pyrotechnics for signalling and illumination. White-burning mixtures of saltpetre and sulfur, made more combustible by the addition of a small percentage of gunpowder had long been used, in ground flares, hand-held torches and as 'stars' discharged from rockets.

This use of rockets and flares for signalling provided an incentive for the military to take an interest in the new coloured fireworks. A signal rocket displaying white stars could, by pre-arrangement, convey a specific message; one displaying 'golden rains' another. The number of messages conveyed could be increased if more colours or effects could be displayed, so the introduction of new colours would have been advantageous for military communications; on the other hand, there were also reasons for rejecting, or at least delaying, the introduction of the new coloured fires into military service. One reason was the propensity of the new compositions to spontaneous ignition. By 1852 this problem had become so evident that a military manual warned:

> These complicated though beautiful compositions are of so dangerous a nature, that no consideration should admit them into stores or magazines. or aboard ships; since they … are

> liable to take fire by what is termed spontaneous combustion, particularly when exposed to a hot and humid atmosphere, as several accidents from them have proved. [221]

Such technical problems are obvious reasons for rejecting a new development, but social factors can also come into play. For example, the original reason for delaying the introduction of coloured signal rockets lay not in the recognition of technical problems but in more subtle matters, not stated explicitly in the sources. In 1827 the Lambeth pyrotechnist Joseph Southby (1786-1865) modified the original theatrical red fire to make 'stars' for 'crimson star rockets', which he used in his firework displays at the Vauxhall pleasure-gardens and later demonstrated to representatives of the Board of Ordnance for possible use as military signals. The official response from the Board rejected Southby's rockets as no better than ordinary white-star signal rockets. Then, at the end of 1831, two Royal Navy officers publicly demonstrated coloured-star rockets to high-ranking officials. The rockets, according to contemporary reports, displayed 'ten different colours'. The demonstration was widely reported, the invention of the new rockets being attributed to one of the officers, a Lieutenant Hughes. Southby pointed out, in a letter to the editor of one of the publications, that some time earlier he (Southby) had given some rockets of his own manufacture to Hughes for testing, and that whatever credit attached to having invented them belonged to Southby, not to Hughes. It can be inferred that the officers to whom Southby first demonstrated his red rockets submitted an unfavourable report to the Board so that they might make a wider range of colours and then claim credit for the 'invention', earning favour with their superiors. This is a fine example of interactions, and tensions, between a civilian pyrotechnist and the military. The successful demonstration of the rockets shows that the officers, within a few years of their first being shown the red stars, were able to secure a whole range of different coloured star compositions. Exactly how they did this is not documented, but it is at least plausible that they would have turned to the Royal Laboratory at Woolwich Arsenal, the centre of pyrotechnic expertise in Great Britain.

There is one piece of evidence that demonstrates that research into coloured flame compositions did take place at Woolwich, certainly before 1844 and very probably much earlier. This evidence is a collection of rather primitive compositions for coloured fires and coloured stars included in a paper published in 1844 by James Marsh, who at that time had been working at Woolwich Arsenal for some 38 years. Marsh's discussion of coloured fires appears at the end of his 1844 article. The compositions are distinctly 'old fashioned' for the time, but Marsh made no claim for their novelty. He did not say that he invented any of the compositions, but gave instructions for preparing and storing the ingredients and for mixing the compositions. He explained how they should be used, either for stars or for illuminations. The chlorate-based coloured stars described in Marsh's paper have been discussed in Chapter 4. If these compositions are indeed as early as they seem, they constitute a major advance in the development of coloured fires, made by the military chemists at Woolwich Arsenal, and would be an important example of the contribution of the military to the transformation of fireworks by the introduction of new materials.

The introduction of potassium chlorate by John Forster in 1810 had made possible the first effective red and green coloured fires; the Woolwich chemists, seeking a full range of colours, used potassium chlorate only when it was necessary. Satisfactory yellow and white fires could be made without potassium chlorate, so none of the compositions for those colours included it. As explained in Chapter 4, potassium chlorate was used in red and green fires, as well as in the novel blue and purple fires, based on copper salts, that may well have been discovered at Woolwich. The high cost of potassium chlorate is sufficient justification for using it only when it was essential; the tendency of some compositions containing potassium chlorate to ignite spontaneously is another very good reason for

[221] Anonymous, "Pyrotechny, Military" in *Aide-Memoire to the Military Sciences Framed From Contributions of Oficers and Others Connected with the Different Services, Originally Edited by a Committee of the Corps of Royal Engineers, 1850-1852*, Second revised ed., 3 vols., vol. 3 (London: Lockwood & Co., 1862), pp. 170-195, p. 194. I have discussed this in Sturman, "Coloured Fire." p. 57.

avoiding it. As noted previously, this problem was the reason for the British military to reject the new coloured fires, as late as 1852. [222]

The problem of spontaneous ignition of coloured fires was evidently solved, though the details were kept secret, during the development of novel pyrotechnic signals in the United States of America by Martha Coston, as discussed in Chapter 6. The evidence suggests that the coloured fire compositions used by Coston were a major advance, in view of their freedom from spontaneous combustion, but as their chemical constituents were never disclosed it is not possible to say how that was achieved. One possibility is that the compositions were based on potassium perchlorate (discussed in Chapter 5), rather than potassium chlorate. This would account for their stability. If this interpretation is correct, we have an example of an expensive new pyrotechnic ingredient being used for a military application because cost was of less importance to the military than effectiveness, safety and reliability.[223]

Another example can be given from the other side of the Atlantic. At about the same time that Coston's signals were introduced in the United States, the British began using a different technology for military signalling, based on magnesium. As discussed in Chapter 5, magnesium had become available by 1864, at an affordable but still high price, as a light source for photography. Its use for military signalling began in 1864, with the development at the Royal Dockyard at Chatham of a mixture of powdered resin, lycopodium and powdered magnesium called 'Chatham Powder'. The developers specified that the mixture must contain no source of oxygen, lest it become explosive in its own right, so it was clearly not a pyrotechnic composition; it was sprayed into the flame of a specially-designed lantern to produce flashes of light. Magnesium flash signals were extensively used by the British Army in Abyssinia in 1868, 'several hundredweight of magnesium powder having been supplied by Mr Mellor, Director of the Magnesium Metal Company...' The retail price of magnesium powder at this time was around 6s. per troy ounce, so the price per hundredweight would have been close to £490. Even if Mellor had given the military a good discount, he can be presumed to have made a tidy profit. This is an example of a mutually beneficial interaction between a civilian entrepreneur and the military - the entrepreneur supplying an essential ingredient for a military invention.[224]

This use of magnesium in non-pyrotechnic military signals soon led to its application in pyrotechnic signal lights. In 1865 the two officers who had developed the flash signals (Captain Philip Howard Colomb (1831-1899) of the Royal Navy and Captain Francis John Bolton (1831-1887) of the Royal Artillery) used magnesium powder in white-burning flares for use on ships entering port in time of fog. Subsequently, they introduced red, and then green, magnesium flares. The compositions were not disclosed.

In 1874 a British military manual specified a 'Light, Signal, Magnesium', to burn for one minute with a brilliant white flame. This is shown in Table 7.1: [225]

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[222] For more about Marsh and his work, see "The Early Use of Potassium Chlorate in Pyrotechny: Part III. Applications of Early Chlorate-based Coloured Flame Compositions".

[223] For the store of expensive chemicals, see Coston, *A Signal Success*. p. 141. The advantages of potassium perchlorate had been published in 1850, albeit in German; see Websky, *Martin Websky's Schule der Lustfeuerwerkerei*, pp. 166-170. It is plausible that Detwiller, a pyrotechnist and 'clever chemist', would have known about it.

[224] For details of the flashing light signals, see Commander P. H. Colomb, "Signal Lights of Captains Colomb and Bolton," *Journal of the Royal United Service Institution, Whitehall Yard* 12 (1868), pp.373-377. Captain Colomb and Major Bolton, *The System of Flashing Signals Adopted in Her Majesty's Army and Navy* (London: W. Mitchell and Co, 1870). The quote about the source of the magnesium powder is from Rudolf Wagner, *A Handbook of Chemical Technology* trans. William Crookes (London: J. & A. Churchill, 1872). p. 680.

[225] W. R. Barlow, *Treatise on Ammunition* (London: Her Majesty's Stationery Office, 1874), p.79.

Ingredient	Parts by weight
Magnesium containing 25% paraffin	1
Saltpetre	28
Sulphur	7
Red Orpiment	2

Table 7.1 British military signal light of 1874

A composition for white stars for a star shell, from the same source, is shown in Table 7.2:

Ingredient	Parts by weight
Magnesium Powder	8
Nitrate of Baryta	9
Chlorate of Potash	6
Boiled (linseed) oil , 3% added	

Table 7.2 British star-shell composition of 1874

The application of magnesium in military pyrotechnics is another instance of an expensive material being used by the military when it was still too costly for wide application on fireworks.

This section has shown how the interest of the military in pyrotechnic signals contributed to the introduction of some of the new materials that transformed fireworks during the 19th century. Sometimes dissemination of knowledge of the use of new materials was delayed, or even prevented; the most notable example being knowledge of how Martha Coston's pyrotechnists overcame the problem of spontaneous combustion, as discussed in Chapter 6. In other cases, such as the paper published by Marsh in 1844, sufficient information was published to permit the developments to be understood in detail. Other manuscripts and publications that contributed to the dissemination of pyrotechnic knowledge, and which were written by people associated with the military, will be reviewed in the next section.

7.2. The Role of the Military in Transmitting Pyrotechnic Knowledge.

Military people contributed to the dissemination of knowledge about pyrotechnics in two distinct but related ways: they trained cadets in pyrotechny, and they documented military pyrotechnic practices for internal use. Although such training and documentation was intended for military purposes, much of the knowledge soon reached the general public. The former military officer Chertier, for example, continued his enthusiasm for pyrotechny in civilian life and published the results of his work. Some serving military men, too, wrote books about pyrotechny for a general readership. The first two books in English on fireworks (published in 1635) were written by military gunners. Their motivation seems to have included gratifying curiosity about how fireworks were made, and providing information for amateur pyrotechnists. These military authors spread knowledge of firework-making beyond the artillerymen's workshops to the public at large – a favourable development for the advancement of pyrotechny.[226]

[226] Bate, *The Second Booke Teaching most plainly, and withall most exactly, the composing of all manner of Fire-works for Tryumph and Recreation*. John Babington, *Pyrotechnia, or a Discourse of Artificiall Fire workes for Pleasure* (1635; repr., Amsterdam: Theatrum Orbis Terrarum Ltd, 1971 and New York: Da Capo Press, 1971).

Over 60 years later, in 1696, Robert Anderson of London published a booklet on the making of rockets, dedicated to the Master-General of Ordnance. This is an example of a civilian amateur attempting to ingratiate himself with the most senior military person in the field of pyrotechnics. Anderson was a former silk-weaver, and was sufficiently wealthy to indulge in private researches on the application of mathematics to gunnery and rocketry. One section of his booklet was addressed to amateur rocket-makers; the other section was highly mathematical and provided formulae for finding the proper dimensions and correct compositions for rockets of all sizes, up to hitherto unprecedented diameters (12 inches). Such huge rockets were presumably intended for military use, so Anderson's work is another instance of the productive influence of the military in the dissemination of pyrotechnic knowledge, though in this instance the influence was indirect.[227]

The next English book on fireworks was published 70 years after Anderson's booklet. The author was a military officer: Lieutenant Robert Jones (ca 1740 – 1???), of the Royal Artillery. As a boy Jones somehow came to the attention of the statesman William Pitt (1708-1778), who arranged for him to join the Royal Artillery at Woolwich Arsenal as a boy cadet. The breadth of Jones' interests is indicated by his having published, in 1772, the first known book on figure-skating. In July 1772 Jones was charged with having sodomized a 12 year old boy. He was convicted, sentenced to death and committed to prison to await the hangman. His friends managed to persuade King George III to pardon him, on condition that Jones should leave the United Kingdom, never to return. He was released on October 30, 1772; his career from this point is unknown. The case has attracted the attention of those who take an interest in the history of homosexuality; it is not appropriate to take up that discussion here, but it is perhaps worth noting this unexpected intersection of pyrotechnic history with 'queer studies'.[228]

As an officer at Woolwich Arsenal, Jones was in a position to know the state of the art of British pyrotechny in the mid 1760s. Whether it would be reasonable to expect that Jones would reveal that knowledge in his book depends on his intentions when he wrote it. In his preface he claimed that existing treatises on the subject were translations of foreign works, and often erroneous; he hoped to instruct British readers so that ignorance could not be used to justify the habitual recourse to foreigners whenever a firework display was required. These statements lead to the expectation that Jones's book, which was dedicated to Sir Charles Ferederick, Comptroller of the Royal Laboratory, would indeed be an up-to-date technical treatise on firework-making, but that expectation is only partially fulfilled. Brock commented that Jones' book is 'of some merit, displaying considerable knowledge of the subject'. Kentish, on the other hand, wrote of Jones' book: 'The greater part of it is absurd and impracticable, and shows that it was written by a person who undertook to teach what he had not learnt'. Despite the shortcomings of his book, Jones is noteworthy as a military man who attempted to disseminate knowledge of fireworks to a general readership.[229]

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[227] Robert Anderson, *The Making of Rockets* (London: Robert Morden, 1696). Henry Sydney (Sidney), 1st Earl of Romney (1641-1704) was Master-General of the Ordnance from 1693 to 1702.

[228] Jones, *Artificial Fireworks, Improved to the Modern Practice*. For Jone's career, see Rictor Norton, "The First Public Debate about Homosexuality in England: The Case of Captain Jones, 1772. *The Gay Subculture in Georgian England*," http://rictornorton.co.uk/eighteen/jones1.htm, accessed 9th March, 2017.
Contemporary newspaper items about Jones are reproduced at "The First Public Debate about Homosexuality in England: News Reports concerning the Case of Captain Jones, 1772, *Homosexuality in Eighteenth-Century England: A Sourcebook* "
http://rictornorton.co.uk/eighteen/jones3.htm, accessed 9th March, 2017.

[229] Sir Charles Frederick (1709-1785) OB, FRS, served at Woolwich Arsenal as the Comptroller of the Laboratory from 1746 and in 1750 he was also made Surveyor General of the Ordnance, holding both positions until 1782. See Buchanan, Buchanan, Brenda J. "'The Art and Mystery of Making Gunpowder': The English Experience in the Seventeenth and Eighteenth Centuries." in *The Heirs of Archimedes: Science and the Art of War Through the Age of Enlightenment*, edited by Brett D. Steele and Tamaara Dorland. Cambridge, MA: MIT Press, 2005, pp.233-274, pp. 257-260. Frederick's name is also included in the long list of subscribers to Jones's book. See Jones, *Artificial Fireworks, Improved to the Modern Practice*. pp. ix-xiv

The details of exactly what took place in military and naval technical institutions are difficult to find. We are fortunate that a remarkable document does exist that tells us a great deal about firework-making at Woolwich Arsenal in the mid 1780s. This is a three-volume manuscript by one John Maskall (dates unknown). Produced in 1785, it provides an insight into the state of the art before the introduction of potassium chlorate. Maskall's manuscript shows that he was involved with the manufacture of fireworks at Woolwich and knew all the practical aspects of the craft. The work is meticulously detailed, down to such specifics as the number of times a mixture needed to be passed through a sieve to ensure that it was sufficiently mixed, and the number components that a man could produce in a day. The tools needed for the work were all specified in carefully dimensioned drawings, as were the various mechanical components for fireworks. An example is shown in Figure 7.2:

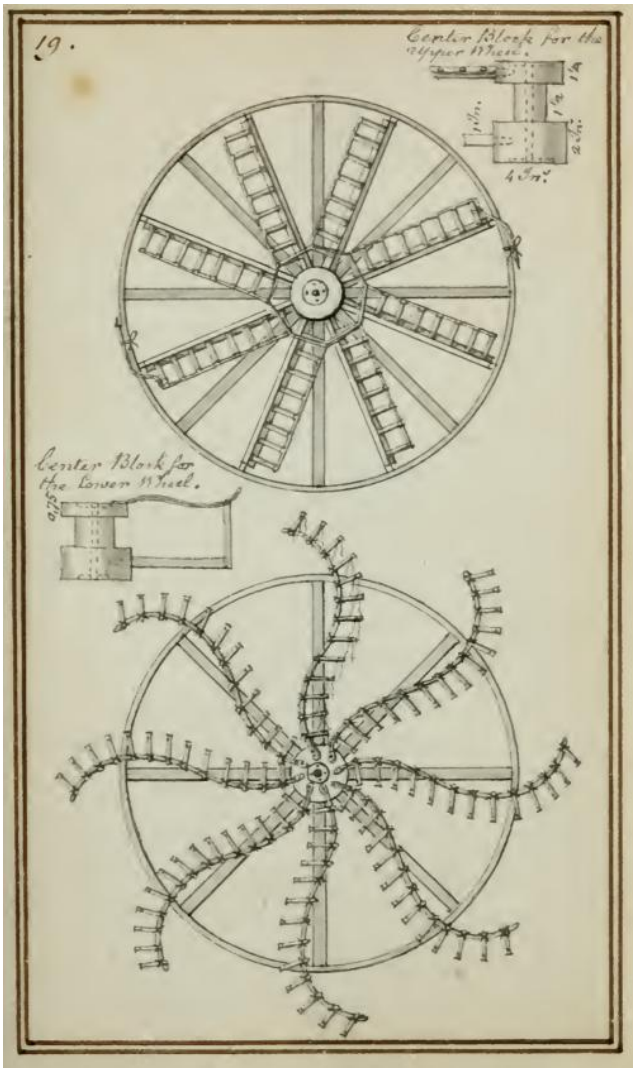

Figure 7.2. Illustration from John Maskall's manuscript, showing details of the construction of firework wheels. [230]

Maskall's work was a technical handbook of firework-making, presumably written for the benefit of workers at the Laboratory. There is no indication that the work was ever intended for publication.[231]

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[230] Maskall, "Artificial Fireworks Vol. 2 ", p. 19.

[231] "Artificial Fireworks Vol. 1," The Getty Research Institute, http://www.archive.org/details/artificialfirewo01mask, accessed 9 March, 2017; "Artificial Fireworks Vol. 2 ";

Most of the fireworks that Maskall described were made with the long-established compositions that Brock called 'force and spark' mixtures. There were also a number of flame compositions, including white stars for signal rockets, and several compositions for what Maskall called 'Specchis'. These, which correspond to modern lances or colour cases, were thin paper cases charged with flame compositions. Specchis were used to outline letters and pictures, exactly as modern lancework; they were also used, like modern colour cases, to decorate firework wheels, as shown in Figure 7.2.[232]

A remarkable coloured flame composition was used by Maskall in his 'Wheels in Azure Fire'. This composition was used in cases attached radially to a vertical wheel, so that when they were fired they projected radial jets of flame, forming a contrast to the tangential jets of sparks produced by the wheel drivers. These radial cases were charged with two compositions that burned one after the other, providing a pleasing change of effects. The two compositions are shown in Table 7.3:

	'Rayonnant'or White Fire'[233]	Blue[234]
Potassium nitrate	2	65
Sulfur	1	33
Meal powder	2	132
Zinc filings	-	192

Table 7.3. Two of John Maskall's Compositions of 1785.

The ingredients of the 'Rayonnant' or white composition are nothing unusual, but the effect that it produced was described by Maskall as:

> always beautifull, the body of the fire being white and the Rays yellow, like the sunbeams, from whence it is called Rayonnant Fire.[235]

Maskall mentions that this composition improves when cases charged with it are kept for some time. The yellow 'Rays' thrown out by the burning composition would have been caused by molten globules of combustion products.

Maskall's 'blue' composition is rich in zinc, which Lavoisier had introduced into fireworks to make blue flames less than 20 years before, as discussed in Chapter 2. The flame of the burning composition was described by Maskall as 'Sometimes blue and sometimes Green, much like the flame which arises from melted brass or Gun metal.' This to be expected: the flame in each case is produced by burning zinc vapour. Maskall mentioned that his blue composition does not keep beyond nine or ten days, after which time it 'becomes hard and uninflammable'. Despite this disadvantage, and the rather pale and ambiguous colour of the zinc flame, it must have been an impressive addition to the rather limited range of firework effects that were possible at the time. Maskall gave no clues as to the origin of the composition, but he did offer an explanation for its deterioration:

"Artificial Fireworks Vol. 3," The Getty Research Institute, https://archive.org/details/artificialfirewo03mask, accessed 9 March, 2017.

[232] For 'Force and Spark', see Brock, *A History of Fireworks*. chapter XV.

[233] Maskall, "Artificial Fireworks Vol. 2 ".p. 245.

[234] Ibid., p. 246.

[235] Ibid., p. 263.

> The Effect seems produced by the antipathy between Sulphur and Zinck – the Sulphur consuming that Semi-metal intirely.[236]

Maskall's manuscript comes to a sudden halt in the middle of the third volume. Blank pages have been ruled up in preparation, but the text stops in mid-sentence on page 52, as if the writer had been called away and never returned. The manuscript provides the best record that we have of late 18th century firework-making at the Woolwich Arsenal. Another 45 years would pass before any detailed descriptions of fireworks (as distinct from military pyrotechnics) would be provided by someone associated with Woolwich Arsenal.

In 1830 The Edinburgh Encyclopaedia included a lengthy entry on pyrotechny written by Dr John MacCulloch (1773-1835), Chemist to the Board of Ordnance from 1803 to 1825. MacCulloch is discussed here because he worked for the military when he wrote about pyrotechny. The opening paragraph of his encyclopaedia entry begins: 'Like many other arts, the present has been chiefly confined to the workshops of artisans, has perhaps never been fairly treated of by any one who, to general principles, united practical knowledge.' The unification of pyrotechnic practice and general principles would have been a major contribution, had it been accomplished.

MacCulloch classified the effects produced by firework compositions into four types: blast or explosion, motion by recoil, flame, and sparks. The first of these is achieved by gunpowder, the second by various mixtures of the three ingredients of gunpowder. Flame compositions require slowness of burning, and the absence of sparks. They must 'exclude charcoal as far as it is possible', and the mixtures must also 'be as minute and intimate as can be effected'. Charcoal, if needed, is added only as mealed gunpowder, in which form it is sufficiently fine not to produce sparks. The speed of burning is reduced by decreasing the proportion of saltpetre in the mixture, and various ingredients intended to modify the colours of the flame are added. Spark compositions are based on the mixtures used for recoil, most simply by adding coarsely-ground charcoal, but also by 'the addition of other sparkling substances, and principally of iron'. The latter can also be added to a flame composition, to produce a flame 'accompanied by brilliant white sparks.'

This is good information, but is essentially all that MacCulloch has to offer as the 'General Principles of Composition for Fireworks'. The reader, having been promised a unification of practical knowledge and general principles, might hope to find some discussion of the chemistry of the various compositions. This is not asking too much, considering Lavoisier's remark, published some 35 years before:

> All combustible substances may likewise be oxygenated by means of mixing them with nitrat of potash or of soda, or with oxygenated muriat of potash, and subjecting the mixture to a certain degree of heat ; the oxygen, in this case quits the nitrate or the muriat, and combines with the combustible body.

MacCulloch discussed the various ingredients of firework compositions without once mentioning oxygen. The most he had to say was 'All pyrotechny depends on the property which nitrate of potash possesses of accelerating the combustion of inflammable substances, even when excluded from air.' This invites the question: what about potassium chlorate?

Lavoisier had mentioned 'oxygenated muriat of potash' and in MacCulloch's day potassium chlorate was well known from the French attempt to use it in gunpowder and from its use in matches and in percussion primers. Even more relevant to MacCulloch's subject was its application in coloured fires. Yet, MacCulloch ignored it, apart from a description of the red fire reported by Faraday in 1820, transcribed almost word-for-word from the original. He made no further comment, possibly because he was fearful of discussing matters of current interest at Woolwich that ought to be kept secret. If so, it would be an example of military secrecy inhibiting the transmission of information that might have

[236] Ibid., p. 262.

assisted the development of improved coloured fires. Despite its shortcomings, MacCulloch's encyclopedia entry is an important example of a person employed by the military disseminating information about fireworks to the general public.

A few years before MacCulloch's entry was published, the military in the United States of America had contributed to the dissemination of knowledge of pyrotechnics through the work of a young chemist, James Cutbush (1788-1823), who taught chemistry and pyrotechnics to cadets at the United States Military Academy at West Point. According to his biographer Edgar Fahs Smith, Cutbush was an enthusiastic writer on chemistry from an early age. By 1813 he was Professor of Natural Philosophy, Chemistry and Mineralogy at St John's College, Annapolis. Cutbush became Acting Professor of Chemistry and Mineralogy at the Military Academy at West Point in 1820 and remained in that role until his death in 1823 at the age of 35. In 1822 Cutbush submitted a paper to the American Journal of Science. Ostensibly about Chinese Fire and Brilliant Fire, the article (which was not published until 1824) was a compendium of just about everything that was known about firework compositions. After his death, Cutbush's widow published his notes on pyrotechnics as a large book that reveals what chemistry students at West Point were taught about pyrotechnics in the 1820s, as well as providing Cutbush's views on every substance known at that time that was used, or conceivably could be used, in pyrotechnic compositions. As discussed elsewhere, Cutbush took the position of the prominent chemists of his day that potassium chlorate was too dangerous for practical use. Consequently, despite having successfully experimented with it as an ingredient in coloured fires, and having published the formula for the original English chlorate-based red fire, Cutbush taught that potassium chlorate was useful only for what he termed 'experimental fireworks': in other words, pyrotechnic lecture demonstrations. Thus, Cutbush's work contributed to the delay in the eventual recognition of potassium chlorate as the key to the production of a full range of coloured pyrotechnic flames. This is an example of the dissemination of expert knowledge by a teacher at a major military academy having the paradoxical effect of inhibiting the acceptance of a valuable new material.[237]

A notable step in the dissemination of practical knowledge of how that new material could be applied to good effect in fireworks was taken by a French artillery officer some three years after the publication of Cutbush's book. Chlorate-based colours were introduced into French firework displays in 1828 when the French Captain of Artillery Domenique-Nicolas Munier (1790-1838) used a modified version of the original English theatrical red fire in a display at Metz for the King and Queen of France. The display was prepared by students at the École Centrale de Pyrotechnie Militaire, under Munier's direction. Student at the recently-established École were taught the art of making and displaying fireworks to give them mastery of what was then the most challenging branch of pyrotechnics. Munier wanted to impress the royal visitors, so he adapted the theatrical red fire to produce designs outlined in points of brilliant red – a novel effect, which received the anticipated Royal approval. Full details of the compositions used, and of the difficulties experienced with their preparation as a result of the inconsistent purity of commercial chemicals, were published in a technical journal. What better example could there be of the contribution of the military to the dissemination of new pyrotechnic knowledge? [238]

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[237] For Cutbush and his career, see Edgar Fahs Smith, *James Cutbush; An American Chemist 1788-1823* (Philadelphia: J. B. Lippincott Company, 1919; repr., BiblioBazaar, LLC, 2008). Cutbush's writings on fireworks are Cutbush, "Remarks on the composition and properties of the Chinese fire, and the so-called Brilliant fires."; *A System of Pyrotechny*. For a discussion of Cutbush's views on potassium chlorate, see Sturman, "Coloured Fire", pp. 35-36.

[238]"Coloured Fire." "The Early Use of Potassium Chlorate in Pyrotechny: Part III. Applications of Early Chlorate-based Coloured Flame Compositions ". For the military pyrotechnic school at Metz see M. Vauchelle, *Cours d'Administration Militaire* 4ème ed., vol. 1 (Paris: J. Dumaine, 1861), pp. 190-194. For the royal order for the founding of the school, Baron de Demas, "Ordonnance du Roi portant création d'une École Centrale de Pyrotechnie militaire près de l'une des école régimentaires d'artillerie " *Annales Maritimes et Coloniales* (1824), p. 351-353. See also Marquis de Clermont-Tonnere, "Réglement sur le Service et l'instruction de l'École centrale de Pyrotechnie militaire," ibid., pp. 560-565. On the staging of public firework displays by pupils of the school, see Joachim Ambert, *Equisses historiques, psychologiques et critiques de l'armée Français*

At about the same time another French artillery officer, Chertier, had acquired an enthusiasm for the artistic application of pyrotechnics. It can be presumed that he, like Munier's men, had received his pyrotechnic training as part of his military duties; in his case, it developed into a life-long passion. In his retirement, the former artillery officer would become one of the foremost amateur pyrotechnists of the 19th century. [239]

A few years previously, in Germany, another artillery officer had published some innovative work on fireworks. Franz Eduard Moritz Meyer, an artillery officer who had earned a doctorate in chemistry as part of his military training, was employed by the Prussian War Ministry to study and document any technical developments that might be useful for military purposes. In 1833 he published detailed studies of coloured flame compositions based on potassium chlorate, including compositions for each of the principal colours. This was part of a much broader project to apply new scientific knowledge to the rationalization and simplification of pyrotechnics. At that time, pyrotechnics was a technical handicraft, founded on hard-won empirical knowledge and practical skill in the manipulation of materials. Meyer saw scope for improvement by purging pyrotechny of unscientific encumbrances and re-building it on a firm scientific foundation

Meyer's rationalization of pyrotechny was founded on his application of stoichiometry to the formulation of pyrotechnic mixtures. The term 'stoichiometry' had been introduced in 1792 by the German chemist Jeremias Benjamin Richter (1762 –1807) to refer to the ratios of the masses of reactants and products in a chemical reaction. Before Meyer, pyrotechnic compositions had been developed by trial and error. Meyer recognized that such an approach was necessary when dealing with charcoal, the properties of which varied from batch to batch. Meyer preferred pure substances (potassium nitrate, potassium chlorate, sulfur) as pyrotechnic ingredients and used stoichiometry to find the optimum proportions of fuel and oxidizer. In addition to this chemically-based rationalization of the craft, Meyer experimented with different substances as colour-producing agents, suggested improvements to the processes involved in the manufacture of fireworks and pointed out opportunities to enhance the aesthetic impact of firework displays.

In 1833 he wrote:

> Fireworks may offer only brief, fleeting pleasure, but, reproducing the intense fiery phenomena of the atmosphere, they possess a more magical power over the senses than other, milder art forms. They have a magical charm and, more than any other art, they lead into the realm of dreams and fairyland. They certainly do not deserve to be entirely neglected, as has happened so far. [240]

As a military technologist, he was also aware of the applications of pyrotechnics in warfare, and he also foresaw possible uses in science and industry:

(Bruxelles: Librairie Militaire de J.-B. Petit, 1840), p. 212. Munier, "Extrait d'une note sur le feu d'artifice tire à Metz le 4 September 1828, par M. Munier, Capitaine d'Artillerie", p. 184.

[239] Sturman, B. "The Early Use of Potassium Chlorate in Pyrotechny. Part VII. F. – M. Chertier and the Development of Chlorate-based Coloured Fires in France." *PGI Bulletin (Bulletin of the Pyrotechnics Guild International, Inc.)*, no. 193 (March/April 2015), pp. 29-46.

[240] Sturman, "The Early Use of Potassium Chlorate in Pyrotechny. Part V. Moritz Meyer And His Application of Chemical Theory To Pyrotechnics"; Franz Eduard Moritz Meyer, "Ueber einige Verbesserungen in der Lustfeuerwerkerei," *Erdmanns Journal für technische und ökonomische Chemie* 16 (1833). p. 440.

> In addition, the principles of pyrotechnics that we will develop will later be of the highest importance for science, especially in the field of optics, for signaling, and indeed in industry for the provision of mechanical force, or for obtaining higher temperatures.…[241]

Having stated the artistic and practical value of pyrotechnics, Meyer explained his intentions as follows:

> We therefore hope that by simplifying the work, and by ensuring first and foremost that the desired results can be achieved, the artistic aspects of pyrotechny will once again be widely taken up by amateurs. The more serious applications will then certainly not be neglected.[242]

Meyer's advocacy of amateur pyrotechny is surprising from a modern perspective. We would expect an army officer and member of the State bureaucracy to disapprove of amateurs, especially amateurs in a technical field relevant to the military. Meyer's enthusiasm for amateurism in firework making stands in sharp contrast to his recommendation concerning the proper ordering of fire brigades, for which he advocated central control and disciplined administration. His military preference for control, order and discipline can perhaps be seen, too, in his project to place pyrotechnic chemistry on a rational footing. Meyer's stated justification for the encouragement of amateur firework-making was that pyrotechnic expertise would be valuable to the State; it is obvious, too, that Meyer liked fireworks and saw their artistic development as valuable in its own right.[243]

Meyer's simplification of pyrotechnics began with the compositions, which he proposed to base on just four mixtures of four ingredients. The latter consisted of two oxidizing agents (potassium nitrate and potassium chlorate) and two fuels (sulfur and charcoal). One of his four compositions, *Chlorkalischwefel*, was the basis of his novel coloured flame compositions. *Chlorkalischwefel* is an example of Meyer's application of the principles of chemical stoichiometry to the development of pyrotechnic mixtures. This was a new development in pyrotechnics; it required him to postulate the products of the combustion reaction and, from these, to calculate the quantity of each reactant required to form those products, with no reactant in excess. *Chlorkalischwefel* was theoretically a mixture of 79 part of potassium chlorate with 21 parts of sulfur, but a simple 4:1 mixture was used in practice. There is evidence, presented elsewhere, that Meyer's *Chlorkalischwefel* is not stoichiometric according to modern understanding of the combustion reaction, but it was perfectly adequate as a basis for coloured flame compositions. Meyer used it to make compositions that introduced many new colour-producing materials, as discussed in Chapter 4 and elsewhere. Meyer's work is an outstanding example of the contribution of the military to the transformation of fireworks in the 19th century by the introduction of new materials. It is also important for its explicit application of chemical theory to the formulation of pyrotechnic compositions.[244]

Some 5 years after the publication of Meyer's book a French artillery officer, Amand Denis Vergnaud (1791-1885) published a book on fireworks that showed that the French practice of the day was considerably behind the state of the art in Germany, as revealed by Meyer. This was the 3rd edition of a work originally published in 1826. As noted by Swisher in his 1982 review of a reprint of Vergnaud's 1838 book, Vergnaud did not draw on the work of his contemporary Chertier, published only two years before. Vergnaud gave recipes red and green theatre fires with nitrate of potash

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[241] *Die Feurewerkerei in ihrer Anwendung auf Kunst, Wißenschaft und Gewerbe*. p. 2.

[242] Ibid., p. 3.

[243] Moritz Meyer, *Die Feuer-Lösch-Anstalten in Paris und Mailand im Vergleiche mit den unseren* (Berlin: Im Verlage von Adolph Martin Schlesinger, 1832), pp. 5-10, 19-20.

[244] B. Sturman, "The Early Use of Potassium Chlorate in Pyrotechny. Part VI. Moritz Meyer's Work on Coloured Pyrotechnic Flames," *PGI Bulletin (Bulletin of the Pyrotechnics Guild International, Inc.)*, no. 189 (2014).

instead of chlorate of potash. These could not have worked, so Vergnaud could not have tested them. Strangely, he gave the original (1822) Green Fire mixture (with chlorate) as a green 'jet of coloured fire'. The same peculiarities were repeated in the 1852 edition of Vergnaud's book, which is most odd given that Chertier's original (1836) work and his subsequent (1843) book had both been available for some years. In 1865 Vergnaud and a P. Vergnaud (presumably his son Paul, born 1818) published an excellent manual on fireworks that took into account the works of Chertier (1836, 1843) and Tessier (1859) and included a comprehensive section on coloured fires. As both the Vergnauds were artillery officers, this work stands as an example of the contribution of military men to the dissemination of pyrotechnic knowledge.[245]

Yet another military officer who made a valuable contribution to the transmission of knowledge about fireworks was the Austrian artillery officer Josef Uchatius (1809-1875). His 1848 book is an impressive, highly detailed treatment of fireworks, and, as noted by Philip, contains the first published discussion of electrical firing of fireworks – a practice that had been used by Southby in London in 1843 and which was a natural adaptation of the military's electrical firing of explosives, introduced in Russia during the Napoleonic Wars.[246]

7.3. Military-civilian connections.

The contributions of the military to the introduction of the new materials that brought brilliant colours and other revolutionary new effects into fireworks were much more effective than they might otherwise have been, as a result of the participation of military personnel in social networks that extended well beyond the military, and which permitted civilians to have access to matters that we might expect to have been kept strictly within the military. An example of such a network was touched upon when we noticed that James Marsh, the military employee, knew the chemist and pyrotechnist George Southby and his father, Joseph Southby. Thanks to James Marsh's courtesy in acknowledging George Southby as the source of his knowledge of the value of manganese dioxide in the preparation of oxygen from potassium chlorate we have a glimpse of a network of personal acquaintances linking a surgeryman working as a military chemist (Marsh) to a professional pyrotechnist who was also an amateur chemist (George Southby) and a professional pyrotechnist who was also an actor, a clown and a cabinet-maker (Joseph Southby) to a medical student who was also an amateur chemist (John Forster). The link that connects all these diverse characters is a common interest in potassium chlorate. This illustrates the point that the introduction of the new materials into pyrotechny in the first half of the 19th century happened somewhat haphazardly and in ways that might seem surprising.

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[245] Philip, *A Bibliography of Firework Books: Works on recreative fireworks from the sixteenth to the twentieth century*, p. 154. Amand Denis Vergnaud, *Nouveau manuel de l'artificier, du poudrier et du salpêtrier* (Paris: Roret, 1838). The theatre fires are on page 234, the 'green jets' on p. 229. For Swisher's review, see Michael S. Swisher, "Review of 'Nouveau manuel de l'artificier, du poudrier et du salpêtrier' by A. D. Vergnaud," *Pyrotechnica*, no. VIII (1982), pp. 39-40. Amand Denis Vergnaud, *Nouveau manuel de l'artificier, du poudrier et du salpêtrier* (Paris: Roret, 1852). The theatre fires are on p. 279, the 'green jets' on p. 274. Vergnaud and Vergnaud, *Nouveau manuel complet de l'artificier. Seconde partie: pyrotechnie civile*. The section on colours is pp. 102-123. For Vergnaud's biography, see A.-M. Gossez, *Souvenirs du Colonel Vergnaud officier d'artillerie 1791-1885. Analyse et extraits*, Bibliothèque de " La Revolution de 1848 " (Paris: Rieder, 1937).

[246] Philip, *A Bibliography of Firework Books: Works on recreative fireworks from the sixteenth to the twentieth century*, p.149; Josef Uchatius, *Die Kunst-Feuerwerkerei zu Lande basirt auf wissenschaftlichen Principien* (Wien: F. Tendler & Comp., 1848). Electrical firing is discussed on pages 159-162. For Southby firing with electricity, see Anonymous, "New Picture-Model at the Surrey Zoological Gardens," *The Illustrated London News* 2, no. 58 (1843), p. 396. For early military firing of explosives with electricity, see Robert W. Tolf, *The Russian Rockefellers: The Saga of the Nobel Family and the Russian Oil Industry* (Stanford, California: Hoover Institution Press, Stanford University, 1976), p. 11.

We might expect evidence of a military man, for instance, recognizing a requirement for coloured flares for signalling and consulting a chemist, or a professional pyrotechnist. Before anything like that is even hinted at, we find a theatrical manager (John Astley) approaching a medical student (John Forster), known to be an amateur chemist, and asking the student if he can find a more reliable red fire than the mixtures of strontium nitrate, gunpowder and various combustibles that were currently in use as stage effects. The student succeeds, using potassium chlorate, a chemical thought to be too dangerous to use. The new red fire attracts the attention of one of the theatre's actors (Joseph Southby), who also happens to be a firework-maker. He adapts it to make stars for sky-rockets, and uses them to great effect at the local pleasure gardens. Being of patriotic (and entrepreneurial) disposition, he shows his rockets to some navy officers in the hope that the rockets would be accepted by the Navy for use as signals at sea. The officers tell their superiors that the rockets are not worth having. Only then do they go to the Royal Laboratory and tell the chemists there (perhaps including Marsh?) to get busy cracking the formula for the red stars and, while they are about it, make the other colours as well. Soon afterwards, the officers are demonstrating a full range of coloured rockets to top-ranking military men, and claim the invention as their own. The actor-pyrotechnist is not pleased.

Meanwhile, a Prussian military chemist (Meyer) learns of the coloured rockets, and begins to pay serious attention to what might be achieved with the help of potassium chlorate. The actor-pyrotechnist's son George Southby (a pyrotechnist-chemist) has been experimenting with potassium chlorate, probably to gain a better understanding of how it behaved in fireworks. He noticed that addition of manganese dioxide makes it part with its oxygen at a conveniently low temperature, providing a useful source of oxygen for chemical experiments. He mentions this to Marsh, the surgeryman-chemist from Woolwich Arsenal, who is interested in potassium chlorate because of its use in coloured fires. The Woolwich chemist decides that the new method of making oxygen is worth publishing and does the right thing by acknowledging his source.

All these things involved interactions between people from different walks of life. Such interactions would have been difficult in circumstances where there were strong class divisions, and it is no coincidence that such divisions, though still powerful, were not quite as rigid in the big cities of early nineteenth century Europe as they had been in earlier times. For example, the London theatres and pleasure gardens in which Southby applied his pyrotechnic talents were attended by members of all classes, and this loosened class distinctions to some degree. Joseph Southby was a cabinet maker, a clown, an actor and a firework-maker – all rather humble callings. But Southby was also 'Artist in Fireworks to the Royal Gardens, Vauxhall', and as such was sufficiently well-regarded and self-confident that he was able to interact with officers of His Majesty's Royal Navy and to criticise them in letters to a military publication.

In a different field, James Marsh was originally a humble wheelwright, and officially never more than a 'dispenser of medicines' but thanks to his training by the military he was able to develop and apply his chemical talents to an extent that earned him the respect of professional chemists and the right to participate in the activities of the Chemical Society. Without such possibilities of social interactions beyond the stratum into which one had been born, the chain of productive acquaintances outlined above could never have been formed.

This chain of acquaintances can be extended further, even to France. To do this, we must look back to 1856, to the last involvement of the British military with firework displays. The displays on May 26 for the end of the Crimean War were under the direction of Captain Edward Mounier Boxer (1822-1898), Superintendent of the Royal Laboratory, Woolwich, but according to Brock the actual manufacture of the fireworks was carried out at the Royal Laboratory under the direction of 'Mr Southby, pyrotechnist to the Surrey Gardens'. Again according to Brock, Southby was assisted by Thomas Kentish, a schoolmaster and amateur firework-maker. In his book on fireworks published in 1878, Kentish mentions that Southby had told him that he had met Chertier in Paris, and had derived much useful information from him; the network thus crossed the Channel and included the most productive pyrotechnic innovator of the century. With Kentish, the network extends to include two men who were responsible for putting commercial firework manufacture in Britain on a footing

commensurate with its use of the transformative but dangerous material, potassium chlorate. Kentish, according to Brock, was a close friend of the pyrotechnist and entrepreneur Charles Thomas Brock (1843-1881), who in turn was associated in the early 1870s with the artilleryman Captain (later Colonel Sir) Vivian Dering Majendie RA (1836-1898) in recommending the provisions that needed to be laid down to permit the new materials that had transformed fireworks to be used with reasonable safety. This would culminate in the Explosives Act of 1875. Captain Majendie was Assistant Superintendant of the Royal Arsenal until 1871, when he was appointed Her Majesty's Chief Inspector of Explosives. His role in the framing of the Explosives Act of 1875 can be seen as the final contribution of the military to the transformation of fireworks in the 19th century.[247]

7.4. Conclusion

Military people were part of the tangled web that constitutes the history of the transformation of fireworks in the 19th century. They interacted with civilian pyrotechnists, both professional and amateur, and with chemists. The transformation of fireworks always depended on the introduction of materials new to the art; sometimes the involvement of the military facilitated this, sometimes it did not. The comparative insensitivity of the military to the cost of materials was facilitating, as exemplified by the use of magnesium in military signals at a time when the metal was too costly for general use in civilian fireworks.

The contributions of the military to the transformation of fireworks were often indirect, and almost always involved interactions with civilians. Interactions were both positive and negative, depending on the circumstances. At the beginning of the century fireworks and military weapons were all based on gunpowder; by the end of the century military gunpowder was being supplanted by new propellants and explosives, a process that had begun in the late 1840s but proceeded very slowly until the 1880s, when nitrocellulose-based propellants began to be introduced. Well before then the skills involved in making and displaying fireworks had become irrelevant to warfare and the time had come for the military to abandon its involvement with fireworks. Pyrotechnics for signalling were of continuing interest to the military and led to the introduction of some new materials that were subsequently adopted by civilian firework-makers. By the end of the 19th century the military had surrendered its former responsibility for fireworks to civilians. In the intervening decades it had made important contributions to the development and application of the new coloured fires and was central to the application of the transformational new ingredient magnesium. Military men were also active in the application of chemical theory to pyrotechnics and in the dissemination of pyrotechnic knowledge. Chapter 9 will explore the role of civilian chemists in the transformation of fireworks, and review the ways in which knowledge of the new developments was disseminated. Meanwhile, the following chapter addresses the effect of the cost and availability of materials in the development and practical implementation of new firework effects.

[247] For the 1856 displays, see Jocelyn, "The connection of the Ordnance Department with National & Royal fire-works, including some account of Sir Martin Beckman, Colonel Henry John Hopkey, & Sir William Congreve (2nd Baronet.)", p.499. For Southby at Woolwich , see Brock, *A History of Fireworks*, p.78. For Southby and Kentish at Woolwich, see ibid., p. 162, fn. For the Gunpowder Act, see ibid., p. 144. For Kentish, see Sturman, "Thomas Kentish: A Victorian Amateur Pyrotechnist."

Chapter 8: Availability and Cost of Materials as a Limiting Factor in the Transformation of Fireworks.

Previous chapters focussed on knowledge of the properties of chemicals as factors limiting the introduction of new materials into pyrotechny. Such knowledge may be either facilitating (for example knowledge that the chemical can produce interesting effects) or limiting (for example knowledge that the chemical is unacceptably hazardous).[248]

Another influence on the adoption of a new ingredient, perhaps so obvious that it is easily ignored, is the availability of the ingredient at a reasonable cost. How would the availability and price of chemicals have affected their use in firework-making? The intuitive answer would be that scarce, costly materials would have only very limited application, if they were used at all. There certainly were materials that might have been used in principle but were not used in practice, simply because they were too expensive. In 1839, for example, Martin Websky wrote that selenium (which had been discovered some 22 years earlier) 'gives...a very intense blue coloration', but 'the preciousness and rarity' of selenium 'had 'so far precluded its application.' [249]

Similarly, in 1863 the English physicist and chemist William Crookes (1832-1919) published a composition for 'a magnificent green fire for pyrotechnic purposes' based on thallium chlorate. Crookes had discovered thallium only two years previously, and he admitted:

> At the present price of thallium, its employment for pyrotechnic purposes would be out of the question; but a very little reduction in price would enable its magnificent green flame to be advantageously employed for ship signals, as the extraordinary intensity and monochromatic character of the light would enable it to penetrate a hazy atmosphere without the change of colour suffered by the ordinary green lights in which baryta is used.[250]

Selenium and thallium never became sufficiently cheap to be used in fireworks. In other cases, as will be shown here, if an initially limited application of an uncommon, costly material becomes sufficiently popular, increased demand can lead to its becoming less costly. This can lead in turn to further applications, and thus to a further reduction in the rarity and costliness of the ingredient. This is a slow process, and it is to be expected that a material will be more readily adopted as an ingredient in fireworks when it is already available, and inexpensive, as a consequence of its having other applications. How, then, did the prices of pyrotechnically-useful chemicals change over the course of the 19th century? Why were they available at all? In answering these questions, it would have been useful to begin in the late 18th century, shortly after the discovery of important new chemicals such as potassium chlorate and strontium nitrate, but no quantitative information could be found. That potassium chlorate was initially very expensive can be inferred from the comment of the English chemist Thomas Hoyle Jr (no dates) in 1799 that 'many have probably been deterred from the investigation [of potassium chlorate] by the exorbitant price...'[251]

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[248] "Coloured Fire", pp 33-36, discusses the consequences of late 18th and early 19th century chemists teaching that potassium chlorate was unacceptably hazardous.

[249] Websky, *Lustfeuerwerkerei für Dilettanten*. p. 82. For the discovery of selenium, see Jan Trofast, "Berzelius' Discovery of Selenium," *Chemistry International* 33, no. 5 (2011) https://www.iupac.org/publications/ci/2011/3305/5_trofast.html, accessed 9th March 2017.

[250] William Crookes, "On the Extraction of Thallium on a Large Scale from the Flue Dust of Pyrite Burners," *The Chemical News* 8 (1863), pp. 159-161, p.161.

[251] Thomas Hoyle, "Experiments and Observations on the Preparation, and some remarkable Properties of the Oxygenated Muriate of Pot-ash," *A Journal of Natural Philosophy, Chemistry and the Arts: Illustrated with Engravings; by William Nicholson* 2, no. October 1798 (1798), pp. 290-297, p. 290.

It was necessary to begin where the available data began: in the second decade of the 19th century. At that time chemistry was a popular pastime among those having the luxury of enough time and money to indulge in such activities. The formal study of chemistry was also undertaken at various universities, to cater for the requirements of the medical profession and the demands of rapidly growing chemically-based industries. Accordingly, many chemicals and minerals were available commercially, primarily for laboratory use. Almost any chemical known to science was available – at a price; unless a chemical had other uses, production would be small (possibly 'on demand'), and costs would be high. Once a use had been established, production would be scaled up and prices would fall.

The chemicals that would be needed in the new red and green coloured fires were commercially available early in the century, but they were costly. Table 8.1 shows the prices in 1817 from a London dealer in laboratory supplies: This was the earliest listing of the prices of these chemicals that could be found after extensive searching. As explained in Chapter 4, all three of these chemicals were discovered in the late 18th century.[252]

Chemical	Price per Ounce
Potassium chlorate	4 shillings
Barium nitrate	1 shilling and 6 pence
Strontium nitrate	3 shillings

Table 8.1. Prices charged in 1817 by a London supplier of laboratory equipment for some chemicals needed to make coloured fire.

An indication of just how costly these chemicals were is given by a comparison of the cost of some of the more common pyrotechnic chemicals from the same supplier:

Chemical	Price per Ounce
Antimony sulfide	6 pence
Iron filings	3 pence
Potassium nitrate	6 pence
Sulfur	3 pence
Zinc filings	6 pence

Table 8.2. Prices charged in 1817 by a London supplier of laboratory equipment for some traditional pyrotechnic chemicals.

The chemicals shown in Table 8.2 were far less expensive than the three new chemicals shown in Table 8.1. The chemicals in Table 8.2 were common industrial materials, or even waste products, at the time, and they seem to have been grossly marked-up. Evidence for this is that a barrel of gunpowder, containing 100 lbs, cost about £6/6/- (i.e 126 shillings) at that time. This corresponds to about 1 shilling and three pence per pound, or a little less than a penny an ounce. Gunpowder contains 75% potassium nitrate, so the makers of gunpowder were obviously obtaining potassium nitrate at far, far less than the 6d. per ounce that the chemical supplier was advertising. Naturally the chemical supplier claimed that his products were 'absolutely pure', and presumably he incurred costs in packaging the materials in small quantities, and presumably too he hoped to make a handsome profit.

[252] For an example of laboratory chemicals being commercially available in the early 19th century, see Accum, "A Descriptive Catalogue of the Apparatus and Instruments employed in Experimental and Operative Chemistry, in Analytical Mineralogy and in the Pursuits of the Recent Discoveries of Voltaic Electricity." This was published bound as an Appendix to his book *Chemical Amusement, Comprising a Series of Curious and Instructive Experiments in Chemistry, which are Easily Performed, and Unattended by Danger* (London: Thomas Boys, 1817).

In considering the cost of materials at different periods in history, it is possible to obtain a quick impression from the price in the currency of the day. The real cost of the chemicals in Table 8.2 can be better appreciated with the knowledge that the wages of a skilled building craftsman in London in 1817 were 6 shillings a day. Economic historian Robert C. Allen has shown that it is more informative to express the cost not in currency but in the time that would have to be taken for a person of a particular station in life (such as a skilled building craftsman) to earn enough to purchase a specified quantity of the material. This approach has been followed in this chapter unless specifically stated otherwise.[253]

In 1817 the new materials that would be needed to make coloured fires were luxury items; a skilled craftsman would not have been able to afford them, and it is easy to see why the earliest of the modern coloured fires (introduced in 1810) would have been not just a novelty, but a very costly one. Table 8.3 shows the how the price of each chemical contributed to the cost of the new Red Fire:

Chemical	Amount in Red Fire, parts by weight	Price, pennies per ounce of chemical	Price, pennies per ounce of Red Fire
Strontium nitrate	40	36	23.2
Sulfur	13	3	0.6
Antimony sulfide	4	6	0.4
Potassium chlorate	5	48	3.9
		Total:	28.1 pence per ounce.

Table 8.3. Prices of the chemicals used in one ounce of the original chlorate-based Red Fire, as charged in 1817 by a London supplier of laboratory equipment.

The chemicals in just one ounce of Red Fire would have cost two shillings and fourpence, at a time when a day's wage for a skilled craftsman was only six shillings. An ounce of Red Fire would probably have been sufficient for one firing, lasting for a few seconds, in a theatrical performance; an ambitious stage manager would probably have wanted to use more, but for the cost (and the noxious smoke). Despite its high price, there is evidence that Red Fire was in use in the theatre from 1810 and in firework displays in 1817.[254]

While the more common pyrotechnic ingredients could have been obtained much more inexpensively elsewhere, the laboratory suppliers were probably the only commercial source of the newer chemicals.

[253] The price of a barrel of gunpowder in 1816 is given in "African Forts. Report from the Select Committee on Papers relating to the African Forts. Ordered, by the House of Commons, to be printed, 25 June 1816," *The Colonial Journal*, no. V (1817), p. 188. The silver price is for an Avoirdupois ounce, not the heavier Troy ounce normally used for precious metals, so it is directly comparable to the prices for the chemicals. At the time the price of gold was fixed by the Gold Act of 1816 at £46/14/6 per troy pound; the ratio of the price of gold to that of silver in 1817 was 15.11, which allows the price of silver to be calculated. For tabulated gold to silver price ratios, see Marc Flandreau, *The Glitter of Gold: France, Bimetallism, and the Emergence of the International Gold Standard, 1848-1873*, trans. Owen Leeming (Oxford: Oxford University Press, 2004), p. 243. Robert C. Allen has compared historical prices and wages by converting them to grams of silver. Robert C. Allen, "The Great Divergence in European Wages and Prices from the Middle Ages to the First World War," *Explorations in Economic History* 38 (2001), pp. 411-447. He presented data for the wages of a skilled London building craftsman in grams of silver at different times in the 19th century. For the purposes of this chapter, Allen's data were either used directly, or, when he did not give a number for a particular year, it was estimated by interpolation using a second-order polynomial fit to his data (R^2 =0.9961). Conversion between currencies, and between silver and currencies, was done using the on-line converter available at http://www.historicalstatistics.org/Currencyconverter.html,accessed 9th March 2017.

[254] For the introduction of Red Fire, see Sturman, "Coloured Fire.", and "The Early Use of Potassium Chlorate in Pyrotechny: Part I. John Forster and the First Chlorate-based Colored Fire."

The only other way of obtaining them would have been to make them from minerals, and recipes for doing so can be found in contemporary chemistry texts. This would require time, equipment, chemicals, a suitable work space and a supply of the necessary minerals. If the latter had to be purchased from a dealer, they would not have been cheap. It seems, then, that access to the new chemicals was effectively restricted to the rich. Over the next several decades, this would change greatly.

Table 8.4 shows the prices of a selection of pyrotechnic chemicals in 1817 and 1878. Prices are given in days' wages for a skilled London building craftsman per pound (16 ounces) of chemical.

Chemical	1817	1878	Price in 1878 as % of price in 1817
Antimony sulfide	1.45	0.06	4.17%
Barium nitrate	4.41	0.08	1.84%
Iron filings	0.73	0.08	11.13%
Potassium chlorate	11.68	0.12	1.04%
Potassium nitrate	1.45	0.06	4.17%
Strontium nitrate	8.78	0.08	0.92%
Sulfur	0.73	0.04	5.51%
Zinc filings	0.73	0.36	50.08%

Table 8.4. Changes in the prices of some pyrotechnic ingredients in London from 1817 to 1878

The real prices of all these materials fell over that time. The greatest falls were for the newer chemicals – products of the chemical laboratory or the industrial chemical plant. Falls in prices were least for iron filings and zinc filings, which were essentially waste products of other manufacturing processes. The prices of antimony sulfide, sulfur and potassium nitrate fell less than those of the new chemicals but much more than those of the metal filings. These three materials are refined natural products. Potassium nitrate and sulfur had long been important in commerce as ingredients of gunpowder, and natural antimony sulfide was the only source of antimony. While Table 8.4 indicates the general trend, it is worth examining the changes in more detail. The discussion that follows focuses on London, because the available data related most directly to that city. It is presumed that prices elsewhere in Europe would have been broadly similar to those in London. As will be seen, data from Paris and London plotted on the same graphs show no glaring anomalies.

Figure 8.1 shows the price per pound of five important pyrotechnic ingredients, expressed in a London craftsman's days' wages per pound. Apart from the data for 1817, prices were taken from books about amateur firework-making. Those for 1859 and 1883 were from French books, the rest were from British sources. The prices are for materials bought by the pound (or by the ounce for the more costly ones). Professional firework makers, who would have bought chemicals by the hundredweight, would presumably have paid less, but no illustrative data could be found.

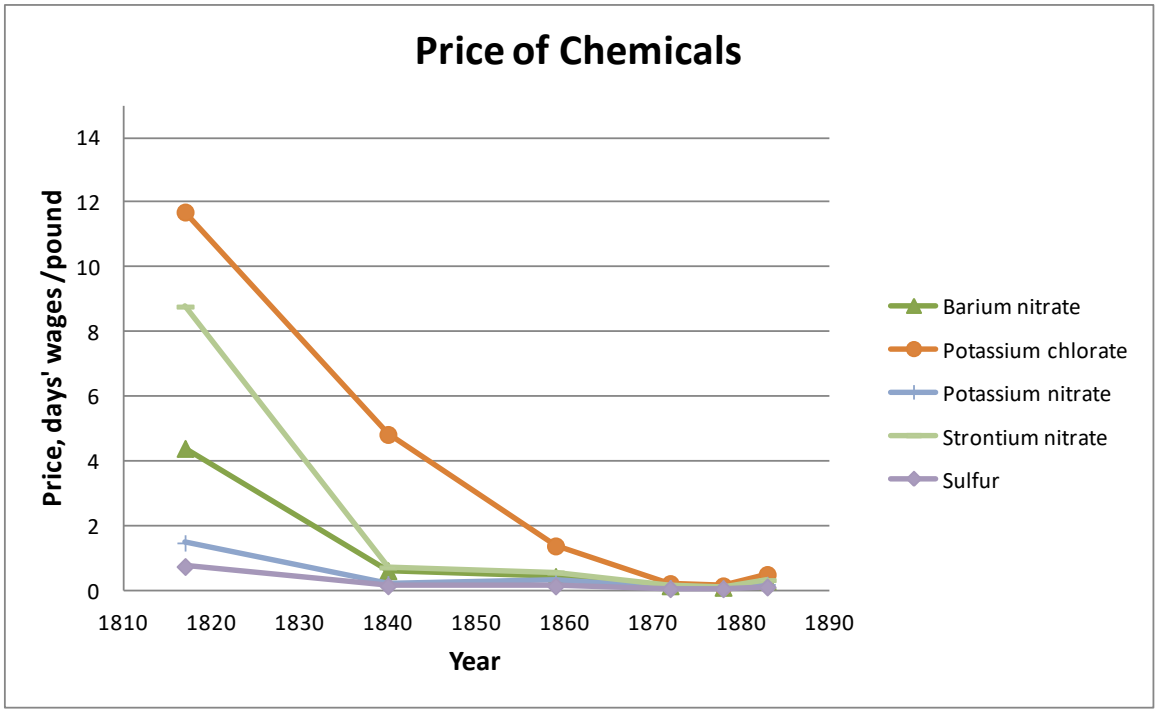

Figure 8.1. Prices of five pyrotechnic chemicals, 1817-1883.

The obvious trend is that prices of all these chemicals fell; closer inspection shows that the prices of the two traditional ingredients (potassium nitrate and sulfur) fell much less than did those of the three new ingredients. Indeed, if allowance be made for the 1817 values being from a laboratory supplier, who would charge more than a chemical manufacturer, the price of the two traditional ingredients did not change much at all. This is evident in Figure 8.1, which shows the same data as Figure 8.2 with an expanded vertical scale.

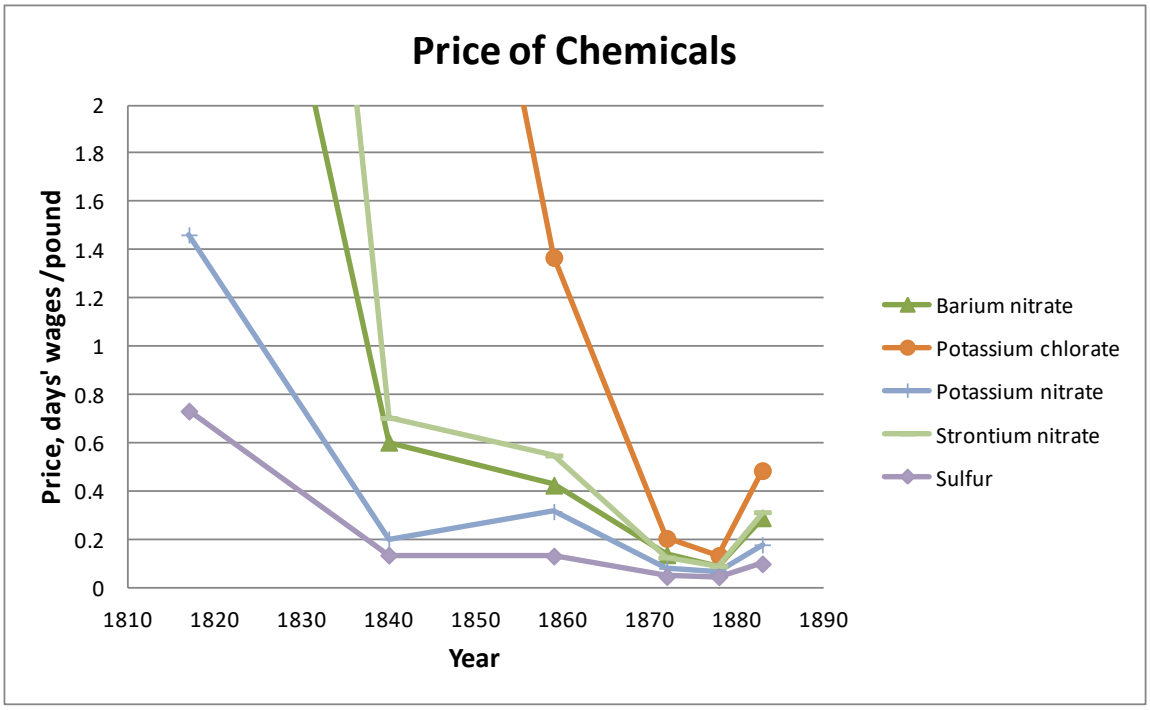

Figure 8.2. Prices of five pyrotechnic chemicals, 1817-1883. Scale expanded to show the trend from 1840.

8.1. Barium Nitrate and Strontium Nitrate

The prices of barium nitrate and strontium nitrate fell rapidly between 1817 and 1840, but after that fell much more slowly. This reflects the transition of these chemicals from laboratory supplies to industrial products. The principal use of these two chemicals was in pyrotechnics, and the relatively small decrease in their real price from 1840 indicates that supply and demand were more or less in balance. The details of the transformation of barium nitrate from a laboratory chemical to a raw material for the firework trade have survived, and it is worth taking a closer look at what happened. In 1838 The German scientist Karl Friedrich Mohr (1806-79) wrote a short paper that began:

> A significant amount of nitrate of baryta is used in recent times in fireworks, and its economical procurement is therefore probably a matter for technical chemistry. But since it is also the material used to prepare caustic baryta, it is also of relevance to the chemist..[255]

Mohr explained the inefficiency of the usual way of making barium nitrate, and described how barium nitrate can be crystallized from a mixture of the solutions of sodium nitrate and barium sulfide; the latter can be made from the most common barium mineral (barite, barium sulfate, $BaSO_4$) by heating it with charcoal.[256]

Mohr was to become a vey distinguished scientist. A year before publishing his short paper on barium nitrate, he had published the first explicit statement of the principle of the conservation of energy. In later years, he would become the founder of volumetric analysis. In his introductory remarks, Mohr seems to be excusing his paying attention to a subject 'probably a matter for 'technical chemistry' by pointing out that the chemical was useful to chemists. Is this an early example of scholarly chemists distancing themselves from (and even looking askance at) the practical applications of their science? [257]

Once an economical way of preparing barium nitrate had been developed, there would have been little scope for chemical manufacturers to reduce its price other than by increasing the scale of production. This would not have been attractive because there would have been little scope for increasing the size of the market. None the less, there was a modest decrease in price, in line with the general trend for real prices of commodities to fall.

Barium nitrate and strontium nitrate are examples of formerly rare and costly materials becoming available in larger quantities and at lower prices specifically to meet a demand for them in pyrotechny. This was possible because the relevant minerals, though uncommon, occurred in readily-accessible deposits and the chemical processes involved in converting them to the nitrates were not particularly difficult. The carbonate minerals (witherite, strontianite) had simply to be dissolved in nitric acid; the sulfate minerals (barite, celestine) had first to be heated with charcoal or coke to make the sulfides, which were then processed as outlined by Mohr. The crude nitrates obtained in this way were not suitable for firework-making without careful purification. Even small amounts of calcium, strontium or sodium in barium nitrate would make the flame yellow, not green; strontium nitrate normally presented itself as the hydrated salt, which had to be dehydrated before it was fit for use. Unless carefully freed from calcium nitrate impurity, strontium nitrate would be even more

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[255] Karl Friedrich Mohr, "Leichteste Darstellung des salpetersauren Baryts " *Annalen der Pharmacie* XXV (1838), pp. 290-292.

[256] Webster, *A manual of chemistry, on the basis of Professor Brande's: containing the principal facts of the science, arranged in the order in which they are discussed and illustrated in the lectures at Harvard University, N.E; the United States Military Acadamy, West Point; Brown Univerity, Amherst, and several other colleges in the United States. Compiled from the works of the most distinguished chemists,* p. 307. Thomson, *A System of Chemistry of Inorganic Bodies*, 1, p. 422.

[257] Charles Frederick Hoffmann, "Sketch of Friedrich Mohr," *Popular Science Monthly* 17 (1880), pp. 402-404.

hygroscopic and would be useless. Munier wrote of his difficulties in this regard; Chertier gave a procedure for purifying strontium nitrate, which must have added considerably to its effective cost. If pure materials were available, they were much more expensive. For example, as late as 1854 the catalogue price of 'common' strontium nitrate from a London supplier of laboratory equipment was 1s per pound; the same supplier offered 'pure' strontium nitrate at 4d per ounce – over 5 times the price.[258]

Later in the century, when increased competition led chemical manufacturers to take more notice of their customers' needs, firework-makers were able to purchase materials that had been specially prepared to their requirements, and needed no further treatment. This must have resulted in a substantial reduction in the real costs. The reduction in the catalogue price is thus only one component in the reduction of the real cost of these materials that resulted from their change from laboratory supplies to industrial commodities.

8.2. Potassium Chlorate and Potassium Perchlorate

The modest declines in the prices of barium nitrate and strontium nitrate after 1840 contrast with the trend for the price of potassium chlorate. This chemical was still very expensive in 1840 and, although its price continued to fall over the next 30 years, it remained the most expensive of the three new chemicals. There were two reasons for this. One is that the manufacture of potassium chlorate was inherently expensive and inefficient. It is not appropriate here to review its production in full detail, but by way of an example Figure 8.3 shows a schematic representation of apparatus used in France for the industrial preparation of potassium chlorate in 1824. At that time, potassium chlorate was in demand, albeit on a rather small scale, as an ingredient of percussion powders and percussion caps for firearms, and as a component of the very popular and widely-used 'oxygenated tinder-box' – an early chemical fire-making device invented in 1805 by Frenchman Jean-Louis Chancel. (1779-1837).[259]

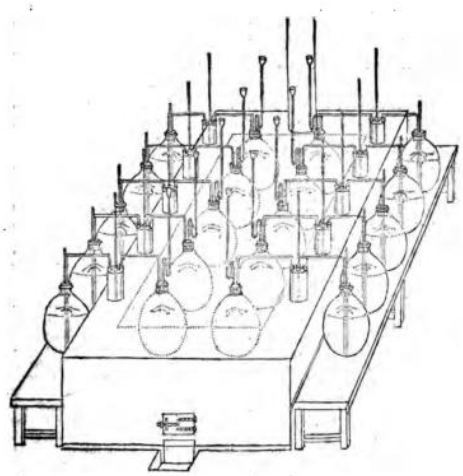

Figure 8.3. Industrial production of potassium chlorate in 1824[260]

The equipment shown in Figure 8.3 was used to carry out the same process that Berthollet used in 1786 in his original preparation of potassium chlorate. It was a batch process, requiring constant supervision and intervention by an operator. The glass vessels could be no larger than a person could

[258] "Descriptive and General Catalogue of Philosophical Apparatus and Chemical Preparations, Manufactured and Sold by Bland & Long, Opticians, Philosophical, Photographical, & Chemical Instrument Makers and Operative Chemists, 153, Fleet Street, London.," (London: Bland & Long, 1854), p. 57.

[259] For Chancel's device, see J. Nicklès, "Sur l'histoire de l'industrie des allumettes chimiques," *Le Moniteur Scientifique* 8 (1866), pp. 67-73, pp. 68-69.

[260] Anonymous, "To Prepare Chlorate of Potash," *The Chemist*, no. 20 (1824), pp. 306-307, p. 305.

handle, and the scale of production would necessarily have been small. None the less, it was sufficient to make potassium chlorate a practical, if rather costly, ingredient in coloured fires. As noted above, it was available in 1817 from a London dealer in laboratory supplies at 4 shillings per ounce. [261]

From the early 1830s potassium chlorate was in great demand for the manufacture of matches and it also had applications in the printing of textiles and in medicine. The chemical remained costly predominantly because of the complexity and inefficiency of the processes used to make it. The manufacture of potassium chlorate required the use of chlorine gas, at a time when the production of chlorine was inherently costly. Reduction in the price of potassium chlorate was achieved by increasing the scale of production and modifying the processes to improve efficiency. This combination of more efficient production and high demand resulted in high, but rapidly falling, real prices between 1840 and 1880. The possibility of less costly production of potassium chlorate began with the invention of an electrolytic process in France in 1886, but efficient, economical electrolytic manufacture of potassium chlorate awaited further developments in the 1890s and beyond.[262]

As explained in Chapter 5, potassium perchlorate was shown to be a potentially useful pyrotechnic ingredient as early as 1850, but it had the great disadvantage that it was manufactured from costly potassium chlorate. This made the price of potassium perchlorate so high that it precluded commercial use of the chemical in firework-making. In 1849 potassium perchlorate was being sold in London at 64s per pound; this corresponds to 12.8 day's wages for a skilled craftsman – clearly an exorbitant price for practical application in fireworks. For comparison, the price of potassium chlorate in that year is estimated by interpolation of the data used in Figure 8.1 to have been about 3.6 days' wages per pound, which would make potassium perchlorate about 3.5 times as costly as potassium chlorate. [263]

Potassium perchlorate is not listed in any of the 19th century tables of prices for firework ingredients found during this project. German pyrotechnist Karl Gellingsham wrote in a book published as late as 1913 that the price of potassium perchlorate was twice as high as that of potassium chlorate. Potassium perchlorate did not become available at prices conducive for its use in fireworks until well after the introduction of electrolytic processes for its manufacture. This development seems to have been the consequence of an alert entrepreneur seeing an opportunity where others might have seen only a problem. In 1890 Swedish industrialist Oskar Fredrik Carlson (1844-1916), founder of a factory (Stockholms Superfosfat Fabriks Aktiebolag) for the manufacture of phosphate fertilizers, applied for a patent for the electrolytic production of sodium chlorate from common salt. Sodium

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[261] Ibid.. For the cost in 1817, see Accum, "A Descriptive Catalogue of the Apparatus and Instruments employed in Experimental and Operative Chemistry, in Analytical Mineralogy and in the Pursuits of the Recent Discoveries of Voltaic Electricity", pp. 52-54.

[262]For methods of preparing potassium chlorate in the 19th century, see F. Crace-Calvert, "On the preparation of certain Chlorates, particularly of Chlorate of Potash," *The Quarterly Journal of the Chemical Society of London* 3 (1851), pp. 106-111 and Henry Watts, *A Dictionary of Chemistry and the Allied Branches of Other Sciences*, vol. 1 (New York: D. Van Nostrand, 1872), pp. 887-888. For the electrolytic methods, see S.P.S., "Manufacture of Chlorates by Electrolysis," *Journal of the Franklin Institute* 129, no. 3 (1890), p. 256; Henry Gall and Amaury de Villardey de Montlaur. Manufacture of Chlorates of the Alkaline Metals and Metals of the Alkaline Earths. United States Patent 492,003, filed July 21 1892, and issued February 21, 1893; William T. Gibbs and Stanislaus P. Franchot. Process of Obtaining Chlorates of the Alkalies or of the Alkaline Earth Metals by Electrolysis. United States Patent 493,023, filed August 29 1892, and issued March 7, 1893; Henry Blumenberg Jr. Electrolysis. United States Patent 519,400, filed May 6 1893, and issued May 8, 1904; William T. Gibbs. Art of Obtaining Chlorates by Electrolysis. United States Patent 665,426, filed September 9 1895, and issued January 8, 1901; Electrolytic Apparatus. United States Patent 655,427, filed September 9 1895, and issued January 8, 1901. The prior art in the Gall and de Montlaur patent gives the date of the original French application as September 23, 1886.

[263] Damberger, "On the Preparation of Perchlorate of Potassa", pp. 251-253.

chlorate was used for making potassium chlorate, an essential ingredient in the manufacture of matches – a well-established Swedish industry. During early trials of the process Carlson observed the formation of sodium perchlorate as well as the intended sodium chlorate. Despite this being undesirable from the point of view of producing chlorates, Carlson modified the process to optimize the production of perchlorate, set up a pilot plant in 1892 and built a commercial plant in 1893. By 1904 it was routinely producing sodium perchlorate. This was converted into either ammonium perchlorate or potassium perchlorate, which Carlson intended to use as ingredients for explosives. Sodium perchlorate, being deliquescent, was unsuitable for this purpose. Carlson was granted a patent in 1897 for a new class of explosives that consisted of 40%-98% ammonium perchlorate, the remainder being an inflammable substance such as petroleum tar, naphthalene, powdered wood, powdered carbon, sugar or Vaseline. Ammonium perchlorate produces only gaseous products and thus provides a more powerful explosion than potassium perchlorate, but it has the disadvantage of generating hydrogen chloride, a toxic, irritating and corrosive gas. Later, other inventors (including Carlson's son Oscar Birger Carlson (1873-1928)) were awarded patents for various explosives that contained potassium perchlorate. The subsequent applications of potassium perchlorate in fireworks are discussed in Chapter 5.[264]

8.3. Magnesium

Following the developments outlined in Chapter 5, the price of magnesium fell from over 600 dollars per pound in 1860 to around 40 dollars per pound in 1867. From 1888 much less expensive magnesium (ca. 5 dollars per pound) began to appear on the market from the new electrochemical plant in Germany. It was not possible to find price data for magnesium over the whole 19th century; Figure 8.4 shows the price per pound in US dollars, unadjusted for inflation. The price scale is logarithmic – necessary because of the huge range of prices. The scale was chosen to be consistent with Figure 8.6, which shows the price of aluminium over the same period.

[264]Joseph C. Schumacher, "History of Establishing a Source of Potassium and Ammonium Perchlorates for Use in Solid Rocket Propellants," Paper 99-2926, *35th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit* (Los Angeles, California American Institute of Aeronautics and Astronautics, 1999), pp. 1-9; "Carlson. 1. Oskar Fredrik C.," in *Nordisk familjebok, vol. 35 supplement*, (1923), pp. 27-29. Oscar Fredrik Carlson. Improvements in Explosives. Great Britain Patent 10362 of 1897 filed 26 April 1897 and issued 3 July 1897. For early explosives containing potassium perchlorate, see Joseph Sayers, Walter Atkinson Wilson, and James Thorburn. Explosive. United States of America Patent 995,187, filed November 15 1910 and issued June 13 1911; Oscar Birger Carlson. Method of Producing Explosives Containing Common Resin. United States of America Patent 1,038,847, filed February 12 1910 and issued September 17 1912; Method of Producing Explosives Containing Nitro Derivatives of Common Resin. United States of America Patent 1,043,042, filed February 12 1910 and issued October 29 1912.

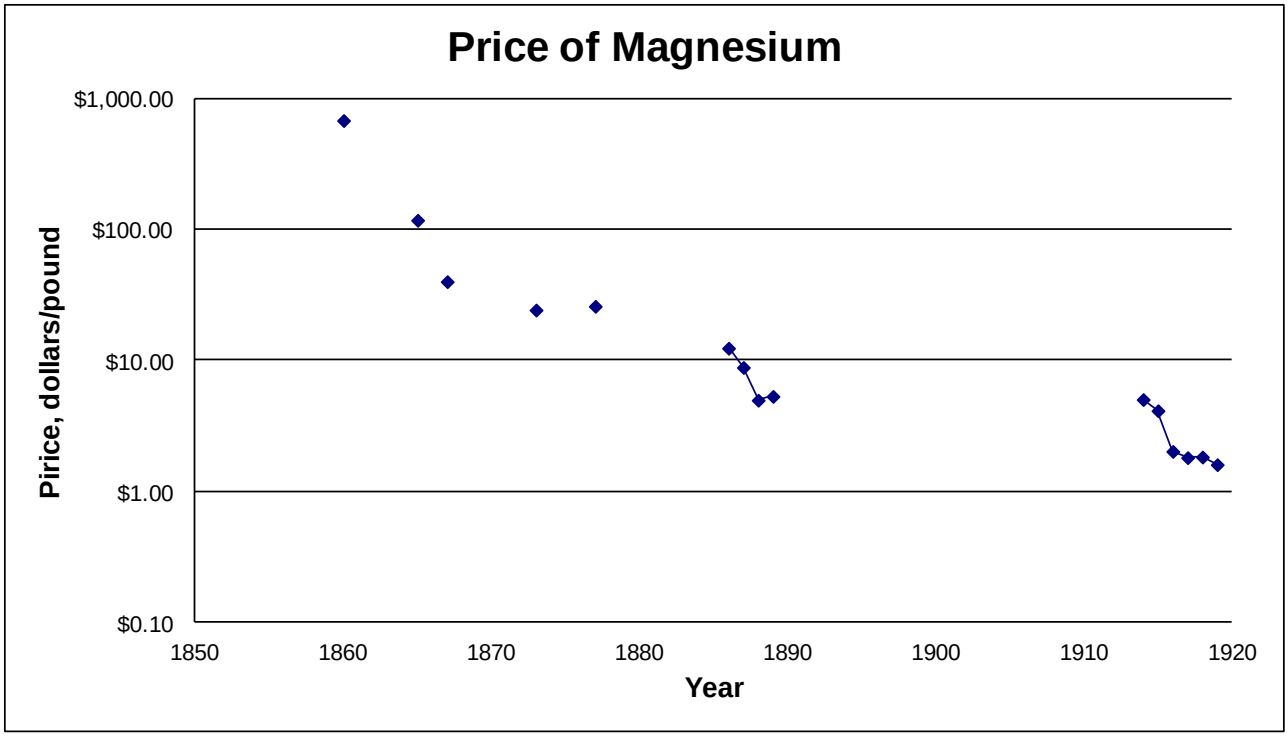

Figure 8.4. Price of magnesium in unadjusted US dollars per pound, 1850-1920.

Figure 8.5 shows the price of magnesium expressed as the number of days that a skilled London building craftsman would have had to work during that year to purchase a pound of the metal. Even after the fall in prices from 1888, magnesium was still much more expensive than other pyrotechnic chemicals, as can be seen by comparison to Figure 8.1, which has the same vertical scale

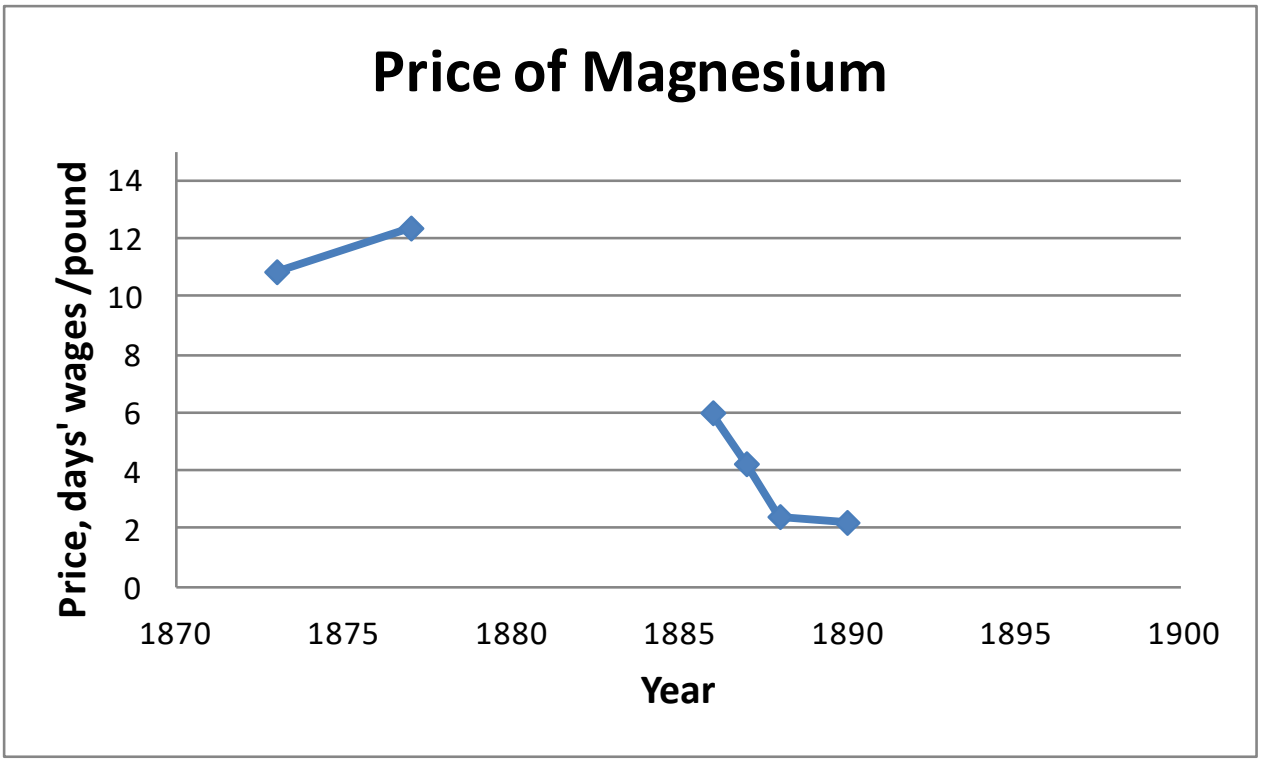

Figure 8.5. Price of magnesium in days of a London craftsman's wages per pound, 1870-1900.

The price of magnesium was greater than those of other pyrotechnic chemicals throughout the 19th century. As soon as it ceased to be prohibitively expensive, its use in fireworks was explored in detail and a range of new compositions and effects were discovered and introduced, as outlined in Chapter 5. Its effectiveness was such that despite its high cost, it became a standard component of European fireworks by the end of the 19th century.

8.4. Aluminium

Figure 8.6 summizes the evolution of the price of aluminium from 1850 to 1920. Like Figure 8.4, Figure 8.6 shows the price per pound in US dollars, unadjusted for inflation, and again the price scale is logarithmic. Originally aluminium was about the same price as gold, which cost $301.44/lb throughout this period. The price of aluminium fell tremendously between 1854 and 1856 with the introduction of Sainte-Claire Deville's process, as noted in Chapter 5. Aluminium then remained a semi-precious metal, costing about $10/lb and used mainly for luxury goods, until about 1887. With the introduction of the Hall-Héroult electrolytic process, the price fell rapidly and by the end of the century had stabilized at around 30 cents per pound.

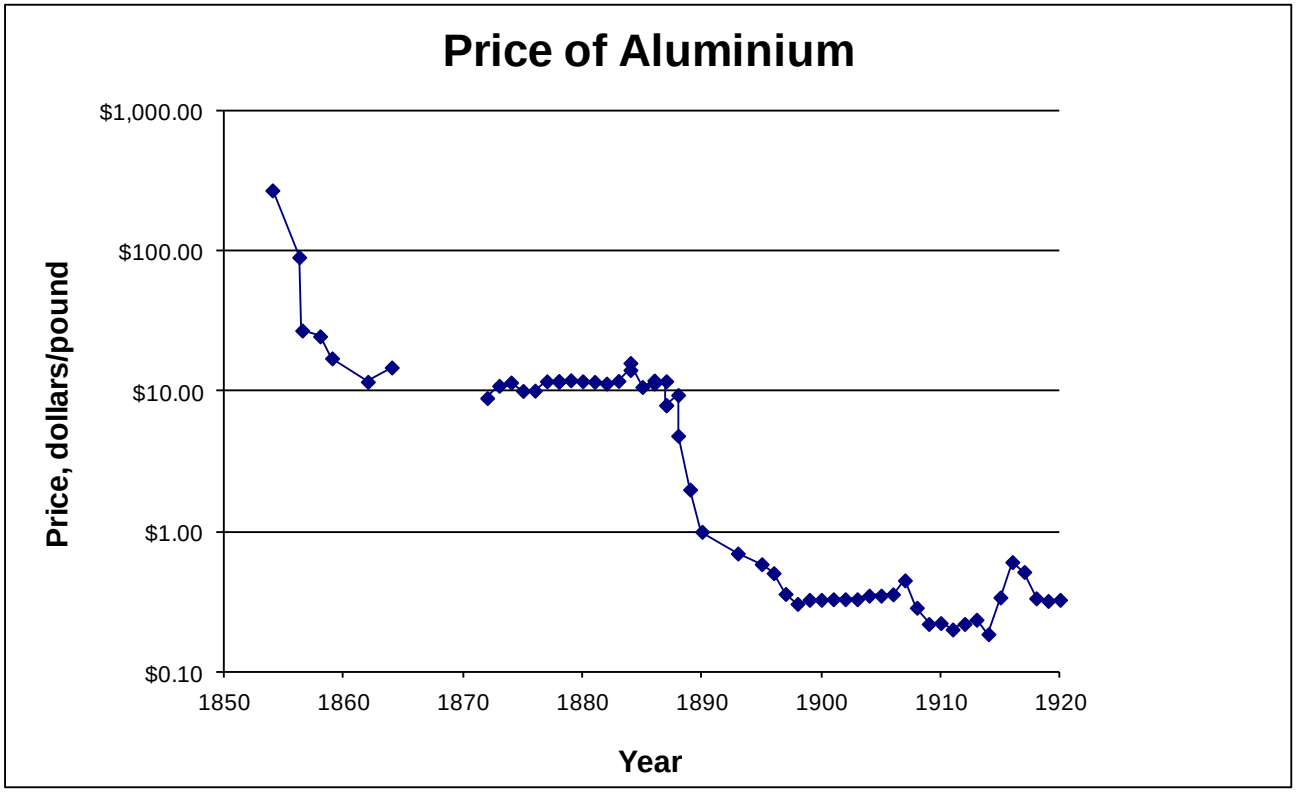

Figure 8.6. Price of aluminium in unadjusted US dollars per pound, 1850-1920.

Figure 8.7 shows the price of aluminium, expressed as the number of days that a skilled London building craftsman would have to work to purchase a pound of the metal. This graph is directly comparable to Figure 8.4. After 1890 the bulk price of aluminium was similar to the price for pyrotechnic chemicals. The price of aluminium powder would have been much higher than that of the bulk metal, but it was still sufficiently affordable for aluminium to assume an important place in the pyrotechnists' stock of ingredients, as outlined in Chapter 5.

Comparison of Figures 8.5 and 8.7 reveals that the price of magnesium remained much higher than that of aluminium after the late 1880s, even though by that time efficient electrolytic processes had been developed for the production of both metals. Aluminium, a strong, light, corrosion-resistant

metal, was in great demand for applications ranging from building material to silver pigment. Magnesium, in contrast, was limited in its usefulness by its great susceptibility to corrosion. Demand for magnesium was essentially restricted to photographic illumination, pyrotechnics and laboratory demonstrations. Magnesium was consequently produced on a far smaller scale than was aluminium, and its price remained relatively high.

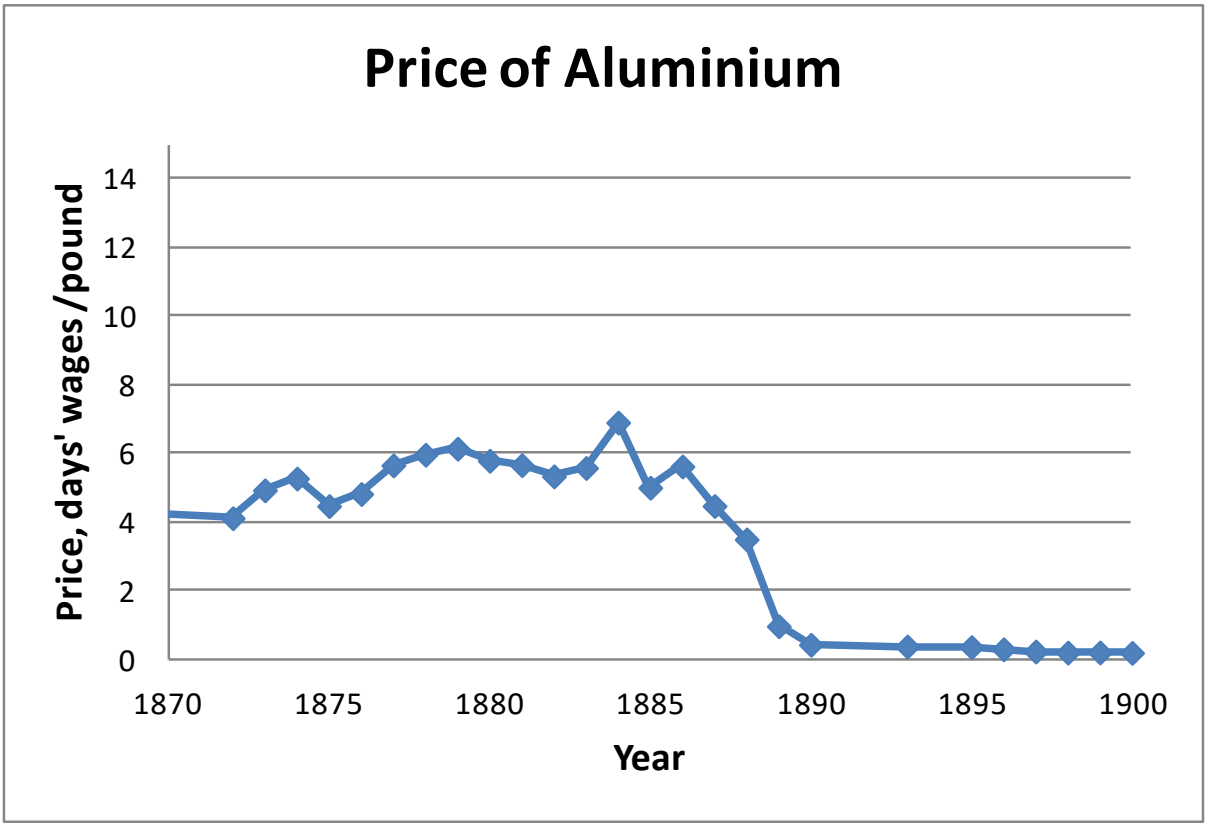

Figure 8.7. Price of aluminium in days of a London craftsman's wages per pound, 1872-1900.

8.5. Concluding Remarks

The real prices of the chemicals shown in Figures 8.2, 8.5 and 8.7 can be correlated with developments in pyrotechny. Figure 8.2 shows that from about 1840 the prices of the three new chemicals used in red and green fires were considerably lower than they had been some 20 years earlier. In the case of potassium chlorate, this was largely because of a demand for it in the manufacture of matches; with barium nitrate and strontium nitrate, it was the result of their application in coloured fires. The use of these coloured fires in the theatre and in fireworks, despite the high cost of the essential ingredients, seems to have inspired several investigators to look for new colours and for better ingredients; indeed, from 1831 to 1859 we see the pioneering publications of Websky, Meyer, Chertier and Tessier on coloured fireworks. These publications were all written for amateur firework-makers, indicating that there were enough amateur pyrotechnists to justify the publication of books for their benefit. This could not have happened unless the essential materials for firework-making were affordable. It is evident that the writers were well aware that costs of materials were important to their readers. Chertier commented on the costliness of several new ingredients, such as barium chlorate, sodium chlorate and 'chlorate de cuivre et d'ammoniaque'. Tessier went further; he included the cost of each ingredient in all his tables of compositions and calculated the cost per kilo of each composition. These pyrotechnists were well aware that there sometimes had to be a compromise between technical excellence and cost, but none the less they presented some quite

expensive compositions, perhaps in anticipation that future developments might make them affordable.[265]

Potassium perchlorate provides a regrettable example of the high cost of a chemical inhibiting its use in fireworks. Despite Websky's demonstration in 1850 of the value of this chemical in removing the problem of spontaneous combustion, its high price precluded its wide application in fireworks until after the First World War.

As shown in Chapter 5 the striking new effects produced by magnesium led to its introduction into lavish public firework displays at a time when it was much more expensive than other pyrotechnic ingredients, but its more general use in commercial fireworks was inhibited by its high price. Its main pyrotechnic applications, as explained in Chapter 7, were in military signal lights and illuminating flares, where its performance compensated for its high price. The application of aluminium in fireworks, discussed in Chapter 5, was first recorded within a short time of the metal becoming commercially available as a powder, manufactured as a silver pigment. This happened soon after the price of the metal fell with the introduction of the new electrolytic smelting process. Aluminium thus provides another example of the importance of the cost of a material to its application in fireworks.

The availability of chemicals at an affordable price was central to the transformation of fireworks during the 19th century. In the second and third decades of the century, the new chemicals used in coloured fires were still very costly and the extent to which they could be used in pyrotechnic stage effects or in fireworks was limited by their cost. By the end of the century they had become so cheap that cost was no longer an issue. It might even be argued that the chemicals were so inexpensive that the new colours were over-used, and consequently lost some of their artistic and aesthetic appeal. From the mid 1860s the introduction of magnesium, and later of aluminium, supplemented the now-familiar colours with novel effects that helped to maintain enthusiasm for fireworks into the new century. The pyrotechnic potential of these two metals, obvious from the early 1830s, lay unexplored until developments in chemical metallurgy transformed the metals from expensive curiosities to affordable commodities.

[265] Websky, *Grundlich und fasstliche Anweisung zur Verfertigung kleiner Lustfeuerwerke*; *Praktisches Handbuch der Lustfeuerwerkkunst*; *Lustfeuerwerkerei für Dilettanten*; *Lustfeurwerkkunst; oder, Leicht fassliche und bewahrte Anweisung zur Verfertigung von Lustfeuerwerken*; *Martin Websky's Lustfeuerwerkerei insbesondere Dilettanten und Freunde dieser Kunst. Nebst einem Doppel-Anhang: (I) Die Stoffe und Substanzen der Lustfeuerwerkerei in ihrem chemischen und physikalischen Verhalten theoretisch betrachtet von Ernst Schnell; (II) Auszug des Neuen und Beachtenswerthen aus F. M. Chertier's Lustfeuerwerkerei nach dem Französischen mit Anmerkungen von Martin Websky*; *Martin Websky's Schule der Lustfeuerwerkerei. Ein Vermachtniss an die Freunde und Dilettanten dieser Kunst*. Franz Eduard Moritz Meyer, "Uber Schiesspulver und schiesspulverartige Mischungen zu bunten Flammen,"; *Die Feurewerkerei in ihrer Anwendung auf Kunst, Wißenschaft und Gewerbe*; "Ueber einige Verbesserungen in der Lustfeuerwerkerei."; "Bunten Flammen zur Theaterbeleuchtung"; "Feuerwerkerei," in *Technologische Encyklopadie, oder alphabetisches Handbuch der Technologie, der technischen Chemie und des Maschinenwesens*, ed. Johann Joseph Prechtl (Stuttgart: J. G. Cotta'schen Buchhandlung, 1835), vol. 6, pp. 41-70; Chertier, *Essai sur les compositions qui donnent les plus belles couleurs dans les feux d'artifice*; *Nouvelles recherches sur les feux d'artifice* (1843,1850); Tessier, *Chimie pyrotechnique* (1859).

Chapter 9: The Role of Chemists in the Chemical Transformation of Fireworks in the 19th Century

Previous chapters have shown that the transformation of fireworks from the late 18th century to the close of the 19th century was, in the final analysis, the result of the introduction of new materials. Given that chemistry is the science of materials and the changes that they undergo, it is easy to assume that chemists would have played a central part in this transformation of fireworks. Such an assumption was made by some 19th century pyrotechnists. In 1845, for example, the Italian pyrotechnist Vincenzo Pacini (n.d.) wrote: 'coloured fires are a beautiful discovery of the chemical art....' Some 43 years earlier, and 18 years before the disclosure of the first of the chlorate-based colours that that inspired Pacini's comment, Claude-Fortuné Ruggieri (1777 – 1841) had written of pyrotechny: 'A knowledge of chemistry is … an absolute necessity...' This claim, the possible motivations for which have been discussed by Simon Werrett, is easily refuted by noticing that whenever Ruggieri discussed anything related to chemistry he was either in a muddle or downright wrong by the standards of his day. Ruggieri's knowledge of chemistry was vague and out-of-date. Yet, he was one of the greatest pyrotechnists of his day. [266]

Earlier still, the young Lavoisier had written:

'There are few arts whose existence depends so essentially on chemistry as that of fireworks. It owes its origin uniquely to chemistry; it is on chemistry only that it must rely for its progress and its perfection.' [267]

At the time, Lavoisier had yet to make his own transformational contributions to chemical science, so the 'chemistry' that he had in mind was very different to that to which Ruggieri referred at the beginning of the 19th century. The present chapter argues that the contribution of chemists to the transformation of fireworks in the 19th century was in fact very much less than might have been expected, both from 'common sense' and from the remarks of Lavoisier and Ruggieri. The explanation for this begins by noting that the science of chemistry has three aspects: 'descriptive' chemistry, which documents materials, their properties, and their interactions, 'theoretical' chemistry, which attempts to explain the accumulated knowledge of descriptive chemistry with reference to a unifying theory, and 'applied' chemistry, which puts knowledge of materials to practical use. In the nineteenth century theoretical chemistry was not sufficiently advanced to be helpful in explaining the phenomena seen in fireworks. Descriptive chemistry and applied chemistry, in contrast, were advancing tremendously, and they led to the discovery of new materials, of new applications for them, and of means of providing them at prices that made them affordable [268]

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[266] Ruggieri, *Elémens de pyrotechnie, divisés en cinq parties; avec un vocabulaire des termes compris dans cet ouvrage*. p. xiii. For Werrett on Ruggieri, see Werrett, *Fireworks*. pp. 226-229.

[267] Lavoisier, "No. 67: Remarques sur la Composition de quelques feux d'artifice Colorés en bleu et en jaune, dont je remets cacheteé entre les mains de l'Académie. Archives de l'Acadédmie des Sciences, 333 A."

[268] For 'applied' and 'pure' chemistry, see for example Ursula Klein, "Not a Pure Science: Chemistry in the 18th and 19th Centuries," *Science* 306, no. 5698 (2004), p. 981-982; "Technoscience *avant la lettre*," *Perspectives on Science* 13, no. 2 (2005), pp. 226-266. 'Applied Chemistry' was called 'technical and economic chemistry' and then 'practical chemistry' by Otto Linné Erdmann (1804–1869), who founded the *Journal für technische und ökonomische Chemie* in 1828 and in 1834 changed its name to *Journal für prakitsche Chemie*. 'Applied chemistry' was used in William Francis and Henry Croft, *The Chemical Gazette or Journal of Practical Chemistry in all its applications to Pharmacy, Arts and Manufactures*, vol. 1 (London: Richard and John E. Taylor, 1843). p. iii. The term 'pure chemistry' was in use by 1851, for example, in C. G. Lehmann, *Physiological Chemistry*, vol. 1 (London: The Cavendish Society, 1851), pp. 10, 25, 26, 28, 29, 52, 72, 74, 183, 361. The division of 'pure' chemistry into 'theoretical' and 'descriptive' chemistry had been made by 1876. The

Thus, as noted by Brock, the main role of chemists in the transformation of fireworks was in making new materials and documenting their properties, – in other words, the chemists' contributions came from the field of descriptive chemistry. The production of materials at affordable prices, discussed in Chapter 8, came about through the efforts of applied chemists who nearly always had other than pyrotechnic applications of the materials in mind. There are a couple of instances where we know that a chemist worked on improving manufacturing processes for a material specifically to make it more readily available for use in fireworks. Mohr did this for barium nitrate, and Hutstein for potassium perchlorate, as discussed in Chapter 5. [269]

The actual introduction of new materials into fireworks was only rarely done by a person who defined himself as a chemist – Lavoisier, who introduced sodium nitrate and zinc is one example, as discussed in Chapter 3, Tessier, discussed in Chapter 6, is another. There were also instances of chemists suggesting that new materials might be useful in fireworks. Sometimes these suggestions were explicit, as with Lavoisier suggesting the use of potassium chlorate, Fourcroy suggesting that strontium nitrate 'mixed with gunpowder' could produce red flames, and Proust's independent discovery of the value of sodium nitrate in yellow fires. An indirect suggestion is found in Damberger's comments on potassium perchlorate, quoted in Chapter 5.

Once Lavoisier had established the nature of combustion in 1783, chemical theory had little to contribute to pyrotechny. In 1833 Meyer made much of the application of the new theory of stoichiometry in optimizing fuel-to-oxidant ratios in firework compositions, but in practice the stoichiometric approach was useful only for two-component mixtures and only then if the chemistry of the combustion process were known. Even then its benefits are questionable: a binary mixture is easily optimized by trial and error. When more than two components were involved, the problem was beyond the capability of 19th century chemistry. The attempts of several 19th century scientists to understand and optimize gunpowder did little more than confirm the validity of the traditional composition.

For other phenomena, such as the production of colours, chemical theory was next to useless. Meyer understood that the production of colour was somehow related to the vaporization of certain chemicals into the flame, but details of the processes involved in the emission of coloured light were simply beyond the reach of the science of the day. Even such ancient phenomena as the colour of incandescent sparks turned out to be explicable only with the invention, at the very end of the 19th century, of quantum theory. The theoretical understanding of coloured flames had to await the application of quantum theory to molecular spectroscopy, and the application of chemical thermodynamics to high-temperature gas-phase chemical reactions, in the 20th century. Also in the 20th century, science was applied to the understanding of a superficially simple pyrotechnic device (the rocket) with the intention of optimizing its performance for military and space-flight purposes. The resulting analysis turned out to be so complicated that 'rocket science' entered the vernacular to indicate a particularly difficult and challenging field of study.

Nineteenth 19th century science was of little value in establishing a theoretical foundation for pyrotechny. Despite this, 19th century books on pyrotechny sometimes give the impression that the writers thought that chemists understood how pyrotechnic mixtures functioned, even though they themselves did not. The English pyrotechnist and entrepreneur Charles Thomas Brock (1843-1881) even claimed, reflecting on his experiences in the mid 1860s, to have succeeded 'in placing the matter of the combinations of pyrotechnic chemicals on a scientific basis', but there is no evidence to support this claim. Books on chemistry mentioned fireworks only in passing, if at all. They sometimes stated that certain materials were used in pyrotechny, and sometimes mentioned for what purposes they were

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terms were used, for example, by M. M. Pattison Muir, "Our Book Shelf. A Class-book of Chemistry. By Edward L. Youmans, M.D. (London : Henry S. King and Co., 1876)" *Nature* 13 (1876), p. 424.

[269] Brock, *Pyrotechnics: The History and Art of Firework Making*, p. 137.

used, but they did not discuss how the materials performed their particular function (such as producing red light, for example) for the very good reason that nobody knew. [270]

Towards the end of the 19th century there is evidence that some of Brock's commercial competitors had retreated to the old artisanal traditions of the craft, and made no pretences of any application of chemistry in their work. In 1882 the English pyrotechnist William Wilder (1852-1904), testified at an inquest into a fatal firework accident:

> "I have no chemical knowledge whatever, I make compositions simply by receipts and do not know anything about the results of putting chemical substances together. We have no one on the establishment with chemical knowledge." [271]

Wilder also remarked that he did not think that one firework maker in ten had any more chemical knowledge than he had. Wilder made these comments in response to a question by Captain John Ponsonby Cundill, R.A. (1843-1894), Her Majesty's Inspector of Explosives. Cundill was taken aback to learn that Wilder's firework 'stars' contained potassium chlorate and sulfur, a combination that the chemist and explosives expert Frederick Augustus Abel (1827-1902) had told Cundhill was 'always liable to explode when subjected to friction developed by a blow or concussion' After hearing Wilder's evidence, Cundill wrote 'It is much to be feared that some pyrotechnists at least are remarkably ignorant of the chemical properties of the mixtures made by them.' [272]

A rare example of experienced amateur pyrotechnists explicitly recording that they did not understand the chemistry that explained how a particular composition functioned occurred in 1882, when Amédée Denisse published an account of a tiny firework, introduced from Japan and paradoxically known as 'Mèche Italienne'. This firework consisted of a thin piece of twisted paper, containing at one end a small quantity of a secret black powder. In use, the end opposite the powder was held between the fingers, so that the device hung vertically. The free end was then ignited, whereupon after an 'insignificant deflagration' a red-hot ball of molten dross developed, slowly consuming its paper support as it ascended. After a while the molten ball appeared to be boiling, and then it began to discharge large sparks, reminiscent of those displayed by firework fountains, before gradually subsiding.[273]

This firework had been known in Europe for some time before Denisse described it, but was somewhat of a novelty in 1864 when the renowned German chemist August Wilhlem von Hofmann (1818-1892) demonstrated some specimens to the Chemical Society in London. Hofmann had been given some of these tiny fireworks, or 'matches' as he called them, that had supposedly been brought back from Japan. He analysed them, and successfully reproduced them. After the demonstration Hofmann distributed some of the 'matches' to the audience. Not one of those learned chemists appears to have been able to work out a chemical explanation for the performance of the firework – a subject that Hofmann tactfully avoided in his talk. Shortly afterwards a letter was published from R. Trevor Clarke describing a

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[270] C. T. Brock's claim is quoted by Brock, *A History of Fireworks*, p.160.

[271] Captain J. P. Cundill, "The Circumstances attending an Explosion which occurred at the Hull Botanic Gardens, on the 25th September 1882," ed. The Right Hon. the Secretary of State for the Home Department (London: Home Office, 1882), p. 7. Wilder was, with his brother, a proprietor of a family-owned firework manufacturing business in Birmingham, England that had been founded in 1834. At the time Wilder testified to the lack of chemical knowledge in the firework business, the industry had been transformed by the requirements of the Explosives Act of 1875.

[272] Ibid.

[273] Denisse, *Traité pratique complet des feux d'artifice,* pp 383-389.

variation of the 'curious little Japanese firework' that he had known since his boyhood, when he had obtained some from an Italian juggler. They performed in the same way as those demonstrated by Hofmann but were of different construction. A mixture of lampblack, sulfur and gunpowder, ground finely and made into a paste with alcohol, was formed into little (¼ inch) cubes and thoroughly dried. In use, the little cube was held in a cleft in a lavender-stalk or a carpet-broom straw and ignited, whereupon it performed as described above for the twisted-paper version. Clarke perceptively wrote: 'it is a form of the beautiful and very curious spur fire of the Chinese, - so curious as to be worth scientific investigation.' Clarke enclosed some specimens that he had made; according to the editor, they gave 'coruscations of extraordinary beauty.' [274]

Clarke turned out to be Richard Trevor Clarke (1813-1897), a member of the landed gentry. He was a Justice of the Peace, a Deputy Lieutenant of Northamptonshire and a senior officer in the Northamptonshire Militia, but he also engaged in regular correspondence with the naturalist Charles Darwin (1809-1882). Clarke's main contributions were to horticulture and plant breeding, but he was also knowledgeable in pyrotechny. As we shall see, in 1869 he wrote a letter to 'The Times' explaining the dangers of spontaneous combustion of firework compositions that was reprinted in several periodicals. Clarke provides yet another example of the skilled amateur pyrotechnists who flourished in the 19th century, as discussed in Chapter 6.[275]

Denisse did not mention the English work on the Japanese fireworks in his 1882 book. He and Tessier analysed the mysterious black powder, and found that it contained nothing but saltpetre, sulfur and charcoal. Their attempts to duplicate the effect initially proved futile, but they eventually succeeded, after realizing that the choice of paper was important, as was the type of charcoal. They plausibly speculated that the effect must have been discovered accidentally, as a consequence of the Oriental custom of making firework fuses from twisted paper enclosing a trace of a crude gunpowder mixture. The second edition of Tessier's book (published a year after Denisse's) included a chapter on Japanese fireworks. Tessier acknowledged the work of Hofmann and Clarke, which had been reprinted in French in 1865. He spent much time researching the composition, and recorded his unsuccessful efforts to make red-burning versions with lithium nitrate and yellow-burning ones with sodium nitrate. He presented several rather complicated formulae, all based on potassium nitrate, which worked very well, but he did not attempt to provide an explanation of their performance. These little fireworks, much admired in Japan and called there 'senko hanabi' (incense-stick fireworks), attracted the attention of Japanese, and then American, pyrotechnists in the 20th century and some insights were obtained into the way they function. Despite this, the questions posed by Denisse remained unanswered: 'What is going on in that minute sphere?

[274] Anonymous, "Proceedings of the Meeting of the Chemical Society, Thursday 15th December 1864." *The Chemical News and Journal of Physical Science* X (1864), pp. 305-306; R. Trevor Clarke, "Japanese Matches," ibid. XI (1865), p. 24..

[275] Sir Bernard Burke, "Clarke of Welton Place," in *A Genealogical and Heraldic History of the Landed Gentry of Great Britain & Ireland*, ed. Sir Bernard Burke (London: Harrison, 1879), p. 319. See also David Saint, "Our link to Darwin, kings and coronets," *Northampton Chronicle and Echo*, 4 April 2011. http://www.northamptonchron.co.uk/news/opinion/david-saint-our-link-to-darwin-kings-and-coronets-1-2564023 Accessed 23 December 2016.

How can it be that the components of gunpowder, or rather their simple residue, produce such an astonishing effect?' [276]

Very recently, Denisse's questions were answered in full detail in a paper by a team of four authors (three Japanese and one French) published in one of the most prestigious scientific journals. The work involved chemistry, photography, two-wavelength pyrometry, thermal analysis, computational fluid dynamics and statistics. It was clearly beyond the capacity of 19th century science. The impossibility of 19th century chemistry providing a satisfactory explanation of the effects produced by fireworks was a good reason for chemists to avoid the subject, which is exactly what almost all of them did.[277]

Three exceptions, James Cutbush, Moritz Meyer and Paul Tessier, have already been discussed in Chapters 7 and 6 respectively. Only one other example could be found. In 1851 a lengthy paper on coloured fires was published in *Dingler's Polytechnisches Journal* by Professor Karl Georg Winkelblech (1810-1865) of the Higher Technical School at Kassel, in the Electorate of Hesse-Kassel. Six years later, a French translation of the same article was published in Paris.[278]

9.1 A German Professor of Chemistry Writing on Coloured Fires in 1848

This paper is important because, apart from the writings of Meyer and Tessier, it is the only work that has come to light in which a professional chemist commented in detail on the new coloured fires and the only one in which the writer was actually a Professor of Chemistry. The main point that emerges from the paper is that despite its author's status it actually contains very little chemistry. It invites comparison with the writings of Winkelblech's French contemporary Chertier, who, according to several commentators, was conspicuously ignorant of chemistry. Here we have two men, one a highly qualified chemist and the other a retired artillery officer, writing on coloured fires at about the same time. Chertier introduced a range of new materials, many of which remain in use to this day. Winkelbelch did the opposite: he arbitrarily dismissed many of the useful materials that had been introduced by Meyer, Websky and Chertier as useless or even detrimental, apparently for no better reason that he could see no chemical reason for using them. He cited no sources, so we do not know where he obtained his information. His red fire compositions are clearly derived from the original chlorate-based red fire first published in 1820, but the others seem to be his own. The ingredients that he rejected show that he was familiar with recent developments in coloured fires, but he seems to have decided to start anew, guided by his chemical expertise. The resulting compositions are all based on the usual dangerous combination of potassium chlorate and sulfur, and there is nothing in the compositions or in his assessment of them to suggest that he had made any worthwhile contribution to pyrotechny. This could not be attributed to any shortcoming in his chemical knowledge.

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[276] Denisse, *Traité pratique complet des feux d'artifice,* pp. 385-389. Tessier, *Chimie pyrotechnique ou traité pratique des feux colorés* (1889), pp. 438-439. For modern commentary on the effect, see Shimizu, *Fireworks: The Art, Science and Technique,* pp. 68-67, also the entry 'Senko Hanabi' in Kosanke et al., *Encyclopedic Dictionary of Pyrotechnics (and Related Subjects),* pp. 985-987.

[277] Chihiro Inoue et al., "Direct Self-Sustained Fragmentation Cascade of Reactive Droplets," *Physical Review Letters* 118 (2017). pp. 074502-1- 074502-5; "Supplemental Material for "Direct Self-Sustained Fragmentation Cascade of Reactive Droplets." Physical Review Letters 118 (17 February 2017): 074502-1- 02-5.," http://journals.aps.org/prl/abstract/10.1103/PhysRevLett.118.074502#supplemental, Accessed 6 March, 2017.

[278] Winkelblech, "Ueber Farbige Feuer." *Dingler's Polytechnisches Journal* 19, no. 3 (1851): 208-17; ibid., no. 4, pp. 94-302. "Sur les feux d'artifice," *Le Moniteur Scientifique* 1, no. 1 (1857), pp. 161-174. In the original article Winkelblech's affiliation is given as *Aus dessen Programm der höheren Gewerbeschule in Kassel* (p. 208, fn.). In the French version the original German publication is incorrectly given as *Journal für prakt. Chim. 1851* (p. 161, fn.) It was not unusual for articles to be published in more than one journal; I consulted the bound volumes of *Journal für praktische Chimie* in the Hargrave-Andrew Library at Monash University and there is no such article. This is consistent with the record of Winkelblech's papers in *Catalogue of Scientific Papers (1800-1863). Compiled by The Royal Society of London*, 17 vols., vol. 6 (Cambridge: Cambridge University Press, 1872). p. 395.

As one would expect of a Professor of Chemistry, Winkelblech was well-educated in the science. Furthermore, he commenced his doctoral studies under the renowned Professor of Chemistry Justus Freiherr von Liebig (1803-1873), one of the greatest chemists of the nineteenth century. Despite his chemical expertise, Winkelblech became more widely known under the pseudonym Karl Marlo, under which he published works on economic theory and socialism. Writers interested in his social theories have provided quite detailed accounts of his life, revealing his educational background and giving insights into his character. Winkelblech received his early education first at home, then under the tutelage of a Protestant pastor. He was deeply religious throughout his life. At the age of 15 he was apprenticed to an apothecary, in 1829 he attended the university *Alma Mater Philippina* at Marburg (now *Philipps-Universität Marburg*) where he studied in the pharmaceutical and chemical science institute headed by the chemist Ferdinand Wurzer (1765-1844). In 1832 Winkelblech left Marburg for a semester to study chemistry under Liebig at the University of Giessen. He began the research into the cobalt oxides that would later be written up as his doctoral dissertation. In October 1832 he returned to Marburg; he was awarded his doctorate there in 1835. Three years later Winkelblech visited Paris for three months and made many friends amongst Parisian academics. The following year he obtained a professorship at the *Höherer Gewerbeschule*, in Kassel, the capital city of Hesse. In that same year he published a textbook of analytical chemistry. For the remainder of his life he taught chemistry, but devoted his spare time to writing a book expounding his political and social views. [279]

A portrait of Winkelblech in his early 50s is shown in Figure 9.2. He died suddenly on January 10, 1865, at the age of 55, while still working on the book on social issues that had preoccupied him for the previous 20 years. This turned out to be without lasting influence.[280]

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[279] William Harbutt Dawson, *German Socialism and Ferdinand Lasalle: A Biographical History of German Socialistic Movements During This Century*, 2nd ed. (London: Swan Sonnenschein & Co., 1891). pp. 48-52 Edgard Allix, *L'Œuvre Économique de Karl Marlo (Karl-Georg Winkelblech 1810-1865)* (Paris: V. Giard & E. Brière, 1898). Wilhelm Eduard Biermann, *Karl Georg Winkelblech (Karl Marlo) Sein Leben und Sein Werk*, 2 vols., vol. 1 (Leipzig: A. Deichert'sche Verlagsbuchhandlung Nachf (Georg Böhme), 1909). G. D. H. Cole, *Socialist Thought: Marxism and Anarchism 1850-1890*, 7 vols., vol. 2, A History of Socialist Thought (London: Macmillan & Co. Ltd, 1953-1958). pp. 24-31. John Weiss, "Karl Marlo, Guild Socialism, and The Revolutions of 1848," *International Review of Social History* 5, no. 1 (1960). For Liebig's research school at Giessen, see Catherine M. Jackson, "Visible Work: The Role of Students in the Creation of Liebig's Giessen Research School," *Notes and Records of the Royal Society* 62 (2008), pp. 31-49. Winkelblech's work on cobalt oxides is Karl Georg Winkelblech, "De Oxydis Cobalticis " (1835) and C. Winkelblech, "Ueber die Cobaltoxyde," *Annalen der Pharmacie* 13, no. 2 (1835) 148-168, completed in ibid. 3 (1835) 253-283. His textbook is *"Elemente der analytischen Chemie. Von C. Winkelblech, Professor in Marburg. Marburg und Leipzig. Druck und Verlag von Elwert 1838," Archiv der Pharmacie 18 (1839).* For his social theories, see Weiss, "Karl Marlo, Guild Socialism, and The Revolutions of 1848." Karl Marlo, *Untersuchungen über die Organisation der Arbeit; oder, System der Weltökonomie* vol. 1 (Kassel: Wilhelm Appel, 1848).

[280] In 1990 Ruth Levitas, referring to a 19th century work on Utopias by English clergyman Moritz Kaupfmann (1839-1920), mentions that Kaupfmann discussed a ' totally obscure and pseudonymous German cooperative socialist, Karl Marlo..." Ruth Levitas, *The Concept of Utopia* (London: Philip Alan, 1990; repr., Bern: Peter Lang AG, 2010). p. 14.

Figure 9.2. Portrait of Karl Georg Winkelblech, 1862.[281]

Winkelblech's legacy to chemistry is also rather small. His book on analytical chemistry was well-received, but his proposed book on technical chemistry was never completed. He published papers on the oxides of cobalt and of lead, the combustion of metals in sulfur, and coloured fires. According to Biermann, the paper on coloured fires was written in 1847-1848; Winkelblech was at that time involved in the political ferment leading up to the events of 1848. It would be fascinating to know what led him to turn his mind to pyrotechny, especially when his passion for social reform must have been intensified by the possibility of putting some of his ideas into practice, but no evidence as to his motivation could be found. [282]

The paper begins by stating that coloured fires are 'the most difficult part of pyrotechny'. Published recipes are 'abundant', but 'promise...more than they deliver.' Practical firework-makers are 'very secretive', and 'most often know only how to produce white fires and red fires properly.' The

[281] Biermann, *Karl Georg Winkelblech (Karl Marlo) Sein Leben und Sein Werk*, 1. Frontispiece.

[282] *Catalogue of Scientific Papers (1800-1863). Compiled by The Royal Society of London*, 6. p. 395. The papers are: Winkelblech, "Ueber die Cobaltoxyde", "Ueber die Bleioxyde," *Annalen der Pharmacie* 21 (1837), pp. 21-33; "Ueber die Verbrennung einiger Metalles durch Schwefel," *Annalen der Pharmacie* 21 (1837), pp. 34-40. The pamphlets are Karl Winkelblech, "Ueber Liebig's Theorie der Pflanzenernährung und Schlieden's Einwendungen gegen dieselbe," (Kassel: Theodor Fischer, 1842). and "Bemerkungen zu Schleiden's offenem Sendschreiben an Herrn Dr. Justus Liebig," (Braunschweig: Friedrich Vieweg und Sohn, 1842).

implications are that the authors of published recipes were incompetent and the practical firework-makers even more so, justifying Winkelblech's intervention, as a learned chemist, into pyrotechny. The accuracy of his assessment of the state of the art can be judged by noting that he was writing some 16 years after the publication of Websky's work, 14 years after that of Meyer and 11 years after the publication of Chertier's *Essai*. If Winkelblech had researched the literature, as he implies, and as is suggested by the ingredients that he mentions as being used by firework-makers, he would have been aware of these publications; they are certainly not consistent with his comments. His statement that most firework makers only knew how to make white and red properly is very bold, as many of his readers would have seen firework displays and theatrical coloured fires and formed their own opinions. Winkleblech's aim 'was to establish which fires can actually be produced and the mixtures that furnish them best.' He implied that had done extensive research and would restrict himself to 'summarizing, as briefly as possible, the results of this work that will be of interest to practical firework-makers.' Here we have a clear implication that he, the academic chemist, has something to teach the firework-makers. In fact, his work reads more like a chemist's exposition of coloured fires to fellow chemists. A firework-maker, for example, would not need to be told that 'Coloured fires are commonly produced in three forms: *flames, lights* and *stars*.'[283]

Here is Winkelblech's explanation of coloured fires:

> The principle of the production of coloured fires is based on the property of certain substances of burning with a light of a specific colour depending on the temperature and changing with it and even disappearing entirely in certain cases. On introducing such a substance, in the form of an impalpable powder, into a flame, the substance becomes luminous and imparts a specific colour to the flame....All the mixtures for coloured fires are made from a *combustible substance* and an *igniting substance* that decompose themselves, just like gunpowder, with fire and produce a very lively flame. The gaseous products resulting from the decomposition, and which produce the flame, entrain within themselves the molecules of the colouring substance, giving rise to the phenomenon that is seen when these same substances are projected into a hydrogen flame.[284]

This description is no better than that given by Meyer in 1833.[285] And it is nowhere near the standard set by Lavoisier, who wrote as long ago as 1789:

> 'One can also oxidize all combustible bodies by combining them with some nitrate of potash or of soda, or with some oxygenated muriate of potash [i.e. potassium chlorate]. At a certain level of heat, the oxygen leaves the nitrate and the muriate to combine with the combustible body: but these sorts of oxidation must only be done with extreme precautions and on very small quantities. Oxygen enters into the combination of nitrates, and especially of oxygenated muriates, with a quantity of caloric almost equal to that necessary for it to form oxygen gas. That immense quantity of caloric must be suddenly liberated at the moment of its

[283] This three-fold division of coloured fires, with different composition for each type, was adopted by Websky, *Grundlich und fasstliche Anweisung zur Verfertigung kleiner Lustfeuerwerke, zunachst für Dilettanten der Feuerwerkskunst.* but not specifically addressed by Meyer, *Die Feurewerkerei in ihrer Anwendung auf Kunst, Wißenschaft und Gewerbe*.. Chertier (1836) added two more categories" 'little grains' (granules of colour composition added to fountain compositions to enhance the spray of fiery sparks with points of coloured light), and 'little suns' (long thin cases of colour composition added to pinwheels to augment the performance with a circle of coloured light).Chertier, *Essai sur les compositions qui donnent les plus belles couleurs dans les feux d'artifice*.

[284] Winkelblech, "Ueber Farbige Feuer", pp. 209-210.

[285] Meyer, *Die Feurewerkerei in ihrer Anwendung auf Kunst, Wißenschaft und Gewerbe*, p. 26.

> combination with the combustible bodies and produces terrible explosions that nothing can resist.' [286]

Lavoisier was discussing the ways in which substances can be oxidized in the laboratory, but the relevance to pyrotechnic combustion is obvious. Winkelblech referred to the substances that provide oxygen as 'igniting substances', almost as if he wished to avoid mentioning oxygen. He commented:

> If one is fortunate enough to find in a single colouring material the combustible material or that which ignites, that could not be better; but otherwise it is necessary to search for a mixture that gives, as much as possible, a colourless flame and to add the colouring substance to it in fine powder.

Winkelblech then discussed the requirements of mixtures to have a suitable burning time, an appropriate flame temperature, a sufficient flame volume. The residue left after combustion must not disrupt the flame. All of these are excellent points. He explained the usefulness of potassium chlorate:

> On burning with combustible substances, chlorate of potash gives a larger flame, a higher temperature and a more fusible slag than does nitre; mixtures that contain chlorate are more flammable and are consumed more rapidly than those based on nitre.

Sulphur was his preferred combustible; mastic was used only as a binder for stars.

Winkelblech then discussed the individual coloured fires and presented his recommended compositions. He gave several compositions for each colour, but they will not be reproduced here unless there is something particularly noteworthy about them.

9.1.1. Green Fires

Having noted the unsuitability of compounds of boron or of copper for colouring firework flames green, Winklblech wrote: 'Barium is the only body that gives useful green colours in pyrotechny. The oxygenated compounds yield a very distinct greenish blue, and its chlorinated compounds give a very lively yellowish green flame.' The nitrate and chlorate, he correctly stated, are best for green fires as they simultaneously 'serve as igniting bodies and colouring bodies'; he mentioned that the nitrate does not burn with sulfur unless it is mixed with potassium chlorate, a point noted by Meyer in 1833. A mixture of 7 part barium chlorate with 3 parts sulfur burns quickly, with a 'very lively and very beautiful green flame'.[287]

Winkelblech emphasized the difficulty of making green, and correctly indicated the importance of using only pure barium salts. He erroneously wrote that, of all the pyrotechnic fuels 'none but sulfur yields the green colour in all its purity.' The section concludes with the observation that pyrotechnists 'generally use nitrate of baryta to produce all types of green fire...with little success with respect to the coloration.' This he attributed in part to the 'poor distribution of the ingredients', in part to the use of charcoal, organic substances such as stearine, shellac or sugar of milk, or of chloride of mercury, 'all substances that exert a disastrous influence on the purity of colour.' If Winkelblech had

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[286] Antoine - Laurent Lavoisier, *Traité Élémentaire de Chimie, Présenté dans un ordre nouveau et d'après les découvertes modernes*, vol. 1 (Paris: Cuchet, 1789), pp. 206-207.

[287] Meyer, *Die Feurewerkerei in ihrer Anwendung auf Kunst, Wißenschaft und Gewerbe*, p. 54. Chertier, who introduced barium chlorate, gave this mixture with the ratio barium chlorate : sulfur ranging from 4:1 to 3.5:1.. Chertier, *Essai sur les compositions qui donnent les plus belles couleurs dans les feux d'artifice*, p. 33. Winkelblech's recipe gives only 2.333:1. The stoichiometric ratio is 3.35:1, so Chertier preferred somewhat fuel-lean mixtures, Winkelblech a very fuel-rich one. Winkelblech must have arrived at this ratio empirically, as it is nowhere near the ratio that a chemist would calculate.

tried the sulfur-free green compositions presented by Chertier in 1843, he would not have written this. These compositions contain large amounts of 'chloride of mercury', and its influence on the colour is the opposite of 'disastrous'.[288]

9.1.2. Red Fires

This section begins with a statement that red can be produced with compounds of lithium, strontium and calcium. Having commented on the deep red that lithium salts impart to the alcohol flame, Winkelblech wrote 'Lithia being too expensive, we shall not deal with it here, and we shall only say that it gives much less colour than one would suppose, considering its alcohol flame.'[289]

He stated that calcium produces a red flame that tends towards violet, but then gave no further discussion of calcium (which actually produces orange-red). The choice for red fire is between strontium chlorate and strontium nitrate; the former, being deliquescent, must be rejected. Winkelblech's red compositions are shown in Table 9.1. His recipes for lights and for flames are rather direct modifications of the original chlorate-based red fire, first published in 1820.[290]

Application→	Stars	Lights	Flames
Ingredient↓	Parts by weight		
Chlorate of potash	15	10	5
Nitrate of strontia	25	40	40
Sulphur	12	13	13
Charcoal	2	2	2
Sulphide of antimony	2	5	-
Mastic	1	-	-

Table 9.1. Winkelblech's red compositions of 1847-1848.

9.1.3. Yellow Fires

Winkelblech correctly identified sodium as the only known element that produces a distinct yellow colour. The choice is between the chlorate and the nitrate; the chlorate must be rejected because it is deliquescent. Potassium chlorate is not necessary: mixtures of sodium nitrate with sulfur, charcoal and antimony sulfide are perfectly satisfactory; the only shortcoming being a tendency to absorb water on storage. This problem can be avoided by using a composition based on potassium chlorate, with a non-hygroscopic sodium salt: Winkelblech recommended sodium bicarbonate. All this is sound advice, but nothing new.

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[288] *Nouvelles recherches sur les feux d'artifice* (1843), p. 450.

[289] The remark about the colour is very much to the point. See Ernst-Christian Koch and C. Jennings-White, "Is it possible to Obtain a Deep Red Pyrotechnic Flame Based on Lithium? ," in *36th International Pyrotechnics Seminar* (Rotterdam, Netherlands, 2009), pp. 105-109.

[290] The original is:

Strontium nitrate	40
Potassium chlorate	5
Sulfur	13
Antimony sulfide	4

Winkelblech's *flame* recipe substitutes 2 parts of charcoal for the 4 parts of antimony sulfide in the original recipe. His *lights* recipe augments the original recipe by adding 5 parts potassium chlorate, 2 parts charcoal and 1 part antimony sulfide. See "Red fire." For the history of this red fire, see Sturman, "Coloured Fire." and "The Early Use of Potassium Chlorate in Pyrotechny: Part I. John Forster and the First Chlorate-based Colored Fire."

9.1.4. White Fires

According to Winkelblech, antimony and arsenic are the only practical substances for producing white fires. This is not right: as explained by Meyer, a stoichiometric mixture of potassium nitrate and sulfur gives an intense white flame, but is very difficult to ignite. Meyer solved this problem by adding a little gunpowder, and thus produced a brilliant white flame that he deemed superior to that produced with antimony sulfide. It seems that the role of antimony sulfide or arsenic sulfide in white flame compositions is to improve the combustibility. Winkelblech noted that antimony 'imparts a white light with a blue tinge; arsenic produces one that is yellowish'. This is probably due to emission from gaseous monoxides. The source of the white light from burning mixtures of potassium nitrate and sulfur has not yet been identified.[291]

9.1.5. Blue Fires

Winkelblech correctly stated that a useful blue flame can only be produced with copper, which 'colours hydrated flames green, it only colours a flame blue under the influence of a very high temperature; in the contrary case, it produces red. This explains why blue fires are generally bordered with red, and seen from a distance tend to become violet.' Here he is mistaken; we now know that the different colours are produced by different copper-containing gases formed in different chemical environments within the flame. Green is produced by CuOH, blue by CuCl and red by CuO.

Winkelblech wrote that copper sulfate gives the best blue, but must be rejected because it has to be anhydrous, and in this form is hygroscopic. He did not mention that in the process of absorbing water anhydrous copper sulfate becomes very hot, and the resulting hydrated copper sulfate is acidic. Consequently, spontaneous ignition of a mixture containing copper sulfate, potassium chlorate and sulfur is inevitable, sooner or later. The problem of spontaneous combustion will be discussed later in this chapter. Winkelblech recommended copper oxide as the blue colour agent. According to Winkelblech, antimony sulfide and charcoal must never be used in blue fire compositions. Firework-makers, he wrote, rarely make satisfactory blue fires, partly because they do not use the correct proportions of materials, partly because 'instead of pure oxide of copper they use carbonated or hydrogenated compounds [including] crystallized verdigris, ammoniacal sulfate of copper, mountain blue, as well as other copper-containing pigments to be met with in commerce. Sometimes they add zinc, antimony, sal ammoniac and organic materials.'

9.1.6. Other colours

Winkelblech stated that the only satisfactory mixed colour is violet, made by mixing blue and red compositions. He mentioned that although plaster makes 'a very pure pink', and sulfate of potash gives a 'blue violet of great beauty', these ingredients 'can scarcely be used because the flame is small and accompanied by solid residue.'

[291] See Meyer, *Die Feurewerkerei in ihrer Anwendung auf Kunst, Wißenschaft und Gewerbe*. p. 25; Clifford J. Rotz, "Thermochemical Modeling of Classical Arsenic-based White Firework Flames." (paper presented at the 38th International Pyrotechnics Seminar, Denver, Colorado June 10 -15 2012).

9.2. Winkelblech's Choice of Materials

The materials in Winkelblech's recommended compositions are shown in Table 9.2:

Antimony sulfide
Bicarbonate of potash
Bicarbonate of soda
Carbonate of baryta
Charcoal
Chlorate of baryta
Chlorate of potash
Lampblack
Mastic
Meal powder
Nitrate of baryta
Nitrate of potash
Nitrate of soda
Nitrate of strontian
Oxide of copper
Sulphur

Table 9.2. Winkelblech's recommended ingredients.

Materials that he discussed, but rejected, are shown in Table 9.3:

Ammoniacal sulfate of copper
Antimony
Chlorate of soda
Chlorate of strontian
Crystallised verdigris
Mercury chloride
Mountain blue
Plaster
Sal ammoniac
Shellac
Stearine
Sugar of milk
Sulphate of copper
Sulphate of copper and potash
Sulphate of potash
Zinc

Table 9.3. Ingredients rejected by Winkelblech.

Some of these he rightly rejected as deliquescent, others as being in his opinion less than optimum. Some, too, he rejected by simply asserting that they were either useless or detrimental. It has to be suspected that Winkelblech rejected them without testing them, as other authors who did test them found them valuable. For example Winkelblech the chemist mentioned shellac only to dismiss it. Chertier the retired artillery officer tested shellac, and deemed it 'the best fuel I know'. Stearine and sugar of milk turned out to be effective fuels for coloured fires, especially for the notoriously troublesome blue. Most important of all, replacing sulfur with the organic fuels so casually dismissed

by Winkelblech largely eliminated the problem of spontaneous ignition that plagued coloured fires based on sulfur and potassium chlorate.

Winkelblech included 'chloride of mercury' among the ingredients that ignorant firework makers included in their green fires, to the detriment of the colour in Winkelblech's opinion. Chertier, on his own admission, was surprised to find that calomel (mercury(I) chloride) improved coloured fires, but improve them it did. The reason that it improved them (by promoting the formation of the gaseous metal monochlorides that emit the colour) was not established until much later, so neither Winkelblech nor Chertier could have predicted that calomel would be useful. That Chertier discovered its effect by exploratory experimentation stands to his credit; that Winkelblech knew of its use but dismissed it out of hand, presumably because he could see no chemical justification, demonstrates the limitations of applying chemistry to a chemically-based craft at a time when chemistry was not sufficiently advanced to make useful contributions.

Winkelblech's paper contains some relevant information on the properties of some chemicals of pyrotechnic interest, and he presents some practical recipes applying those materials he deems to be useful. Despite being written by a Professor of Chemistry, it does not even explain the fundamental combustion chemistry that underlies all these compositions – Lavoisier and Meyer did a far better job. What effect Winkelblech's chemical expertise had on the work that resulted in this paper is not made explicit, but its influence can be detected, and it is not good. His dismissal of some of the new pyrotechnic fuels (stearine, shellac, milk sugar) and of chloride of mercury gives the impression that he could see no theoretical advantage in using them and therefore did not bother to test them. That is the great disadvantage of the theoretical approach, compared to the exploratory. The theoretically-driven experimenter, such as Winkelblech, begins his work knowing what to expect, and limits his investigations accordingly. The exploratory investigator, well exemplified by Chertier, has fewer preconceptions and is prepared to spend a lot of time investigating all manner of possibilities, knowing full well that most of them will be fruitless – but hoping that some will yield unexpected and valuable results, as indeed they did for Chertier.

Winkelblech, presumably boosted in self-confidence by his status as a Professor of Chemistry, boldly dismissed some valuable materials as useless or even harmful. Firework-makers would have seen through his pretence, but what of his fellow chemists?[292]

9.1.7. A French Editor's Addendum to Winkelblech's Paper

The French translation of Winkelblech's paper is followed by a section entitled 'Recipes and Formulas' that begins: 'Following M. Winkelblech's Memoir...,we must give some compositions used by the pyrotechnists, and which one of them told us deserved confidence.' The French editors, unlike Winkelblech, were prepared, if somewhat condescendingly, to take the opinions of pyrotechnists seriously.[293]

Recipes for all sorts of firework compositions were presented, including the full range of coloured lances and Bengal lights shown in Table 9.4. The French editors must have noticed that some of these recipes contravened the principles set out by Winkelblech.

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[292] For Chertier on shellac, see Chertier, *Nouvelles recherches sur les feux d'artifice(*1843), p. 31; For the spontaneous combustion of coloured fires containing chlorate and sulfur, and the advantages of replacing sulfur with organic fuels, see *Nouvelles recherches sur les feux d'artifice* (1854), pp. 400-401. For Chertier on calomel, see *Essai sur les compositions qui donnent les plus belles couleurs dans les feux d'artifice*, preface, also pp. 7, 55. For the metal monochlorides, see Barrow and Caldin, "Some Spectroscopic Observations on Pyrotechnic Flames"

[293] Winkelblech, "Sur les feux d'artifice." p. 174.

Colour →	White		Yellow		Blue		Red		Green	
Lance or **B**engal Light →	**L**	**B**	**L**	**B**	**L**	**B**	**L**	**B**	**L**	**B**
Ingredient ↓	Parts by weight									
antimony (regulus)		-	-	-	-	-	-	-	2	2
antimony sulfide	1	1	-	6	12	12	6	6	-	-
bicarbonate of soda	-	-	3	-	-	-	-	-	-	-
chlorate of potash		-	-	-	30	25	30	20	10	8
English blue ashes		-	-	-	15	15	-	-	-	-
lampblack		-	-	2 ½	-	-	2 ½	2 ½	2	2
meal powder	-	-	2	-	-	-	-	-	-	-
nitrate of baryta		-	-	-	-	-	-	-	95	95
nitrate of potash	5	6	18	-	-	-	-	-	-	-
nitrate of soda		-	-	60	-	-	-	-	-	-
nitrate of strontian		-	-	-	-	-	60	60	-	-
sulphur	2	2	7	18	18	18	18	18	15	15

Table 9.4. French coloured fires, ca. 1857, appended to the French translation of Winkelblech's paper.

Except for the yellow, the mixtures for lances and Bengal lights of each colour are identical, apart from the lights having a little less potassium chlorate (or potassium nitrate in the case of the white). This indicates a systematic approach to formulation: a satisfactory mixture has been found, and then the burning rate has been optimized for each application by adjusting the amount of oxidizer.

The French blue compositions contravene Winkelblech's recommendations by using not copper oxide, but English blue ashes - a synthetic form of mountain blue, which Winkelblech considered an unsatisfactory source of copper for blue fires. The French blue fires also contain antimony sulfide, which Winkelblech stated must not be used in blue compositions. It is hard to escape the conclusion that the French editors were making the point that French pyrotechnists did not need instruction from a German chemist.

9.2 Transmission of Pyrotechnic Information across Language Barriers.

The translation of Winkelblech's paper into French is a rare example of French interest in German work on pyrotechny. Another is the translation of one of Meyer's works, published in Belgium some years previously. It is instructive to look more closely at the transmission of pyrotechnic information between French, German and English-speaking countries at this important time in the chemical transformation of fireworks. We noticed earlier that the original English recipes for red and green fires were soon published in French and German, and that this seems to have inspired Meyer, Websky and Chertier to begin their independent studies. From that point, the important publications were either in French or German. There is evidence that language barriers inhibited the transmission of information.[294]

Important German publications that escaped notice in French (and English) speaking countries are the works on potassium perchlorate, discussed in Chapter 4. All the early works (Websky, Hutstein, Weber and Frey) on potassium perchlorate in fireworks were in German. The reason for this is very

[294] Franz Eduard Moritz Meyer, *Traité de pyrotechnie par Moritz Meyer Dr, capitaine prussien au ministère de la guerre; edité et augmenté d'un appendice par C. Hoffmann, capitaine de l'artillerie prussiene, traduité d'allemand et augmenté de notes par J. B. C. F. Neuens, capitaine d'artillerie belge*, trans. J. B. C. F. Neuens (Liege: Félix Oudart, 1844).

likely that the original work on this chemical as a pyrotechnic ingredient was published in German and was not noticed by pyrotechnists in other countries. While the German pyrotechnic writers were very interested in the work of French pyrotechnists, the reverse apparently did not apply. Ruggieri's 1821 book was published in German in 1832 and 1845, and Websky translated and commented on the work of Chertier. French writers, in contrast, seem to have ignored (or were simply unaware of) the contributions of their German counterparts. Chertier, writing in 1836, did not know about Websky's and Meyer's work on chlorate-based coloured fires. Nor did Chertier ever mention potassium perchlorate. The second (and final) edition of his book was published in 1854; Websky's book had been available since 1850, but Chertier's only mention of a perchlorate was in a composition for yellow lances that included sodium perchlorate. He clearly had not read Websky's work on potassium perchlorate – a much more useful ingredient. As late as 1882 Denisse said nothing about potassium perchlorate in his otherwise comprehensive book, nor did Tessier mention it in his chemistry-focussed book on coloured fires.[295]

Perhaps the explanation for the French ignorance of German work lies in the attitude expressed by the distinguished Alsatian French chemist Charles-Adolphe Wurtz (1817 – 1884) when he began his *Dictionnaire de chimie pure et appliquée* (1869) with the words *'La chimie est une science française.'* According to Alan J. Rocke, as early as 1832 the German chemist Justus von Liebig (1803-1873) denounced the French chemical establishment for 'arrogance, chauvinism, provincialism, rhetorical bombast and scientific thievery'. The penalty for arrogance and provincialism in science and technology is to fall behind when advances happen to be made by foreigners, which seems to be what happened here. In a counter-example, Tessier, who apparently did not know about the work of the German pyrotechnists on potassium perchlorate, cited the work of the German chemist Alexander Wächter on chlorates. This had been published in German in 1843, and in English and in French the following year. The availability of this paper in French could well account for Tessier knowing about it. The works of the German pyrotechnists were not published in other languages.[296]

Very recently material has come to light to show that one Frenchman (named A. Sonnié-Moret, no details available) was sufficiently interested in the work of a German pyrotechnist to prepare a two-volume translation of the 6th edition of Websky's book. The work was carried out between 1859 and 1861 and survives only in manuscript. According to the bookseller who has possession of this work, '...the translator ... gives much information about the sources of Websky (Meyer, Chertier) and on other authors, on compositions, etc. This translation is a valuable source for the

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[295] Websky, *Martin Websky's Schule der Lustfeuerwerkerei. Ein Vermachtniss an die Freunde und Dilettanten dieser Kunst*. Julius Hutstein, "Bereitung des überchlorsauren Kalis für die Pyrotechnik," *Dinglers Polytechnisches Journal* 20 (1851); "Ueber Bereitung und Anwendung des überchlorsauren Kalis," *Archiv der Pharmacie* 1 (1851). Carl Weber, *Die Lustfeuerwerkerei ; oder, Vollstandige Anweisung zur Anfertigung aller Feuerwerkskorper...Nebst practischer Anweisung zur Erzeugang des electrischen Lichtes, des chinesischen Feuerwerks, bengalische Flammen. Lichter mit verschieden farben & Erklarung uber die verschidenen Ingredienzien...* (Berlin: S. Mode's Verlag, ca. 1866). Oskar Frey, *Die Feuerwerkskunst. Kurzes Lehrbuch zur Anfertigung Land-, Wasser-, Theater und Salon-Feuerwerke,* (Erfurt: Fr. Bartholomäus, 1885). For two examples of German interest in French firework literature see Ruggieri, *Handbüchlein der Lustfeuerwerkerei*, 2 ed. (Quedlinberg und Leipzig: Gottfr. Basse, 1845). and Websky, *Martin Websky's Lustfeuerwerkerei insbesondere Dilettanten und Freunde dieser Kunst. Nebst einem Doppel-Anhang: (I) Die Stoffe und Substanzen der Lustfeuerwerkerei in ihrem chemischen und physikalischen Verhalten theoretisch betrachtet von Ernst Schnell; (II) Auszug des Neuen und Beachtenswerthen aus F. M. Chertier's Lustfeuerwerkerei nach dem Französischen mit Anmerkungen von Martin Websky;* Chertier, *Essai sur les compositions qui donnent les plus belles couleurs dans les feux d'artifice*. *Nouvelles recherches sur les feux d'artifice*. p. 161. Denisse, *Traité pratique complet des feux d'artifice*.

[296] Charles-Adolphe Wurtz and Jules Bouis, *Dictionnaire de chimie pure et appliquée: comprenant la chimie organique et inorganique, la chimie appliquée à l'industrie, à l'agriculture et aux arts, la chimie analytique, la chimie physique et la minéralogie,*, vol. 1 (Paris: Librairie de L. Hachette et Cie, 1869), p. 10; Alan J. Rocke, *Nationalizing Science: Adolphe Wurtz and the Battle for French Chemistry*, Transformations: Studies in the History of Science and Technology (Cambridge, MA: MIT Press, 2001), p. 70.

history of pyrotechnics.' That such a work evidently found no publisher is further evidence of a broad lack of interest on the part of the mid 19th century French in the work of German pyrotechnists. [297]

English pyrotechnists obtained information from their Continental counterparts; 'Practicus' (Denis Times Moore) certainly knew Chertier's work: the flyleaf of the copy of Chertier's 1843 book held at Yale University carries his signature, as shown in Figure 9.3

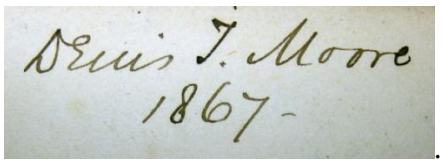

Figure 9.3. Moore's signature on the flyleaf of Chertier's 1843 book.[298]

Kentish mentioned that Southby visited Chertier in Paris and obtained much useful information from him. Kentish also cited Chertier's 1856 book, Tessier's 1859 volume, and Hutstein and Websky's 1873 edition. He commented that he did 'not know that I have been able to learn much from them with which I was not previously acquainted.' This could be just boastfulness, or it could suggest that Kentish had learned his knowledge from other English pyrotechnists, who may have acquired it by their own independent experiments, but more likely obtained much of it from earlier editions of Chertier and Websky. The language barrier may not to have been so severe for the English as it was for the French, perhaps because the English were more willing to learn from foreigners, even if Kentish seemed somewhat reluctant to admit it.[299]

9.3 Chemists, Communication and the Problem of Spontaneous Ignition

An example of an aspect of pyrotechny that could well have benefitted by better communication between pyrotechnists, and between pyrotechnists and chemists, is provided by the long-standing problem of spontaneous ignition of mixtures containing both potassium (or barium) chlorate and sulfur.

Two types of unintended ignition of such mixtures have long been known: ignition associated with shock and friction, and spontaneous ignition of the undisturbed mixture. The first could (in principle at least) be avoided by taking extreme care when making, handling and transporting the mixtures; the second is much more insidious.

It is worth summarizing the modern understanding of why mixtures of a chlorate with sulfur are susceptible to spontaneous ignition. Ordinarily, the oxygen in a chlorate is attached to chlorine atoms, three oxygen atoms to each chlorine atom. These oxygen atoms remain firmly attached to the chlorine until the jiggling (vibrational motion) of the structure, which increases as the material is

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[297] Martin Websky and A. Sonnié-Moret (traduction et notes), "[Manuscrit inédit] Art de la pyrotechnie de joie, ou instruction facile, claire et éprouvée pour la préparation des feux d'artifice, pour tous ceux qui s'occupent de cet art, sous le rapport pratique et théorique, surtout pour les amateurs et amis de la pyrotechnie de joie. Traduit de l'Allemand sur la 6ème édition. Complet en 2 tomes (Breslau 1858 et Paris 1858, 1859 ; Breslau 1858 et Clamecy 1859)." Abebooks.co.uk, https://www.abebooks.co.uk/servlet/BookDetailsPL?bi=18923154111&searchurl=tn%3Dpyrotechnie%2Bpratique%26sortby%3D17, accessed 21 February 2017.

[298] Photographed by B. Sturman on 22 July 2009, from the copy of Chertier, *Nouvelles recherches sur les feux d'artifice* (1843), kindly supplied on inter-library loan by Yale University Library.

[299] Kentish, *The Pyrotechnist's Treasury*, p. iv.

heated, becomes so vigorous that an oxygen atom breaks free. The freed oxygen atom can then join up (react) with some other atom, such as a sulfur atom, causing further heating (more jiggling), with the release of more oxygen atoms and so the process accelerates. The problem with sulfur is that on exposure to moist air it slowly combines with atmospheric oxygen to form sulfur dioxide (SO_2). This in turn reacts with sulfur and moist air to form a series of polythionic acids ($H_2S_nO_3$, where n is a small number greater than 3). When a sufficient quantity has accumulated, the acids decompose into sulfur, sulfuric acid (H_2SO_4) and sulfur dioxide. These react with potassium chlorate to form chloric acid, ($HClO_3$) and chlorine dioxide (ClO_2), in which the oxygen atoms are much less strongly attached to chlorine atoms than they are in potassium chlorate. These products readily release free oxygen atoms that attach themselves to sulfur atoms and thus create more sulfur dioxide in a rapidly accelerating process that increases the temperature and ultimately causes the mixture to ignite. This process was elucidated by the American chemist Herbert Giles Tanner (1893-1967) in 1959.[300]

A further complication is that the extent to which sulfur powder reacts with moist air depends on the chemical nature of the sulfur and the surface area of the powder. Powdered sulfur made by grinding up 'roll' sulfur (rods of solid sulfur made by casting molten sulfur in moulds) consists almost entirely of the most stable and unreactive form of sulfur. Its molecules are puckered rings of 8 sulfur atoms (cyclooctasulfur, S_8). In contrast, the so-called 'flowers of sulfur', made by rapidly condensing sulfur vapour to a very fine powder, contains in addition to the stable (S_8) form of sulfur a variable fraction of 'polymeric' or 'insoluble' sulfur. This consists of long, open chains of sulfur atoms, which are more chemically reactive than the S_8 molecules of 'roll' sulfur. Further, 'flowers of sulfur', because of its very small particle size, has an enormous surface area. This, combined with the presence of a more reactive form of sulfur, makes it much more readily oxidized than powdered 'roll' sulfur. This is shown by 'flowers of sulfur' (or 'sublimed sulfur', as it is sometimes called) giving an acid reaction with moist litmus paper, whereas freshly-powdered roll sulfur does not. With this background information, we can review the history of spontaneous ignition of chlorate-sulphur mixtures.[301]

Spontaneous ignition during mixing led to the abandonment in 1794 of the original French project by the chemists Berthollet, Lavoisier and others to substitute potassium chlorate for saltpetre in gunpowder. Three years later French chemists Fourcroy and Vauquelin reported the detonation of mixtures containing potassium chlorate by friction and shock, and their ignition on contact with sulfuric acid. In 1798 English chemist Thomas Hoyle reported the ease with which mixtures of potassium chlorate and sulfur were ignited by friction and by the action of sulfuric acid. In 1801 Fourcroy warned against the dangers of mixing potassium chlorate with combustibles, including sulfur, noting that a mixture of three parts of potassium chlorate with one part of sulfur ignites spontaneously and produces a violent explosion. The dangers of mixing potassium chlorate and combustibles were widely repeated in chemistry books in the early 19th century, including those intended for a popular and even juvenile readership. I have argued elsewhere that this information, and its endorsement by prominent chemists, was a powerful inhibitor of the use of potassium chlorate in coloured fires.[302]

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[300] Herbert G. Tanner, "Instability of Sulfur-Potassium Chlorate Mixture - A Chemical View," *Journal of Chemical Education* 36, no. 2 (1959), pp. 58-59. See also Ernst Pfantodt, "Chlorates and sulphur - Menace or Bugbear?," *Bulletin of the Pyrotechnics Guild International, Inc.*, no. 76 (1991), pp. 11-14.

[301]For the different molecules in these two forms of sulfur, see Ralf Steudel and Bodo Eckert, "Solid Sulfur Allotropes," *Topics in Current Chemistry* 230 (2003), pp. 1-79. 'Flowers of sulfur' is specifically discussed on p. 15. The specific surface area of commercial flowers of sulfur is quoted as 1700 cm^2g^{-1} in S. J. Chapman, "Oxidation of micronized elemental sulfur in soil," *Plant and Soil* 116 (1989), pp. 69-76. In contrast, I calculated the specific surface area of sulfur powder having a particle diameter of 53 micrometres (i.e., half the aperture size of the finest sieve specified by Tessier in *Chimie pyrotechnique* (1859), p. 308) to be only 539 cm^2g^{-1}.

[302] Bret, "Une tentative d'exploitation militaire de la recherche en chimie: Berthollet et la poudre de muriate oxygéné de potasse (1787-1794)", p. 218 reproduces a letter from Berthollet to Guyton stating the impractical dangerousness of the project. Antoine Francois Fourcroy and Louis Nicolas Vauquelin, "An Account of

Potassium chlorate was eventually introduced as an ingredient in theatrical red fire in 1810. The recipe was not published until 1820, but after that knowledge of the new red fire soon spread. It contained potassium chlorate and sulfur, so it is a little surprising that the earliest published report of its spontaneous combustion came as late as 1835. A packet containing a pound or two of it, left on a shelf in a store-room with no source of ignition, suddenly burst into flames. A similar incident occurred not long afterwards. A third incident, some years later, involved about a pound of the mixture contained in a bottle, wrapped in paper ready to be sent to a customer. This prompted a publication in The Pharmaceutical Journal; it appears that some pharmacists were in the habit of making up the red fire mixture for customers. It soon became clear that red fire was not the only mixture capable of spontaneous ignition. A Yorkshire druggist, Thomas Arnall (1818-1874) wrote to the Pharmaceutical Journal reporting the spontaneous ignition of a small quantity of purple fire containing potassium chlorate, sulfur, anhydrous copper sulfate and anhydrous strontium nitrate. The mix ignited 'with a slight explosion' three days after it was prepared. A second batch, made after more careful and complete drying of the copper sulfate, ignited 12 days after mixing. Arnall proposed two plausible explanations: the copper sulfate, or strontium nitrate, or both, might contain free acid which would then ignite the chlorate-sulphur mixture, as was well known. The second possibility, in modern language, was that some components of the mixture might catalyse the decomposition of potassium chlorate in the same way as manganese oxide and copper oxide were known to do. Arnall had never heard of green fire igniting spontaneously. He suggested that this might be because barium nitrate is anhydrous and unlikely to contain free acid, whereas the smell of nitric acid is 'very perceptible' when strontium nitrate is dehydrated prior to use. [303]

In the same issue of the journal one John Dallas offered some chemical observations relevant to the problem. Noting that the residues from the burning of the red and green fires contain a substantial amount of strontium sulfate or barium sulfate as the case may be, Dallas deduced that during combustion the sulfur takes oxygen rapidly from the chlorate or nitrate, forming sulfuric acid which then combines with the 'baryta or strontia, forming a sulfate, which remains.' The same action, he suggested, takes place slowly as soon as the materials are mixed, generally without the evolution of much heat, but sometimes with sufficient heat to eventually cause ignition. In his experience this is the cause of the coloured fires 'not keeping'. A sample of a coloured fire that had 'lain by for some time' contained 'scarcely a trace of the soluble salt' – i.e. the soluble strontium or barium nitrate had been converted almost completely into the insoluble sulfate. What gave rise to the reaction sometimes taking place so quickly as to ignite the mixture was not known, but Dallas offered some suggestions: the materials were too finely ground, which increases the surface contact and thus 'the chemical action is proportionally active'. 'In coloured fires, properly made, the ingredients are coarsely powdered, and thus present fewer points of contact.' Furthermore, pressure may promote reaction by providing closer contact of the particles, and incomplete mixing might leave portions of the mixture

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Experiments Described, and in part repeated, at the Sitting of the National Institute of France, on the15th Germinal, in the Year 4, by Citizens Fourcroy and Vauquelin, on Detonations Produced by Concussion," *A Journal of Natural Philosophy, Chemistry and the Arts: Illustrated with Engravings; by William Nicholson* 1, no. July 1797 (1797), pp. 168-169. Thomas Hoyle, "Experiments and Observations on the Preparation, and some remarkable Properties of the Oxygenated Muriate of Pot-ash," ibid.2, no. October 1798 (1798), p. 290-297; Antoine Francois Fourcroy, *Système des connaissances chimiques, et de leurs applications aux phénomènes de la nature et de l'art*, vol. 3 (Paris: Badouin, 1801), p. 224. For one example of such warnings in a popular chemistry book, see Samuel Parkes, *A Chymical Catechism, or the Application of Chymistry to the Arts, for the use of Young People, Artists, Tradesmen, and the Amusement of the Leisure Hours* (Philadelphia: James Humphreys, 1807), pp. 153-154. For the inhibiting effect of this information on the development of coloured fires, see Sturman, "Coloured Fire", pp. 32-34.

[303] M. Scanlan, "Instances of Spontaneous Combustion, detailed in a Paper read before the Royal Irish Academy, 25th May, 1835," *Records of General Science* 2, no. 8 (1835), pp. 119-122; Anonymous, "The Spontaneous Ignition of Red Fire " *Pharmaceutical journal: A weekly record of pharmacy and allied sciences* 2 (1843), p. 767 ; Thomas Arnall, "Spontaneous Ignition of Pyrotechnical Compounds," *Pharmaceutical journal and Transactions* 3, 1843-4, no. 1 (1843), p. 38.

with excess potassium chlorate, able to supply more oxygen to the sulfur in that part of the mixture. According to Dallas, 'you never hear of...spontaneous ignition of these fires amongst the firework-makers, though they make them in large quantities'. Another possibility, of course, is that the firework-makers prudently kept their problems to themselves. [304]

We know from the remarks of Chertier that firework-makers were aware of spontaneous ignition. He said nothing about problems with potassium chlorate and sulfur in his 1836 booklet, but he did mention spontaneous ignition of mixtures made with sulfur and impure barium chlorate, saying that several accidents had happened to him in this way. Perhaps one of those accidents caused the fire that destroyed his notes a couple of years previously.[305]

Meyer, in 1833, had warned 'you must not use flowers of sulfur, but only roll sulfur', but he did not say why. Chertier actually specified 'flowers of sulfur' in the recipes in his first (1836) publication, but in his 1843 book, he warned against using it, as it is almost always acidic. This acidity, warned Chertier, can cause spontaneous ignition of compositions containing chlorate. He drew an analogy with the then well-known "oxygenated match', which was tipped with a chlorate mixture and ignited when dipped into sulfuric acid. With firework compositions, the ignition might not take place until some hours, or even several days, had passed. As Chertier explained, ''flowers of sulfur' is made by condensing sulfur vapour, and in the process it forms sulfurous acid' In Chertier's time 'sulphurous acid' referred both to sulfur dioxide (SO_2) and its solution in water. He warned: 'The presence of this acid makes the use of flowers of sulfur (i.e. with chlorate) extremely dangerous.' Pyrotechnists, he wrote, generally use powdered roll sulfur, probably for reasons of economy, and this is a fortunate choice because roll sulfur does not present the same dangers as flowers of sulfur. Chertier's remarks illustrate his peculiar combination of chemical ignorance and accurate chemical intuition. For example, he wrote that sulfurous acid is formed by 'decomposition of the sulfur', a chemically absurd statement, as sulfur had long been known to be a chemical element, incapable of decomposition. On the other hand, his recognition of the formation of 'sulphurous acid' as the start of the problem turned out to be accurate, as Tanner would show over a century later.[306]

Chertier cautioned against keeping large quantities of compositions containing chlorate, because of the risk of spontaneous combustion. It was, he wrote, possible to alleviate this problem by storing the compositions, whether powder, paste, grains or stars, in stoppered glass bottles which were then stored immersed in buckets of water almost up to the top. Thus, in the event of the composition igniting, the bottle would break and the water would put out the fire. To avoid the risk of fire from the flame that escapes before the water has done its job, one should store the compositions in a separate room that is kept perfectly free of combustibles.[307]

The preceding paragraphs indicate the state of knowledge of the problem of spontaneous ignition when Professor Winkelblech commented on it in 1848. He indulged in some chemical speculation, warning not to use flowers of sulfur because it contains free sulfuric acid, which, on acting on chlorates, decomposes them and produces hypochlorous acid, which can sometimes bring about spontaneous combustion of the mixture. This explanation is not correct. The troublesome acidic

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[304] John Dallas, "On the Spontaneous Ignition of Pyrotechnical Compounds," ibid., 3, 1843-44, pp. 39-40. Census records reveal that Dallas was probably the Reverend John Dallas (1798 -1876), Vicar of Laxfield, Suffolk. If so, he is the third example in this project of a clergyman indulging in amateur chemistry or pyrotechny (the others being von Stadion and Denis Times Moore).

[305] Chertier, *Essai sur les compositions qui donnent les plus belles couleurs dans les feux d'artifice*. p.12.

[306] Meyer, *Die Feurewerkerei in ihrer Anwendung auf Kunst, Wißenschaft und Gewerbe*, p. 17 ; Chertier, *Nouvelles recherches sur les feux d'artifice* (1843), pp. 62-64. Tanner, "Instability of Sulfur-Potassium Chlorate Mixture - A Chemical View."

[307] Chertier, *Nouvelles recherches sur les feux d'artifice* (1843), p. 392.

component of flowers of sulfur is, as Chertier correctly stated, sulfurous acid. Winkelblech's identification of the product of the acidification of potassium chlorate with sulfuric acid as hypochlorous acid (HClO) is questionable, to say the least. It is not an error of translation: the German text gives 'Unterchlorsäure', the French 'l'acide hypochloreux'. The expected product is chloric acid ($HClO_3$). Winkelbelch was also aware that mixtures of potassium chlorate and sulfur are dangerous to mix, because of their sensitivity to friction. He wrote: 'The mixing must be done in wooden mortars or on some paper with a wooden spatula. The chlorate of potash is only added at the end, as it can decompose without pressure in the presence of sulfur.' In view of his recognition of the danger of sulfur, it is surprising that Winkelblech was so dismissive of the organic substances that can safely replace sulfur as combustibles in coloured fires. All in all, Winkelblech's contributions did not advance the understanding of the problem.[308]

Spontaneous ignition was investigated by the chemist/pyrotechnist Tessier, who came to the conclusion that flowers of sulfur was always acidic and should not be used; it could be purified by washing with water and drying, but this was not worth the risk. Some firework-makers, he noted, used unwashed flowers of sulfur for ordinary work, and roll sulfur for mixing with chlorates. Tessier advised against this, for two reasons: roll sulfur burns better and with less smoke, and having two sorts of sulfur on hand carries the risk of mistakenly using the wrong one, thus compromising the safety of the whole workshop. Tessier exposed mixtures of powdered roll sulfur with pure potassium chlorate, or with pure barium chlorate, to the temperature of boiling water on a water bath for at least half an hour. No change whatsoever was evident. Then, he wetted the mix with 7 or 8 times its weight of water, evaporated it to dryness on the water bath, and kept the dried mixture on the water bath for a further 45 minutes. There was no spontaneous ignition. More water was added, and the procedure repeated. The only observation was an odour that he attributed to sulfur vapour. After each test he extracted the mixture with water and tested for chloride (and for sulfate in the case of potassium chlorate) as these are the expected reaction products. He found no evidence of reaction. Tessier outlined a detailed set of experiments to investigate the problem more completely, regretted that he had not had the opportunity to carry them out, and asserted his moral right to do so in due course. By the time the second edition of his book appeared, in 1883, Tessier had still not completed that program of experiments; as far as they went, his results allowed him to attribute spontaneous ignition to the use of flowers of sulfur, or impure chlorates, or both. He concluded that with pure materials, the danger was no greater than that inherent in making fireworks. Noting that even ordinary combustibles can self-heat to the point of spontaneous combustion when they are stored in quantity, Tessier advised against keeping large quantities of mixed chlorate-containing compositions. [309]

Meanwhile, Chertier had some unpleasant experiences since the writing of his first book. Despite scrupulously using only roll sulfur, and taking the added precaution of washing it, he found that spontaneous ignition still occurred. Mixtures that had kept safely for even ten years would suddenly burst into flame with no apparent reason. Chertier regretted that sulfur had this defect, because sulfur greatly increased the brightness of coloured fires. None the less, he had to advise that it not be used. When its use was (in his opinion) essential, as in fires for general illumination, the sulfur should be kept separately from the rest of the composition until the last moment. Then, the sulfur and the other, pre-mixed components should be passed together though a small sieve directly into the pan in which the coloured fire was to be burned. He advised that sulfur and chlorates should never be mixed in compositions for firework stars. Chertier felt it his duty to emphasize the danger of using such mixtures, writing: 'If pyrotechnists or amateurs do not heed my advice, they have only themselves to blame. They persist at their risk and peril.' It was all very well for Chertier to offer this advice, but he could not resist tempting his readers into 'risk and peril' by publishing recipes containing the very mixture that he insisted that they should not use. On the evidence of Denisse, Chertier continued to

[308] Winkelblech, "Ueber Farbige Feuer", p. 301; "Sur les feux d'artifice", p. 173.

[309] Tessier, *Chimie pyrotechnique ou traité pratique des feux colorés*, pp. 22, 123-130, 150-152, 156. *Chimie pyrotechnique ou traité pratique des feux colorés* (1883), pp. 133-139, 144-147.

develop compositions containing both chlorate and sulfur to the end of his days. Denisse himself accepted Tessier's advice and used only pure chlorates. He satisfied himself that unwashed flowers of sulfur would cause trouble with even pure chlorates, but claimed that he had never had problems with roll sulfur. He set a precedent for generations of Continental pyrotechnists, who would continue to use mixtures containing chlorate and powdered roll sulfur well into the 20th century. [310]

Developments in Britain followed a different path. With little attention to the problem from chemists or anyone else, problems with spontaneous combustion continued. 'Flowers of sulfur' was commonly used, both by amateurs and by pharmacists who supplied coloured fires. It was readily to hand in pharmacies; as it was already a very fine powder, the operator was spared the tiresome task of pulverizing. The seriousness of the problem of spontaneous ignition can be judged from Arnall's remark in 1866 that he knew of five fatalities from the spontaneous combustion of the purple fire mixture that he had discussed some 23 years previously, 'in addition to other cases not fatal'. It had ignited four times in his own experiments. Arnall, the druggist who had first commented on the problem in 1843, had since 'had to make these "coloured fires" by the hundredweight' (1 cwt = 50.8 kg) and 'had several accidents.' Arnall believed the cause 'to be (in most cases) acidity, either of the sulfur or of some other ingredient'. He explained the acidity of sublimed sulfur, and mentioned that he 'had been informed by practical pyrotechnists that they never use sublimed sulphur, but buy it in roll and powder it for use as wanted'. For indoor use, sulfur had recently been replaced by a mixture of shellac and resin; this was safer, but the 'brilliance of the colours will not bear comparison' with that of colours produced with recipes containing sulfur. Arnall attributed the instability of the purple fire mix to anhydrous copper sulfate attracting moisture from the air, leading to 'double decomposition of the copper salt and chlorate'. By this he meant potassium chlorate and copper sulfate reacting to form potassium sulfate and copper chlorate, the latter decomposing to release oxides of chlorine and chloric acid, which would ignite the sulfur. Replacement of the copper sulfate with copper oxide seemed to remove the tendency to ignition. Not mentioned, but surely relevant, is the fact that copper sulfate becomes very hot as it re-hydrates. It seems incredible that a composition that was known in 1843 to be subject to spontaneous ignition should still be in use almost a quarter of a century later, despite having killed at least five people in the meantime. More effective communication between those making these mixtures and chemists having the skills needed to investigate the problem might well have discovered safer alternatives to this deadly mixture. Arnall recommended that mixtures be tested by preparing a small quantity and smelling it; a 'peculiar, somewhat ozonic odour' is 'considered indicative of danger'. The odour is presumably that of chlorine dioxide, and would certainly indicate danger.[311]

On 5th November 1866 a letter appeared in the Chemical News from one John Spiller, of Woolwich, suggesting that the destruction by fire of the Standard Theatre on October 21 of that year was caused by the spontaneous combustion of Red Fire. He noted that 'several instances are already on record, and I was myself some five years ago witness to a spontaneous igniton of the substance in question'. Spiller referred to a mention of the propensity of Red Fire to ignite spontaneously in '"Fownes' Manual of Chemistry", eighth edition, foot-note, page 284)." In fact, this comment was also present in the 1857 American edition of this work, derived from the 4th (1852) English edition. Spiller concluded: '...inasmuch as similar performances are now going on in at two other theatres in London, and the pantomime season is also fast approaching, it would seem desirable to call attention to the treacherous qualities of a pyrotechnic composition so largely employed.'[312]

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[310] Chertier, *Nouvelles recherches sur les feux d'artifice* (1854), pp. 400-401. For Chertier's continued use of chlorate-sulphur mixtures, see Denisse, *Traité pratique complet des feux d'artifice,* p. 280. For Denisse's views, see ibid., p. 15.

[311] Thomas Arnall, "On the Spontaneous Combustion of Pyrotechnical Compounds," *Pharmaceutical journal and Transactions* 8 (1866).

[312] John Spiller, "Fires of Spontaneous Origin," *The Chemical News and Journal of Physical Science* 23 (1866). George Fownes, *Elementary Chemistry, Theoretical and Practical* (Philadelphia: Blanchard and Lea, 1857).

Also in 1866 R. Trevor Clarke contributed his views on spontaneous combustion in a letter to *The Chemical News*. He considered it 'the probable origin of various terrible fires which have occurred on the premises of firework-makers in London'. Clarke drew attention to mixtures of the nitrate of strontium (or barium), potassium chlorate and sulfur. He had observed that the feared process began with the evolution of an orange-coloured gas, then the mixture began to liquefy in several places, a hissing noise was evident as more gas was generated, then the composition ignited. This shows that Tessier was unduly optimistic in drawing conclusions from simple mixtures of chlorate and sulfur: the presence of strontium or barium nitrate made the mixture much more prone to ignite. Clarke was a magistrate and a naturalist, not a chemist, and he offered no chemical explanation for the phenomenon. He mentioned that purple fires containing black oxide of copper are almost certain to ignite sooner or later. Copper carbonate should be used instead. A couple of years later Clarke repeated these observations in a letter to *The Times*, which he concluded with the observation: 'Our chemists could do no better service to the community than by investigating this matter thoroughly'. There is no evidence that any chemists ever did as he suggested, until Dr Rudolf Gartenmeister (n.d) of Elberfeld, Germany investigated the problem in 1907.[313]

Meanwhile, British amateur pyrotechnists continued to recommend chlorate and sulfur mixtures. In 1872 'Practicus' sometimes, but not always, specified 'washed' sulfur in his recipes. He warned against mixing chlorate with 'common sulfur', because of the risk of spontaneous ignition. Kentish, in 1878, specified 'flowers of sulfur' and gave elaborate instructions for washing it free of acid, not realizing that all he was doing was re-setting the clock on the time-bomb.[314]

In 1874 a British parliamentary committee investigating the explosives industry heard evidence from Charles Thomas Brock, who testified that mixtures containing strontium nitrate, potassium chlorate and sulfur are especially dangerous, particularly if they get damp and then dry out. There are good chemical reasons for this, which were not discussed at the hearing. Strontium nitrate attracts moisture from the air, and moisture is essential for the reaction between sulfur and oxygen that lies at the heart of the problem. Any sulfuric acid formed would react with strontium nitrate to form nitric acid. This is a powerful oxidizing agent that would greatly increase the rate of oxidation of the sulfur, and thus speed up the progression to spontaneous ignition. Strontium nitrate would be worse than barium nitrate, which is not hygroscopic. Once the mixture got damp, the chemistry would be analogous. The orange gas noted by Clarke would contain nitrogen compounds such as yellow NOCl and red-brown NO_2, as well as yellow-green ClO_2 and Cl_2.[315]

As well as sometimes igniting spontaneously, many 19th century colour compositions were sensitive to shock and friction. This led to disasters when the coloured stars in a firework shell ignited and exploded from the shock imparted to the contents by the gunpowder charge intended to propel the shell from its mortar. The resulting explosion often projected fragments of the shattered iron mortar into bystanders, like some gigantic anti-personal grenade. As explained by Brock, such problems eventually led, in 1894, to the British Government's prohibition of the use of mixtures of chlorates

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[313] R. Trevor Clarke, "Spontaneous Ignition," *The Chemical News and Journal of Physical Science* 14 (1866); "Spontaneous Ignition of Fireworks," *Pharmaceutical Journal and Transactions (Second Series)* 10 (1868). The latter quotes at length from the letter to *The Times*. For Gartenmeister's work, see Gelingsheim, *Die moderne Kunstfeuerwerkerei: Eine Anleitung für Dilletanten*. 33-36. Gartenmeister attributed the problem, which he observed with mixtures of chlorate with pure sulfur and sugar, to impurities in the potassium chlorate. See R. Gartenmeister, "Gefährliches Kaliumchlorate," *Chemiker-Zeitung* 31 (1907). p. 174; Rudolf Gartenmeister. Process of Purifying Chlorates. United States Patent 975,613. File August 10 1908 and issued November 15 1910.

[314] Moore ('Practicus'), *A Manual of Pyrotechny*, p. 39; Kentish, *The Pyrotechnist's Treasury* (1878), pp. 50-51.

[315] "Report from the Select Committee on Explosive Substances; together with the Proceedings of the Committee, Minutes of Evidence, and Appendix," (London: The House of Commons, 1874).p. 140, para. 2254-2260. The chemical comments are mine.

and sulfur in fireworks. Similar mixtures continued to be permitted in matches, where they had caused no problems. As noted previously, Continental pyrotechnists continued to use chlorate-sulphur mixtures, with due precautions as to the purity of the chlorates, and with the use only of powdered roll sulfur. Their compositions commonly included colour agents such as carbonates or basic salts that helped prevent acidification. The development of such different approaches in different parts of Europe shows that the problem was essentially solved empirically, rather than by a complete understanding of the chemistry. It was not until the 20th century that chemists such as Gartenmeister and later Tanner provided a proper understanding of this most regrettable and unintended consequence of the chemical transformation of fireworks. [316]

9.4. Concluding remarks

Previous chapters show that, as stated by Brock, the main contribution of chemistry to the transformation of fireworks in the 19th century was the provision the necessary materials at an affordable price. From the perspective of the 19th century taxonomy that divided chemical science into descriptive, theoretical and applied chemistry, the essential contributions of science to the chemical transformation of fireworks came from descriptive chemistry, which discovered and characterized the new materials, and applied chemistry, which found applications for those materials and made them available in quantity at appropriate prices. Meyer, Marsh and Tessier evidently regarded the application of new materials in fireworks as applied chemistry. Chertier and Websky, on the other hand, seem to have considered themselves traditional pyrotechnists who were availing themselves of new resources made available by the chemists. This reflects the dichotomy between artisanal and scientific ways of knowing, but could be taken as an example of the two approaches converging.

This chapter argues that theoretical chemistry had little to offer the art of firework-making, the important exception being the combination of Lavoisier's theory of combustion with Richter's concept of stoichiometry that was central to Meyer's approach. This theory explained why there was an optimum combination of a given fuel and oxidizer, and was thus a huge contribution to the understanding of pyrotechnic combustion, but it was not particularly useful as a tool for developing new compositions. The scientific theories that would eventually provide a full understanding of coloured fires were not developed until the 20th century, and some other phenomena exhibited in fireworks (whistles, and until very recently the 'senko hanabi effect) are still understood only in very broad outline. After Meyer, academic chemists avoided commenting on pyrotechny. A notable exception was Winkelblech, who attempted to help firework-makers by applying his chemical expertise to coloured fires, but succeeded only in showing his ignorance of the value of many useful ingredients.

Winkelblech life-long dedication to what he believed to be the teachings of Christ, which led to an intense commitment to radical social reform, show that he was a sincere, well-meaning person, eager to right the wrongs of the world. His interest in pyrotechny remains a mystery, but there is no doubt that his intention was to help practitioners and to advance the art. His project seems broadly the same as that of Meyer some 15 years earlier – to put coloured fires on a scientific basis, and to purge them of unnecessary ingredients. The 15 years separating the work of these two chemists made a huge difference. Meyer, to the extent possible in his day, explained the principles of coloured fires and introduced several new colour-producing materials. His project to remove unnecessary materials was remarkably successful. Over the next 15 years Websky and Chertier carried out exploratory studies of coloured fires and introduced new materials that proved of lasting value. When Winkelblech addressed the subject, the plethora of materials in use by the pyrotechnists must have seemed to him as it did to Meyer: an indication of pyrotechnists' ignorance of the chemical foundations of their craft. In a sense this was true, but the difference was that in Meyer's time many of the materials were

[316] For the prohibition of 1894, see Brock, *A History of Fireworks*, p. 161. For the explosion of shells in their mortars, see ibid., p. 179. For examples of continuing Continental use of chlorate-sulfur colours, see Gelingsheim, *Die moderne Kunstfeuerwerkerei* .pp. 72-76. On p. 48, Gellingsheim warns that flowers of sulfur, even when washed, must never be used because of the risk of spontaneous ignition with chlorates.

indeed unnecessary baggage carried over from the early days, whereas those that had been introduced since then were of great value, even though nobody at time could have justified their use by referring to chemical theory. Winkelblech's mistake was to assume that because he could see no chemical reason for using a particular material, that material must be either useless or detrimental.

One reason for the lack of interest in fireworks on the part of chemists may have been an unstated recognition that the phenomena were beyond the reach of the science of the day; evidence against this is the largely fruitless efforts that were devoted by chemists to understanding (and improving) the performance of gunpowder. Another reason could be that 19th century chemists considered fireworks beneath their notice as men of dignity, and certainly not worthy of their professional attention. If so, this would contrast with the enthusiasm for fireworks demonstrated a century before by Lavoisier, one of the giants of chemistry. Such a change in attitude can perhaps be understood by noting that over the 19th century there was a definite 'professionalization' of chemistry, whereby 'proper' chemists, who held University qualifications and earned their living by teaching or practicing chemistry, distanced themselves from those lesser beings who engaged in chemistry as a hobby. Chemistry had become a serious business. The professionalization of chemistry in the 19th century has, of course, been discussed in the literature; further exploration would take us too far from our topic.[317]

Recognition that 19th century French pyrotechnists did not know of the work of Websky led to evidence that this was not just a language barrier, but an example of a known tendency of French chemists to hold themselves aloof from the work of foreigners, for reasons of national pride and cultural egoism. The language barrier was also evident. Tessier, for example, cited German work on the chemistry of the chlorates that had been translated into French, but he did not mention much more important work on potassium perchlorate that had been published only in German. Some of the English amateur pyrotechnists are known to have read Chertier and Websky, and there is written evidence of personal transmission of information between the French amateur Chertier and the British professional Southby when Southby visited Chertier in France. Cultural barriers to the transmission of information from the Continent to Britain were, in this context at least, not as rigid as those that hindered the dissemination to France of knowledge created in Germany.

The long persistence of the problem of spontaneous combustion of coloured fires is a scandalous indictment of lack of effective communication between pyrotechnists and chemists. It could have been solved much earlier, had it received the concentrated attention of a chemist. A complete theoretical explanation was not required – an empirical solution, arrived at by exploratory experimentation, would have been perfectly satisfactory. If a competent chemist had focussed on the problem, it is likely that chemical explanations would have come to mind and perhaps would have led to useful advances in chemistry. That this did not happen is explicable by pyrotechnists and chemists each regarding the problem as the province of the other. There is also a puzzling sense that the problem was not given the attention that it deserved, other matters seeming more pressing to the investigator. Tessier, who as a chemist and pyrotechnist was in an ideal position to solve the problem, had proposed a valuable series of experiments in his 1859 book, but still had not completed them in 1883. He had, in contrast, found time to conduct a detailed exploration of the pyrotechnic application of the picrates.

The broad conclusion is that 19th century chemistry was simply not capable of contributing to the extent suggested by the remarks of Ruggieri and Lavoisier quoted at the start of this chapter. Surprising as it may seem, the chemical transformation of fireworks was more the result of exploratory experimentation by amateur pyrotechnists than of any systematic study by chemists. Even today, many phenomena exhibited by fireworks are not fully understood. Firework-making is a technical craft that uses the materials provided by chemistry, without any detailed knowledge of how those materials produce their results. It is perhaps not so surprising that the new firework effects

[317] See, for example, Robert Bud and Gerrylynn K. Roberts, *Science versus practice: chemistry in Victorian Britain* (Manchester: Manchester University Press, 1984).

introduced in the 19th century were discovered by trial and error, or even by accident, and not by the application of chemical theory.

Chapter 10. Conclusions

This project set out to explain the transformation of fireworks in Europe during the 19th century. It argued that the changes came about by the introduction of new materials into the chemical mixtures with which the fireworks were charged. The core question then became: 'Why were these new materials introduced into fireworks in Europe in the 19th century, and not in some other place, at some other time? That people were interested in fireworks, in theatrical stage effects and in military pyrotechnics was centrally important, because without such an interest there would have been no incentive for anyone to improve them. Following Michael Lynn, we remarked on the commercialization of fireworks in late 18th century Europe and noticed their use in popular entertainment, both in their own right and as part of the attractions of the urban pleasure gardens and theatres. The increased wealth and leisure time enjoyed by some Europeans at this time permitted them to indulge in activities not directly related to earning a living; these activities included enjoyment of fireworks and of pyrotechnic stage effects. The European military were involved with pyrotechnics at this time, too, both for war-like applications and for State celebrations. These circumstances all favoured attention being given to the improvement of fireworks, but do not provide a sufficient explanation for the improvement that did in fact take place. To prove this point, it is necessary only to recall the enthusiasm for fireworks in 18th century China, which for a while led to Chinese fireworks being superior to those of Europe. The 18th century Chinese would presumably have appreciated new firework effects that the Europeans had produced by the end of the 19th century, just as the Europeans appreciated those that they learned from the Chinese in the 18th century, but (as explained in Chapter 2) 18th pyrotechny had reached the limits set by the available materials.

To explain why European pyrotechnists were able to use new materials to transform the art, we noted that a material cannot be introduced into technology unless people know about it and the physical and chemical properties that make it potentially useful. There must not be knowledge of any properties that would preclude the material from such use, and the material must be available at a price and in quantities that make its application practicable. All this might seem trivially obvious, but it provides insights not just into the history of fireworks but into the broad history of technology. Rochelle Forrester has shown that the self-evident point that a material cannot be used before people know that it exists and that it has properties that could make it useful explains the sequence in which materials come into use. Time and again in this project it was found that recognition of new materials and the acquisition of knowledge of their properties depended on materials and knowledge that were already available at that time and in that place, exactly as predicted by Forrester's analysis.

Potassium chlorate turned out to be essential in the original production of a full range of coloured fireworks. Potassium chlorate did not exist on Earth until 18th century European chemists accidentally made some in the course of experimenting with chlorine. People could not have experimented with chlorine until they knew how to make it, and they could not have known how to make it before they had techniques to handle gases. Those techniques could not have been developed until people recognized that gases were real materials, not fundamentally different from solids and liquids. Presumably the firework makers of 18th century China would have been delighted with potassium chlorate, for the same reasons that European firework-makers were delighted with it a century later, but in 18th century China there was no such thing as potassium chlorate - the chain of explanation could be taken further, well beyond the scope of this project.

It was shown that the requirements for the introduction of a new material were neither static nor independent. Recognition of a useful application of a material can stimulate efforts to make that material available in the necessary quantities and at an affordable price. Efforts directed at one application can make the material practical for completely different applications. This was shown in Chapter 4 for picric acid, made in quantity first as a yellow dye, then adapted to make potassium picrate for military explosives; potassium picrate then turned out to be useful in fireworks for making pyrotechnic whistles. Similarly, aluminium was developed first as a costly, decorative metal for luxury goods. Next, when new technology reduced its price, it found wide application as a strong,

light structural metal. Then, application of the newly-inexpensive aluminium as a silver pigment for paint led to its transformational use in novel firework effects.

Some new materials make it possible for existing materials to be applied in new ways. A small number of these 'enabling materials' were central to the transformation of fireworks. This is the core of the explanation of why that transformation happened when and where it did. As shown in Chapter 3, the most important enabling material in the transformation of fireworks was potassium chlorate, discovered in France in 1786. Potassium chlorate transformed strontium nitrate from a marginally useful red colour agent to a brilliantly effective one and revealed barium nitrate as a novel green colour agent. It transformed copper compounds from green colour agents for alcohol flames to blue colour agents for fireworks.

Application of a new material can reveal unexpected shortcomings and stimulate searches for a replacement. This was illustrated in Chapter 3; many pyrotechnic compositions containing both potassium chlorate and sulfur turned out to be susceptible to spontaneous ignition. A search for a replacement for potassium chlorate led to potassium perchlorate, but at the time this was too expensive to be widely applicable. Chertier's recognition that sulfur was part of the problem of spontaneous ignition led to his advocacy of alternative fuels, most notably shellac.

These new materials were available to firework makers in Britain, France and Germany between the late 1700s and the late 1800s for two reasons: first, chemists had made people aware that the materials existed, and that each material had a unique set of properties, and second, those materials, or the materials needed to make them, could eventually be obtained relatively easily and at affordable prices because of the changing forms of production that were developing at the time, as explained in Chapter 8. To repeat the insight of Forrester, new materials cannot be produced without the availability of certain other materials and of the knowledge and technical skills acquired by studying and using earlier materials. The more materials that have been studied and used, the more new materials can be made. It is therefore particularly significant that, from the middle of the 18th century, some people, designated as chemists, could spend time, gain prestige and even make a living by investigating materials, making new ones, and publishing the results of their endeavours, irrespective of their immediate practical value. A tradition developed that scientific work published in one European language would be translated and published in at least one other, allowing results established in one country to be built upon in several others. In those days, too, it was customary to publish results in clear language and to present sufficient detail to allow the work to be replicated. This was in contrast to earlier times, when the writings of alchemists were deliberately obscure so that important details were kept secret from those 'unworthy' to know them, and to later times when scientific writing became excessively terse and so filled with jargon as to be accessible only to specialists.

New materials made change possible, but with hindsight it is clear that fireworks could have been transformed sooner had it not been for social conditions that worked against change. The order in which materials are introduced is to a great extent fixed by their chemical properties, but the timing of their introduction is contingent on social factors. Introduction of potassium chlorate was delayed for decades, mainly because chemists taught that it was too dangerous for practical use. It was eventually introduced, as an ingredient in theatrical red fire, in 1810 but the new composition was kept secret for 10 years. When it was finally revealed, a similar green fire was disclosed within a couple of years. Knowledge that potassium chlorate facilitated the production of red fire with strontium nitrate had led to the discovery that it also facilitated the production of a green flame with barium nitrate. Information about the two new coloured fires, originally published in England in 1820 and 1822, was soon available in German and French. This seems to have inspired independent investigations into chlorate-based coloured fires in Germany and France, leading to influential publications by Websky in 1831, by Meyer in 1833 and by Chertier in 1836. Similar, but initially secret, investigations at the Royal Laboratories at Woolwich are suggested by the recipes for coloured fires disclosed by Marsh in 1844. Further researches into materials for coloured fires were conducted by Chertier (1843 and 1854) and by Tessier (1859 and 1883). Their work provided made a full range of colours – not just the generic white, red, yellow, green, blue and violet but a large selection of intermediate hues and

saturations. For social and cultural reasons, German pyrotechnists avidly studied the work of their French counterparts, whereas the French seemed largely unaware of what German pyrotechnists had achieved.

The introduction of a full range of colours did not end the transformation of fireworks. As explained in Chapter 5, by the end of the century the metals magnesium (1867) and aluminium (1894) had brought white sparks and flames of unprecedented brilliance, intensely bright colours and lightning-like explosions. The potassium picrate whistle (1888) completed the list of novel effects brought about by new materials.

Many of the new materials that transformed fireworks in the 19th century were introduced by amateur firework-makers. Indulgence in amateur pyrotechny was but one of the consequences of educated people having time and money to spend on non-essential activities. Firework books written with amateur practitioners in mind can be found from the 17th century, so there was nothing fundamentally new about it. In the 19th century many more people than ever before could afford to engage in leisure-time pursuits. Amateur pyrotechny was one such activity, promoted both by the fireworks at the popular pleasure gardens and the pyrotechnic effects in the theatres, and by a wide popular interest in chemistry. At this time, too, the necessary chemicals were available without restriction to all who could afford them. It is true that fireworks were officially forbidden to all but a select few specifically sanctioned by the State, but until the final quarter of the 19th century that prohibition was widely ignored, particularly if the people involved were 'gentlemen'. Unlike professionals, amateurs who could afford to spend time and money on experiments were not just willing, but eager to share their knowledge – that was how they gained respect, status and admiration, as well as the personal satisfaction of advancing their chosen field. Books written by and for amateurs were very important in disseminating knowledge of the new materials and the details of how they could best be used to produce novel effects.

The new materials introduced problems, the most notable being incompatibility of ingredients. This was eventually solved, but before then mixtures would unpredictably burst into flame, often with disastrous results. Compositions intended to burn with a quiet colourful flame would, under certain conditions, explode. With the introduction of the new ingredients explosions in firework-makers' workshops became all too common, and all too conspicuous, as the shops were often located in busy urban areas. The State could no longer turn a blind eye to firework-making, nor could it enforce its prohibition in the face of the on-going demand for fireworks and pyrotechnic signalling devices. Eventually, as explained by Brock, the prohibition had to be lifted and firework-making was required to be carried out under license in specially designed factories, constructed on the assumption that accidental ignition would occur, and that the consequence of such ignition would be restricted to the single work-room in which it took place, and would necessarily be small on account of the small quantity of material that was permitted in each room. This led to the transformation of firework-making, first in Britain and then elsewhere, from an occupation carried out in small, cramped workshops in big cities to one conducted in purpose-built factories, consisting of many widely-separated small workrooms located in open fields on the outskirts of the cities. In Britain, State supervision of firework-making went so far as to prohibit combinations of potassium chlorate, sulfur and sulfides because of the risk of unintended ignition.

The chemical transformation of fireworks in the 19th century reveals the central role played by chemists, but that role was mostly indirect. Chemists produced new materials and disseminated knowledge of their properties, usually without explicit reference to potential applications. Interacting processes then transformed new materials from obscure chemical curiosities to essential components of technology. Consumer demand and entrepreneurial production worked interactively to make materials available at affordable prices. Materials that were initially costly products of the chemists' laboratories became standard industrial products, and applications that would have been absurdly extravagant became commonplace. Firework makers benefitted when prices of obviously useful materials such as magnesium, aluminium and potassium picrate fell when the materials were produced on a large scale for other applications. Experimenting with the new materials led to the

discovery of new, completely unexpected effects, such as 'glitter' and the pyrotechnic whistle. On the other hand, application of the new materials sometimes revealed unexpected problems, which led to searches for different materials, so the transformation process was iterative rather than linear. Potassium chlorate made new colours possible, but it also introduced the problem of spontaneous ignition. The root of the problem was found to be the combination of potassium chlorate and sulfur; potassium perchlorate could be replaced with potassium perchlorate, and the problem was solved, but potassium perchlorate was too expensive to be practical. Alternatively, sulfur could be replaced with shellac, but shellac was also expensive, and some pyrotechnists preferred the colours produced with sulfur to those produced with other fuels. It was not a simple matter of finding a problem, and solving it by finding a new material.

The research presented here also shows that technical developments took place without any detailed scientific understanding of the processes involved. This point has been made before (brewing and baking were taking place untold centuries before there was any knowledge of the microbiology of yeasts, there were steam engines long before there was thermodynamics) but another example may not go amiss. Another, less expected, insight is the central role played by amateurs in the chemical transformation of fireworks. In this respect firework-making provides a parallel example to photography – another science-based craft (but in this case a new one) that developed tremendously in the 19th century, which depended on the introduction of new materials, and which benefitted greatly from the contributions of amateurs. Another insight is that official prohibition of an activity enjoyed by a significant portion of the population did not cause the activity to disappear – on the contrary, firework-making, both amateur and professional, developed and flourished, irrespective of the prohibition, until ultimately prohibition had to be withdrawn. Amateur firework making seems to have been at its height during prohibition and diminished with the enforcement of new regulations in the last quarter of the century. The publication of books for amateur pyrotechnists at that time is best explained as the culmination of the efforts of authors who had worked just before the new regulations began to be enforced. Amateur pyrotechny would remain an obscure and undocumented activity until the 1970s when it re-emerged in the United States of America and continued the innovative traditions of its precursors in 19th century Europe.

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