

Electroplating the Platinum Metals

AN HISTORICAL REVIEW OF THE EARLY RESEARCHES

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The successful development of gold and silver plating in 1840 led to a number of scientists turning their attention to the electrodeposition of platinum and palladium, but before commercially satisfactory processes could be established they met with considerable difficulties because of the insolubility of the anodes and of the complex nature of the chemical compounds of these metals.

The introduction of gold and silver plating in the 1840s naturally prompted the study of the electroplating of platinum and palladium. It was at first assumed that platinum, having so many similar properties to those of gold, would be equally amenable to electrodeposition, but unfortunately its insolubility as an anode and the complex chemistry of its salts presented

severe technical problems. These were nevertheless tackled with enthusiasm by a number of scientists in England, France, Germany and Russia and attempts to develop a reliable process continued throughout most of the nineteenth century until satisfactory standards of quality were achieved—a veritable triumph of hope over experience.



John Frederick Daniell 1790–1845

The very early attempts at electroplating were gravely handicapped by the lack of a satisfactory battery until Professor J. F. Daniell of King's College, London, devised his self-polarising cell which enabled thin but uniform coatings to be deposited. In this reproduction of an early Daguerrotype in the possession of the Royal Institution he is seen, on the left, demonstrating his new battery to Faraday, to whom he had described it in 1836 as "a voltaic combination which I trust you will think worthy of the name of the CONSTANT BATTERY"

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Interest in electroplating began in the late 1830s, but at this time a reliable source of continuous current was lacking: large and powerful voltaic piles were built in the early years of the century but these were quite unsuitable for an electroplating process which required a low voltage applied at a steady rate over a considerable period. Due to local action the voltaic cell rapidly declined in strength. These early researches, particularly on the electroplating of gold, have been reviewed by Hunt (1), who refers to the major steps forward taken in 1836 when Professor J. F. Daniell of King's College, London, described the first self-polarising cell or constant battery which enabled thin but uniform coatings to be deposited (2).

The Pioneer Work of Alfred Smee

It was one of Daniell's students in the chemistry department at King's College who took up the study of electroplating and who made a major contribution to the subject. Alfred Smee entered King's in 1834, gaining a silver medal for chemistry. Both his grandfather and his father had been employed at the Bank of England, the father becoming Chief Accountant in 1831 (3). At that time the Chief Accountant lived with his family in an official residence in the Bank, the necessary security confining them at home in the evening hours. On leaving college young Alfred therefore set up a laboratory in a room leading out of the family drawing room and next to the ledger office and here, working alone with elementary equipment, some lent by Daniell, he carried out a remarkable series of experiments in electrochemistry (4).

His first self-imposed task was to devise a battery more suitable for work in electrodeposition, and on February 28th, 1840 he was able to read a paper to the Royal Society, "On the Galvanic Properties of the Metallic Elementary Bodies with a description of a new Chemicomechanical Battery" (5). Shortly before this another type of battery had been introduced by W. R. Grove (6), and Smee considered this to be

an improvement on the Daniell Cell, but in discussing those two he wrote:

"I found that although the batteries of Daniell and Grove were admirably contrived instruments, yet it is very desirable to possess one that could be set in action at a moment's notice, and with comparatively little trouble. The platinised silver battery is peculiarly suitable for the operator, for when it is in action it completely talks to its possessor. If the current is very feeble a faint murmur is heard; if a moderate current is passing it hisses; but if a violent one it roars. At this present moment I have nineteen batteries at work in the same room where I am writing and they are each telling me the work they are performing" (7)

He had earlier, in a paper on the battery given to the Royal Society of Arts for which he was awarded their Gold Isis Medal, made something of a disclaimer:

"I wish it to be clearly understood that it does not possess the absolute constancy of Daniell's, or the intensity of Grove's battery" (8)

An amusing aside on this point was made some years later by Clerk Maxwell, who was rather given to composing humorous verses, and who composed an "electric valentine" beginning:

"Constant as Daniell, strong as Grove;
Ebullient through all its depths like Smee;
My heart pours forth its tide of love,
And all its circuits close in thee." (9)

Smee's battery relied upon his observation that an electrode having a roughened surface caused the hydrogen formed during the reaction to disperse, preventing the build-up of a film of bubbles. His cathodes were either of silver etched with acid or of platinum abraded with sandpaper, both being placed in a cell containing "nitro-muriate of platinum" as the electrolyte. This produced a thin layer of platinum in the form of a black powder, yielding an electrode simply and cheaply and one unaffected by the strength of acid in any cell. Banks of cells could be employed varying "from the size of a tumbler to a 10 to 12 gallon vessel". Its success lay, however, in its simplicity, and it aroused great interest in the art of depositing one metal upon another.



Alfred Smee

1818–1877

Born in Camberwell, educated at St. Paul's School and King's College, London, and then trained as a surgeon at St. Bartholomew's Hospital, Smee carried out all his researches in electroplating in a room set aside for him in the Bank of England where his father lived as Chief Accountant. He was elected a fellow of the Royal Society in 1840, the year in which he published his "Elements of Electrometallurgy, or the Art of Working in Metals by the Galvanic Fluid", at the age of 22

By the end of 1840 Smee, still only 22 years old, had compiled and published a remarkable text book, "Elements of Electrometallurgy", a term he himself coined. Dedicated to the Prince Consort, who, with Queen Victoria, had been shown some of Smee's specimens of electroplating, the first edition was soon exhausted and a second and much larger edition was published in parts during the year 1842 while a third revised and enlarged edition appeared in 1851 following upon a French translation published in 1845.

In his first edition Smee described his processes for both platinum and palladium plating, writing that:

"Hitherto the reduction of these metals, in any other state than that of the black powder, has been always considered impossible."

He claimed that processes for "platinating and palladiating" rested upon the authority of his book and went on:

"Platinating metals by the galvanic current is a new feature in science. The process is similar in all respects to gilding but is more difficult. The solution of the nitro-muriate of platinum must be very weak, and the battery must be charged with dilute acid. The object to be coated must be very smooth, and thoroughly cleansed by potash, before the process is commenced. Having proceeded thus far, and the solution of platinum being ready, a very fine platinum wire, in connection with the silver of the battery, must be placed so as to dip into the solution, but must not be immersed beyond a very short distance. The object to be platinated is now ready for connection with the zinc of the battery, after which is effected, it is to be dipped in the solution. Immediately, oxygen gas will be given off from the platinum wire, in connection with the silver. From the copper or other metal to be platinated, no gas will be evolved, provided too much electricity be not generated. In a few minutes the object will be coated with platinum. During the process, the object should be withdrawn from time to time, and rubbed over with a little whiting. The colour of the metal thus reduced is so similar to polished steel that it would be difficult to distinguish the one from the other. It

is needless to say that it has a beautiful appearance. It would be of great value as a coating for telescopes, microscopes, quadrants, and a hundred other articles which must be exposed to the action of the weather." (10)

For palladium plating Smee used a similar electrolyte, nitro-muriate of palladium with a palladium anode:

"This metal is whiter than platinum, but not so bright as silver. It might be used in the same cases, and with the same advantages as platinum; and we have, besides, twice the bulk of metal in the same weight." (10)

In the second edition of his work he proposed the addition of "sufficient soda" to neutralise the acidic platinum solution and of ammonia to the palladium electrolyte. He had to admit, however, that his specimens of platinum plating

"will not resist the action of nitric acid because there are generally some little fissures uncovered, some little crack which admitting the nitric acid tears off the platinum in thin scales."

Smee's reputation as an electrochemist was rapidly established. He was elected a fellow of the Royal Society in June 1841, while earlier in

the same year a special post, somewhat honorary in its duties, was created for him in the Bank of England.

Surgeon to the Bank of England

This appointment was made largely upon the recommendation of Sir Astley Cooper, the distinguished surgeon, who was a friend of Sir John Rae Reid, the Governor, and who had sometimes visited Smee's laboratory to see his experiments. He considered that the Bank should "turn Smee's scientific genius to good account", and accordingly the young man was appointed Surgeon to the Bank of England on January 1st, 1841. (This forecast came to fruition a few years later when Smee devised a new method of printing bank notes by an electrotype process.)

Now Sir Astley Cooper had many years earlier married the sister of Thomas Cock who had worked on platinum with William Allen at Plough Court and who was in turn the brother-in-law of Percival Norton Johnson, with whom he was closely associated in the refining of platinum. There can be little doubt therefore



A sketch of Alfred Smee's laboratory made by his brother-in-law William Hutchinson and autographed by the sole occupant. It lay between the family drawing room and the ledger room of the Bank of England, and the occasional dropping of a ledger would be sufficient to ruin one of Smee's experiments by breaking the contact with his battery. This is taken from "Memoirs of Alfred Smee" written by his daughter Elizabeth Mary who had married William Odling, the distinguished chemist who had put forward a rudimentary Periodic System four years before Mendeleev and who had succeeded Faraday at the Royal Institution, later becoming Professor of Chemistry at Oxford



Sir Astley Paston Cooper

1768–1841

In the last year of his life the distinguished surgeon interested himself in the career of the young Alfred Smee, and it was upon his emphasising to the then Governor of the Bank of England that "you don't know what a treasure you have got in that young man" that Smee was given an appointment there as surgeon. Sir Astley was related by marriage to both Thomas Cock and Percival Norton Johnson and it is likely that Smee's interest in platinum and palladium was encouraged and supported by them

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that Smee's interest in platinum and palladium plating was encouraged by Johnson, who doubtless supplied the necessary metals and salts.

The French Controversy

The commercial development of gold and silver electroplating is closely associated with the name of George Richards Elkington of Birmingham and his cousin Henry. Perhaps because of their early success in this field they did not seriously embark on platinum plating. In 1837 Henry had filed a patent (11) for the immersion coating of sundry metals with platinum or palladium, using a solution of platinum and gold chlorides with excess of sodium and potassium bicarbonates. Later, in 1841, one of Elkington's assistants, Oglethorpe Wakelin Barratt, took a patent in parts of which he claimed a method of "precipitating platinum from its solutions as a covering to other metals" (12). His process is difficult to credit today, as it involved dissolving platinum in a boiling solution of sodium chloride, alum and cream of tartar. This was intended for immersion coating, but he claimed that

"if a stronger coating be required, I attach the battery and an anode of metal platinum and con-

tinue the action until the desired thickness is obtained. Palladium may also be employed in like manner."

But it was the British Patent 8447, filed jointly by George and Henry Elkington in 1840 and mainly covering gold and silver plating from their cyanide solutions, that was to cause great controversy and litigation that spilled over into the area of platinum plating. Only a few days after the corresponding French patent had been published in December of the same year a specification was filed in the French patent office by Henri-Catherine-Camille Ruolz, otherwise known as the Comte de Ruolz-Montchal, while on the following June he filed an addition to his patent covering the use of the battery and "the employment, for the first time, of the compounds of cyanogen with gold and silver". A further patent of addition, published in January 1842, covered the platinum plating of iron, steel, copper, brass and silver, (13). This claimed a solution of platinum chloride neutralised with sodium carbonate with the addition of potassium cyanide, the electrolyte to be operated at 80 to 90°C.

Ruolz was financially embarrassed and sold his patent rights to a Paris dyer, Guillaume-

Edouard Chappée, who filed a further addition to the same patent for the use of the double chloride of platinum and potassium, but Ruolz swiftly repurchased his rights on finding another interested party.

The great possibilities disclosed by Ruolz's main patent were quickly realised by Charles Christoffle, the founder of a then small but enterprising firm of goldsmiths and silversmiths in Paris that still bears his name, and he immediately secured an exclusive license from Ruolz for gold and silver plating, retaining the inventor as a consultant. Only a few months later a further addition to the Ruolz patent was filed in the name of Christoffle claiming the addition of potassium iodide to the electrolyte. Still further additions followed, including one for palladium plating from a cyanide solution.

In the meantime the Académie des Sciences had appointed a commission to examine the methods proposed by Ruolz and by the Elkingtons. This comprised the distinguished scientists Thenard, d'Arcet, Pelouze, Pelletier and Dumas, who managed to complete their

long report rather hastily by the December of 1841 (14). In this they tended to prefer the technique of their countryman Ruolz, although they later awarded a prize of 6,000 francs to each party for the new methods of gold and silver plating. In a section on platinum plating they reported on the extremely slow rate of deposition from a cyanide solution compared with Ruolz's double chloride bath, with which "the deposition of platinum goes with at least the same rapidity as that of gold and silver".

They went on rather fulsomely to extol the potential benefits to science and industry of platinum plating in the areas of chemical and pharmaceutical apparatus, watch and clock making and armaments.

Christoffle now secured a license from the Elkingtons for gold and silver plating, relying upon his license from Ruolz covering the plating of platinum and palladium. He entertained great hopes of making a commercial success with these metals, but was never able so to do, although he became the leading gold and silver plater in France.

Charles Christoffle
1805–1863

Founder of the well known Paris firm of goldsmiths, silversmiths and cutlery manufacturers that still bears his name. Christoffle foresaw a use for the electroplating of platinum but had to engage in extensive litigation to secure his rights and to undergo an examination by a committee of the Académie des Sciences

(From a portrait in the possession of L'Orfèverie Christoffle, Paris)



Leeson's Voluminous Patent

Smee's electrolyte was only one of a number put forward during the course of the next twenty years or so, and his remark that platinum plating was "similar to gilding but more difficult" proved to be well founded.

In 1842 Dr. Henry Beaumont Leeson filed a voluminous patent, "Improvements in the Art of Depositing and Manufacturing Metals and Metal Articles by Electro-Galvanic Agency, and in the Apparatus Connected Therewith". This ran to 28 pages and 12 diagrams and included the idea of agitating either the articles to be plated or the plating solution in order to obtain smooth deposits at higher current densities (15). Leeson was an assistant lecturer in chemistry and forensic medicine at St. Thomas's Hospital in London, later becoming a senior physician and dean, but he evidently gave a great deal of his time to his studies in electroplating. His patent, very soon acquired by the Elkingtons, claimed processes for depositing a whole range of metals and alloys including not only platinum and palladium but also rhodium and iridium! In all there were some 430 possible electrolytes listed, and it is not surprising that W. R. Grove in a critical opinion of the patent in 1844 stated that it "contained so many alleged inventions that it would be dangerous to rest a case on it, and that while many of Leeson's statements were such that chemists might know and discover by experiment, they were not such as a competent workman could apply without many unsuccessful trials." (16)

Leeson did, however, realise the cause of Smee's difficulties:

"The solution must be supplied with a fresh portion of the metal by adding to or placing within such solution or electrolytic fluid a further supply of some suitable salt to be dissolved or taken up from time to time as the fluid becomes exhausted."

Activities in Germany

Contemporarily with Smee, the possibility of electroplating with platinum had been studied by Rudolph Christian Böttger who had studied under Professor Schweigger at

Halle and who for many years taught physics and chemistry at Frankfurt. In 1840 he described the production of electroformed copper plates in relief which were then gilded and platinum plated from the double chloride of platinum and sodium, but his process was not commercially viable (17). Three years later he reported that he had worked at some length with the alkaline solution of potassium chloroplatinate proposed by Ruolz but without success (18). He did however succeed in producing bright deposits on copper and brass from a solution of ammonium chloroplatinate to which a few drops of ammonia had been added.

Similarly good results were obtained by Professor Hermann von Fehling of Stuttgart (19).

Some further work was carried out in Germany a few years later by Joseph Konrad Bromeis of the University of Marburg. Later still, however, in his text book on chemistry published in 1854, he admitted that:

"The platinum deposit obtained on other metals by this method is not sufficiently thick to protect the underlying metal from oxidation or from attack by acids. This can only be achieved by platinum cladding, just as with the rolling of silver onto copper." (21)

George Howell and Thomas Henry

Returning to the development of electroplating in England in the mid-nineteenth century, we find a patent filed by George Howell of London in 1846 (22).

This contains the first reference to a solution that became known as the stabilised platinum electrolyte, made by dissolving platinum chloride in caustic soda and adding oxalic, citric, tartaric or acetic acid followed by caustic potash.

The Great Exhibition of 1851, promoted by the Prince Consort and held in Hyde Park, proved against all forecasts to be a magnificent centre for the display of manufactured goods of all types and included elaborately designed and gold plated items. Among the exhibits of scientific instruments was a balance made by

Ludwig Oertling, the founder of the firm of precision balance makers that still-bears his name, "having a beam three feet in length coated with platinum . . . and another sixteen inches long coated with palladium".

The report of the Juries, who awarded Oertling a Council Medal, adds in a footnote:

"These beams were coated by T. H. Henry Esq., F.R.S., by a peculiar process in which the electric current was employed in depositing these metals. It would seem from this successful application that the same process is applicable to graduated instruments." (23)

The Henry referred to remains a rather shadowy figure, and it is not known by what process or electrolyte he succeeded in plating these balance beams. Thomas Hetherington Henry was for many years from 1837 employed as a chemist in the brewery of Truman Hanbury and Buxton in Spitalfields, London (24). He was among the founder members of the Chemical Society in 1841 (as were Daniell, Grove, Leeson and Johnson as well as Thomas Cock's son William, then Johnson's partner) and had succeeded Robert Warrington, the moving spirit in its foundation, at the brewery. He was elected F.R.S. in 1846, and later established himself as a consulting analytical chemist in Lincoln's Inn Fields. Among his clients was the famous John Percy, Professor of Metallurgy at the Royal School of Mines, who described Henry as:

"certainly one of the most careful, accurate and trustworthy analysts whom I have ever known". (25)

It is to Percy that we owe the only surviving example of Henry's plating technique, now preserved in The Percy Collection of specimens in the Science Museum. It is merely a thin sheet of copper plated on both sides with palladium and accompanied by a note from Percy stating that he was given it by the late T. H. Henry before the year 1855.

Despite the success of the exhibit at the Great Exhibition and the abundant publicity for platinum and palladium that accrued, by 1860 Oertling catalogues no longer offered

beams plated with those metals, nor have any surviving examples been found in a long search. It is possible that the deposits did not withstand constant use and that any beams so treated were returned for the normal re-gilding.

The Roseleur Electrolyte

Once described as one of the landmarks in the history of platinum plating (26), a new formulation was proposed in 1850 by Alfred Roseleur, a chemical manufacturer in Paris who had been active in gold and silver plating for some years, and his colleague Lanaux (27). This was made up as follows:

"We dissolve 750 grams sodium phosphate and 400 grams sodium pyrophosphate in 15 litres of water and filter. We also take 15 grams of platinum chloride, as free as possible from acid, dissolve it in 200 grams distilled water and precipitate the platinum as double salt by adding 160 grams ammonium phosphate. The precipitate together with the supernatant liquid is mixed with the first mentioned solution and the mixture boiled for four hours. Ammonia escapes and the bath, previously alkaline, becomes strongly acid; the liquid loses its yellow colour and can now be used successfully for platinum plating, also for thick deposits."

A platinum anode was used, and the strength of the bath was maintained by additions of platinum chloride.

This phosphate bath, with or without some modification, was used for very many years. It furnished thicker deposits than had previously been obtainable, and some years before the date of his patent—which Roseleur offered openly without royalties—he is said to have presented King Louis Philippe with a ewer and a basin on which he had deposited some 400 grams of platinum.

One measure of its success is found in the correspondence of George Matthey, in which there survive two letters from him to the Birmingham firm of J. and C. Ratcliff, brass founders and lamp and lantern manufacturers who had taken a license under the Elkington patents for gold and silver plating. Dated 1865, these letters urge upon Ratcliffs the merits of platinum plating on gunmetal screws and on brass components in general (28).

A Roseleur electrolyte modified by the addition of common salt and borax was patented in 1886 by William Arthur Thoms of London (29), the founder of the Bright Platinum Plating Company. Thoms claimed in his patent that he obtained a deposit that was so bright that it required no subsequent polishing, but his business was not long lasting and was wound up in 1890.

Interest in America

By this time interest in platinum and palladium plating had developed in the United States and in 1883 Dr. William H. Wahl of Philadelphia, for many years the secretary and editor of the Franklin Institute, published an important text-book, "Galvanoplastic Manipulations" (30). In his chapter on "Platinising" he dealt first with Roseleur's procedure and with the method developed by Professor Böttger and then described an electrolyte advocated by Jewreinoff back in 1853 (31). (Peter von Jewreinoff was a colonel in the Russian Mining Engineers and director of the chemical laboratories of the Mining Department in St. Petersburg, but his platinum bath was virtually that of Howell's of 1846.) On palladium plating he referred to an electrolyte proposed by A. Bertrand in 1876 consisting of neutral ammonium chloropalladate (32). He also referred to a process for electroplating iridium just developed by Dr. W. L. Dudley of Cincinnati but declined to publish the details pending patents being filed.

In a paper read to the Franklin Institute in 1890 (33) Wahl reviewed the whole problem of platinum plating, saying that while each of the earlier baths would yield satisfactory results for a time

"the peculiar difficulties met with in the practice of platinum plating render it impossible to maintain the chemical integrity of those electrolytes and in consequence thereof they soon become inefficient or inoperative by reason of contamination with the secondary products formed therein."

Wahl therefore experimented with anodes consisting of porous carbon impregnated with

platinum to provide a means of dissolution in acidic electrolytes, but his deposits were black and non-adherent. He then turned to alkaline baths containing oxalic acid such as those patented by Howell, of whom he appeared to have no knowledge. He was, however, the first to employ an electrolyte free from chloride and to use "platinic hydrate" to maintain the metal content of his bath, so avoiding the build-up of undesirable compounds.

Twentieth Century Electrolytes

The electrolytes described so far seem to have been found reasonably adequate for the needs of the late nineteenth and early twentieth centuries. The Roseleur and Wahl types of bath were, however, deficient in several respects, low cathode efficiency and short life among them, but not until around 1930 were more satisfactory electrolytes developed. A process developed by W. Keitel and H. E. Zschiegner of the Baker Platinum Company (34) employing diammino dinitro-platinum, colloquially known as Platinum P salt, and free from the build-up of unwanted salts, was the starting point for a number of researchers in the next few years seeking superior electrolytes capable of giving bright adherent deposits in reasonable time. It was quickly followed by the hexa-hydroxy platinate bath of A. R. Powell and A. W. Scott of Johnson Matthey (35). Similar formulations were put forward at the same time for palladium plating and were described by Atkinson and Raper in 1933 (36).

The Advent of Rhodium Plating

At this time it appeared that there might well be a substantial increase in the usefulness of platinum plating, but somewhat unexpectedly a third member of the group now appeared, offering greater hardness, higher reflectivity, greater resistance to wear and reasonable ease of deposition. This was, of course rhodium which, despite the difficulty of getting it into solution—it is insoluble even in aqua regia—began to find applications in the jewellery industry but became of great importance in the

electronic equipment developed so intensively in World War II.

The first description of rhodium plating was given by Professor Colin G. Fink and G. C. Lambros of Columbia University in 1933 (37). They obtained satisfactory deposits from both sulphate and phosphate baths and these, or modifications thereof, have largely remained in use up to the present.

The more recent history of the electrodeposition of the platinum metals has been well reviewed by E. H. Laister (38) and in greater detail by F. H. Reid (39). The emphasis has shifted markedly from decorative to industrial uses more reminiscent of the ideas of the early workers who foresaw the principal applications in the coating of instruments and, as is well

known to readers of this journal, each of these three metals finds a place in modern electronic engineering, while a fourth member of the group, ruthenium, is more recently showing signs of receiving more consideration in the same field.

By the very nature of these applications these electrodeposits generally remain hidden from view inside the components whose performance they enhance—unseen, and in a satisfactory electronic device quite unheard. All of which would have considerably astonished and mystified the pioneers of electrodeposition, Daniell, Leeson and Henry, but probably most of all the young Alfred Smee working away with his nineteen batteries murmuring to him in his small laboratory in the Bank of England.

References

- 1 L. B. Hunt, "The Early History of Gold Plating", *Gold Bull.*, 1973, **6**, (1), 16-27
- 2 J. F. Daniell, *Phil Trans. Roy. Soc.*, 1836, 107
- 3 J. M. Keyworth, Bank of England, private communication
- 4 E. M. Smee, (Mrs Odling), "Memoirs of Alfred Smee", London, 1878
- 5 A. Smee, *Phil. Mag.*, 1840, **16**, 315-321
- 6 W. R. Grove, *Phil. Mag.*, 1839, **14**, 388-390
- 7 A. Smee, "Elements of Electrometallurgy", 1st Edn., London, 1840, p. 23
- 8 A. Smee, *Trans. Roy. Soc. Arts*, 1839-41, **53**, 21-29
- 9 L. Campbell and W. Garnett, "Life of J. C. Maxwell", 1882, p. 630
- 10 A. Smee, *op. cit.*, ref 7, p. 94
- 11 H. Elkington, *British Patent* 7304; 1837
- 12 O. W. Barratt, *British Patent* 9077; 1841
- 13 H. C. C. Ruolz, *French Patent* 10472; 1841
- 14 *Comptes Rendus*, 1841, **13**, 998-1021
- 15 H. B. Leeson, *British Patent* 9374; 1842
- 16 R. E. Leader, "History of Elkington and Co.", unpublished archives in the Victoria and Albert Museum, IV, 11
- 17 R. C. Böttger, *Ann. Chem. (Liebig)*, 1840, **35**, 350; 1841, **39**, 175
- 18 R. C. Böttger, *Ann. Chem. (Liebig)*, 1843, **47**, 342-348
- 19 H. Fehling, *Dingler's Poly. J.*, 1843, **87**, 2016
- 20 J. K. Bromeis, *Dingler's Poly. J.*, 1850, **116**, 283
- 21 J. K. Bromeis, "Die Chemie", Stuttgart, 1853, p. 310
- 22 G. Howell, *British Patent* 11,065; 1846
- 23 Report of the Juries, Exhibition of Work of Industry of All Nations, 1851, p. 258
- 24 Archives of Truman, Hanbury and Buxton, G.L.C. Archives Dept. County Hall, London
- 25 J. Percy, "Metallurgy of Iron and Steel", London, 1864, p. 736
- 26 R. H. Atkinson, *J. Electrodepos. Tech. Soc.*, 1937, **13**, Paper 25
- 27 A. Roseleur and Lanaux, *French Patent* 4648, 1850; "Manipulations Hydroplastiques", Paris, 1855
- 28 Unpublished correspondence of George Matthey, Johnson Matthey & Co. Limited
- 29 W. A. Thoms, *British Patent* 10,477, 1886; *U.S. Patent* 367731, 1886; *German Patent* 42418, 1887
- 30 W. H. Wahl, "Galvanoplastic Manipulations", Philadelphia, 1883, pp. 356-364
- 31 P. Jewreinoff, *Le Technologiste*, 1853, March, 293-294
- 32 A. Bertrand, *Comptes Rendus*, 1876, **83**, 854
- 33 W. H. Wahl, *J. Franklin Inst.*, 1890, **30**, 62-75.
- 34 W. Keitel and H. E. Zschiegner, *Trans. Electrochem. Soc.*, 1931, **59**, 273
- 35 A. R. Powell and A. W. Scott, *British Patent* 363, 569; 1931
- 36 R. H. Atkinson and A. R. Raper, *J. Electrodepos. Tech. Soc.*, 1933, **8**, (10), 1
- 37 C. G. Fink and G. C. Lambros, *Metal Industry (N.Y.)* 1933, **31**, 205
- 38 E. H. Laister, *Metal Industry (London)*, 1954, **85**, 427-429 and 469-470
- 39 F. H. Reid, *Metallurgical Reviews*, 1963, **8**, (30), 167-211