

# Herschel's Cyanotype

## Invention or Discovery?

Mike Ware

Whether it is more apt to describe cyanotype as invented — or discovered — by Sir John Herschel in 1842 is a question the reader may decide by the end of this essay. Whatever the verdict, it is well known that this process of photographic contact-printing in Prussian blue was brought to light just three years after Louis Daguerre and Henry Talbot had announced their independent inventions of photography in silver, using metal and paper substrates, respectively. Their successes in finally securing images of silver represent separate fruitations of an idea that had been gestating for more than a century in the minds and laboratories of several noted natural philosophers.<sup>1</sup> In contrast to this well-known history, the birth of cyanotype was totally unexpected, coming both literally and metaphorically 'out of the blue', to a single parent. The question that this essay will address — at least, by implication — is: why should the circumstances of these two photographic innovations have been so different?

While Talbot was assembling several thousand silver images in an *oeuvre* that is now recognized as the richest vision in early photographic art,<sup>2</sup> his colleague Herschel preferred to experiment with process rather than make new pictures, for his preoccupation was with the medium of photography rather than its message. As one of the leading physical scientists of his day, Herschel was driven by the urge to understand photochemical phenomena, and to harness them as tools for probing the electromagnetic spectrum beyond the narrow optical limits imposed by human vision. Using light-sensitive coatings on paper, he sought to venture below the short-wave end of the visible spectrum, into the region of the ultraviolet or 'actinic' rays discovered in 1801 by Johann Ritter; and above the long-wave visible limit, into the region of the infra-red or 'thermic' rays, which had been discovered in 1800 by his father, Sir William Herschel. In part, the son intended his investigations as a vindication of his father's work: 'thus my father's experiments have full ocular demonstration'.<sup>3</sup> As a practical objective, we shall see that Herschel also entertained the hope of devising a direct photographic process in natural colour. There is no compelling evidence to suggest that he was in pursuit of commercially useful methods of reprography, unlike Talbot, whose aim was clearly to multiply his photographic images in

printers' ink. It is a happy irony, therefore, that Herschel should have been the inventor of the first process of photocopying, which held sway for nearly a century and even in obsolescence has left an indelible new word in our language: the blueprint.

The cyanotype process uses a chemical reaction brought about by the action of light on certain organic salts of iron.<sup>4</sup> The notion that light can promote chemical transformations is, of course, central to the invention of photography, of which the accounts by Eder and others will be familiar to the reader.<sup>5</sup> The response of silver halides to light has long been recognized, and provides the mainstream of this technical history, but the photosensitivity of iron compounds is of more recent origin and less widely understood. The first record of the light-induced decomposition of an organic salt of iron dates from 1831 and is due to Johann Wolfgang Döbereiner (1780–1849), who observed that the irradiation of an aqueous solution of ferric oxalate forms a precipitate of ferrous oxalate (which was shown to be identical with the mineral *Humboldtite*) and evolves a gas, which proves to be carbon dioxide.<sup>6</sup> As we shall see, the published report of this investigation was a spur to Herschel in expediting the publication of his own current photochemical investigations of platinum salts. The standard histories of photography do not record that any connection was made at this time between the light sensitivity of ferric organic salts, and the known chemical properties of Prussian blue, which had been well established as an artists' pigment for over a century.<sup>7</sup> But there was at least one such 'pre-photographic' observation in this respect. It was made in 1828 by John Mercer (1791–1866), a Manchester colour chemist and calico-dyer, who noted the formation of Prussian blue on cotton by a light-induced reaction. The biography of Mercer by his nephew, Edward Parnell, quotes Mercer's own description taken from his experimental notebooks:

I spotted a piece of white cloth with a solution of permanganate of iron, and exposed it to the sun. On testing it afterwards with a solution of red prussiate of potash it gave a blue — but no blue before exposure. This is worthy of note. I have not seen it noticed by any chemical writer.<sup>8</sup>

The pressure of maintaining his business evidently deprived

Mercer of any opportunity to pursue this pioneering observation until the 1840s — by which time the 'invention of photography' had been carried out at the hands of others. So the chance to be counted among the precursors of photography has passed Mercer by, owing to the unfortunate necessity for earning a living — a disadvantage not suffered by financially independent gentlemen-scientists, such as Talbot and Herschel. Later, Mercer contributed significant innovations with toning procedures for cyanotypes, but even these only saw publication in an insubstantial form. If we are seeking to identify an unsung hero of early photography, a worthy candidate might well be John Mercer.<sup>9</sup>

In January 1839, stimulated by Talbot's announcement of his invention of photogenic drawing, Herschel took up the study of photographic phenomena. Within a week he had solved the problem of silver fixation. In contrast with Talbot's single-minded pursuit of the silver image, however, Herschel soon began to widen his investigations in the search for other viable photographic systems.<sup>10</sup> The primary sources for this account of Herschel's work are his handwritten experimental notes, memoranda and test prints, and his published scientific papers that sprang from them. Herschel's experimental notebooks are in the Library of the Science Museum, London, but there is a lacuna in the record over the crucial period of 1841–45. Some original documents spanning this period are held in the Herschel archive of the Harry Ransom Humanities Research Center (HRHRC), at the University of Texas at Austin.<sup>11</sup> For brevity, these will be referred to henceforth as the 'Memoranda'. Some of the specimen prints described in the Memoranda are at HRHRC, but the majority are still in Britain, divided between the Museum of the History of Science at Oxford,<sup>12</sup> and the National Museum of Photography, Film & Television at Bradford.<sup>13</sup> Herschel's correspondence, together with the drafts of his published papers and a few test prints, are held in the library of the Royal Society, London.<sup>14</sup> There is a chronological list of 'prepared papers' in the Memoranda, in which a sequential number is allocated to each preparation of chemicals coated on paper, which might prove light sensitive. It will be convenient to refer to this as the 'prepared paper number'. Herschel's Memoranda reveal that by February of 1840 he had carried out nearly seven hundred such photochemical experiments, using silver salts almost exclusively, although many of these coated sheets were divided up into smaller pieces, and each thereby sufficed for several different tests.

To the enduring benefit of the embryonic science of photography, the spring of 1840 was remarkably brilliant. Herschel had already initiated a new series of exposure tests of 'vegetable colours' using extracts of the juices of plants and flowers, but this work was interrupted in March by the removal of the family home from Slough in Buckinghamshire to Hawkhurst in Kent. Once resettled, Herschel resumed his experiments in August, but by then he frequently found the sun to be 'pale' or 'desultory', requiring long exposures for these very insensitive processes.<sup>15</sup> He pursued them nonetheless, during the very poor summer of 1841 that followed.<sup>16</sup> It seems plain from the nature of Herschel's investigation of the bleaching of these coloured plant juices

by light that he was in pursuit of a direct positive-working colour photographic process, and he stated as much in one of his letters to Talbot,<sup>17</sup> and in a letter to the 1841 Meeting of the British Association for the Advancement of Science, reporting on these experiments: '... a circumstance which ... holds out no slight hope of a solution of the problem of a photographic representation of natural objects in their proper colours'.<sup>18</sup> The most important conclusion that Herschel was able to draw from his observations was that a dye tends to be selectively bleached by the light of its complementary colour.

In the early spring of 1842, Herschel suspended his tests of plant colours in favour of further broadening his search for new photosensitive substances; his attention transferred from these rather evanescent organic dyes (now appropriately called anthocyanins) to deeply coloured inorganic compounds. He was later to explain this shift of interest in a paper to the Royal Society, in the following chemically picturesque terms:

The general instability of organic combinations might lead us to expect the occurrence of numerous and remarkable cases of this affection among bodies of that class, but among metallic and other elements inorganically arranged, instances enough have already appeared, and more are daily presenting themselves, to justify its extension to all cases in which chemical elements may be supposed combined with a certain degree of laxity, and so to speak in a state of tottering equilibrium.<sup>19</sup>

His awareness of these 'lax' inorganic compounds had been heightened by earlier consultations with Dr Alfred Smee (1818–77). Schaaf has directed our attention to the important role played by this talented young surgeon and scientist in enabling the discoveries that were to follow.<sup>20</sup> Smee's interest at the time lay in the exciting new sub-science of electrochemistry, which was then enjoying its golden era, following the invention of the galvanic battery by Alessandro Volta (1745–1827), and the thrilling use made of it in 1807 by Sir Humphry Davy (1778–1829), who had harnessed its electric power to 'tear their elements asunder' and for the first time isolated the alkali metals, potassium and sodium.

By 1840, the *Experimental Researches on Electricity* by Michael Faraday (1791–1867), Davy's assistant and successor at the Royal Institution, had established the quantitative basis for this new branch of science. The design of powerful batteries had been improving steadily at the hands of Wollaston, Daniell and Grove; and Smee himself had introduced a further improvement in the electrode construction of a large battery for his own electrochemical researches.<sup>21</sup> The electrodeposition of metals, then called electrotyping, was becoming a craft industry, producing such curios as the copper-plated cucumber prepared by Smee, which was shown to Queen Victoria — whose enquiring finger promptly poked a hole in it. Like photography, electrotyping could enable the duplication of art works — though from moulds rather than negatives — which explains its designation at the time as 'the sister art of heliography'.<sup>22</sup>

Smee also employed his battery as a new means for preparing chemicals that had previously been rather inaccessible. One such substance was then variously referred to as the 'ferrosesquicyanuret of potassium' or 'red ferrocyanate

of potash' or 'red prussiate of potash',<sup>23</sup> but we can now identify it by the modern name of potassium ferricyanide.<sup>24</sup> Herschel was aware of Smee's achievement, since the latter had read his paper before the Royal Society on 18 June 1840, and had subsequently published it in the *Philosophical Magazine*.<sup>25</sup> The chief outcome of this research was to make this bright-red, soluble chemical much more readily available in a pure form, because previous methods of preparation, dating from the substance's discovery by Leopold Gmelin in 1822,<sup>26</sup> had usually resulted in a product that was contaminated by impurities. In his 1840 paper, Smee described how he could prepare potassium ferricyanide from the commonplace and widely-available potassium ferrocyanide. He stated that this new technique of electrolytic oxidation could also be applied in principle to other analogous inorganic substances — a possibility that must have stimulated Herschel's original enquiry of him for 'deeply-coloured salts'. Shortly after his appointment as surgeon to the Bank of England, Smee responded by sending Herschel a specimen of potassium ferricyanide early in 1842. On 23 April, Herschel made the following entry in his Memoranda:

### Photography. Photochromy.

Non Argentine, Mineral substances (F3/2CP)<sup>27</sup>

Smee's Red Ferrocyanate of Potash washed on paper gives it a fine pale green colour. April 23. 1842. The spectrum thrown on this paper acts slowly but about as fast as on Guaiacum ... When the paper is thrown onto water the impression becomes stronger, loses its Violet ruddiness & turns to a fine prussian blue. ... a wash of very dilute acid ... immediately developed a strong blue impression, having the above character. This paper will prove valuable. Try other metallo-cyanates of Bases.<sup>28</sup>

This is the first recorded observation of Prussian blue being formed for a photographic purpose by the action of light on potassium ferricyanide, so it represents the moment of discovery of the first cyanotype process, although this name still lay in the future. The significance of this observation impressed Herschel sufficiently to mention it also in his general diary entry for 23 April 1842: 'Discovered the Photographic property of the Red Ferro sesquicyanuret of Potassium'.<sup>29</sup>

'Discovery' certainly seems a more appropriate word than 'invention' to describe this moment of photographic innovation.<sup>30</sup> But the next day Herschel was already seeking ways to improve this non-silver photographic process, and he began making images by its means, as is evident from the following entry in the Memoranda:

### Photography.

Non Argentine. Sesqui Ferrocyanate of Potash. F3/2CP

April 24/42. Various modes of improving colour & increasing action tried. 1. Pure water destroys the Dove colr first & washes away the yellowish pink border. It also darkens the impression to a good blue 2. Dilute Sulc Acid developes a much stronger blue. 3. Weak sulphate of soda washes the superfluous salt well away with no injury to the blue wh is quite insoluble in neutral salts. 4. Very weak perchloride of Iron acidulated with S. Acid, develops a deep & most superb blue. But the ground also is somewhat blued. Tried it for

copying engravings It does them very beautifully, but the copies are *negative* in the lights are blue the shades white. They are best fixed by very weak sulphuric acid — a barely perceptible acidulation — If Chlor Iron be added the ground gets blued.<sup>31</sup>

Can we detect in these words a hint of surprised disappointment that this process had proved to be negative-working? Although it would, therefore, be well suited to making positive prints from camera negatives, Herschel's preferred *modus operandi* at the time was to make contact prints of 'positive' images, usually steel engravings (figure 1), by means of positive-working processes such as the bleaching of dyes (figure 2).<sup>32</sup> The pictures resulting from a negative-working process would require a second printing — or 're-transfer' as he called it — to restore their correct tonality and handedness, and he realized that this would entail a loss of definition that was inevitable with a paper substrate (figures 3, 4). Herschel would soon devote considerable effort to devising a positive-working version of the Prussian blue process, in the attempt to circumvent what he saw as this disadvantage. But before that became possible, there was one other chemical ingredient, previously unknown to him, that was destined to be introduced into the process, with the consequence of greatly enhancing the sensitivity to light and the speed of printing in Prussian blue.

The 'list of prepared papers' in the Memoranda shows that Herschel received a further sample of potassium ferricyanide from Smee on 27 April,<sup>33</sup> and promptly employed it to make more Prussian blue negative 'copies' from engravings, one of which he sent to Smee. This brought an acknowledgement from Smee dated 10 May 1842, which reveals that he was already well aware that Prussian blue would result from the action of light on potassium ferricyanide, especially when mixed with a ferric salt:

Allow me to return you my thanks for your beautiful and interesting photograph which I presume was executed with the red salt in conjunction with a persalt of iron as that compound invariably deposits Prussian Blue under the combined action of air and light. I trust that by variety of the manipulation you will be enabled to adopt it to the camera.<sup>34</sup>

Smee was no stranger to the newly invented technology of photography. As early as May 1839, only a few months after Talbot's first disclosure of his achievement, Smee published an account of 'photogenic drawing' in the *Literary Gazette*, in which his observations on the best proportions for the sensitizing chemicals and the choice of the paper were both perceptive and useful.<sup>35</sup> In view of this prior photographic experience, and his awareness of the ferricyanide photochemistry implied in the quotation above, we might speculate why Smee had not employed potassium ferricyanide to make photograms at least; it appears that he very narrowly missed the distinction of himself becoming the inventor of the cyanotype process. It would, however, transpire that his hope it might be usable in the camera proved unfounded. Had matters rested here, it is unlikely that Herschel's discovery would have developed into an important invention — the commercially viable blueprinting process — because potassium ferricyanide, by itself, is of very low sensitivity, and demands inconveniently lengthy exposures even to





Figure 1. A. Penley, *Rosolia*, engraved by P. Lightfoot. Published in: *Friendship's Offering; and Winter's Wreath*, T. Pringle (ed), London: Smith, Elder & Co. 1837, plate X. The deterioration of this engraving used by Herschel for contact-printing is due to waxing, to make the paper base more translucent. National Museum of Photography, Film & Television.



Figure 2. Sir John Herschel, *Rosolia*, positive-working cyanotype (fixed with mercuric chloride) printed by Herschel on 17 August 1842, directly from the engraving shown in Figure 1. This is one of 15 varied specimens sent to Robert Hunt on 2 October 1842. National Museum of Photography, Film & Television.



Figure 3. Sir John Herschel, *Lady and Lute*, silver salted paper print from an engraving by John Cochran, c.1830, printed by Herschel on 13 October 1839. Made on 'thin blue wove post', this 'internegative' has been rendered highly transparent by waxing. Museum of the History of Science, Oxford.



Figure 4. Sir John Herschel, *Lady and Lute*, negative-working cyanotype (using the 'standard' formula) printed by Herschel from the internegative shown in Figure 3, and called by him a 're-transfer'. Museum of the History of Science, Oxford. See A. V. Simcock, *Photography 150: Images from the First Generation*, Oxford: Museum of the History of Science, 1989, 22.

bright sun.<sup>36</sup> But Smee's letter of 10 May went on to suggest the key chemical that was to unlock an entire photographic treasure-trove for Herschel:

There are two salts which of late have been used in Medicine having been vamped up by the Chemists and Druggists. The Ammonio Citrate and Ammonio Tartrate of Iron which are perfectly soluble and give very dark solutions. I mention them thinking it just barely possible that they may not have found their way into your laboratory and should my anticipation be correct it will afford me much pleasure to send some of each.

This deferential tone is what we might expect from the 23-year-old Smee, a newly-elected Fellow of the Royal Society, addressing the 50-year-old Herschel, already one of the most distinguished elder statesmen of British science. Presumably, Smee did not realize that he was placing in Herschel's hands the key to the best method for cyanotype and several other processes besides, but simply thought that the 'dark solutions' might lend themselves to bleaching by light. Although they were not difficult to prepare, the 'Ammonio Citrate and Ammonio Tartrate of Iron' were rather new substances on the chemical scene. Interest in them had been stimulated by the well-appreciated pharmaceutical benefits of iron tonics, dating back to Bestuscheff's 'tincture'.<sup>37</sup> It is evident from his reply to Smee that Herschel had had no prior knowledge of these salts, which is not surprising since they do not feature in the pharmacopoeias until 1842.<sup>38</sup> Thereafter, druggists began to promote them as 'chalybeate remedies' (indeed, they are still valued as iron tonics today),<sup>39</sup> but they did not become commonplace on the pharmacy shelves for another year or two. Herschel soon followed Smee's recommendation to try them — photographically, rather than medicinally — and immediately discovered that they were highly sensitive to light. His tests of the substances that he abbreviated as 'ACI' and 'ATI' are of uncertain date, however, because his Memoranda relating to these experiments appear to have been written up retrospectively. This was an uncharacteristic lapse for such an impeccable keeper of scientific records. Is it possible that the excitement of the discovery was so great as to distract him from a lifetime's discipline of systematic note-keeping? Herschel's letters to Smee are lost,<sup>40</sup> but fortunately he made an approximate copy of his reply, 'Substance of letter to Smee' on 15 June 1842, which clearly displays his excitement and pleasure at the richness and variety of processes that his discovery of light-sensitivity in 'ACI' had made possible:

I cannot help thanking you for your mention in one of your late notes to me of the Ammonio citrate and Ammonio tartrate of Iron as highly coloured salts. The former of these salts I have procured and examined, and it has furnished me with an infinity of beautiful photographic processes, both in conjunction with your Ferrosesquicyanate and with other ingredients. I take the liberty to enclose you a specimen or two, to appreciate which they should be wetted, laid on white paper and examined with a pretty strong magnifier. This process if you should happen to attend next Thursday's meeting of the R. S. you will hear described under a name I have invented to give it in imitation of Mr. Talbot's Calotype — viz. — Chrysotype — from the use of Gold as a stimulant to bring about the dormant picture which the action of light produces on paper prepared with this salt. It is one of the most striking and magical effects which has yet turned up

in photography, the Calotype and Argyrotype (Daguerreotype) themselves not excepted.<sup>41</sup>

The chrysotype process, although startlingly beautiful, never took its promised place in the photographic repertoire: far from rivalling the calotype in general practice, it was destined to be dismissed as impractical, unsatisfactory and obsolete by all the major photographic authorities of the nineteenth century.<sup>42</sup> However, Herschel's original conviction concerning the excellence of printing in gold has finally been vindicated by the writer in recent years.<sup>43</sup>

The 15 June 1842 was also the day on which Herschel's long and important paper, entitled 'On the Action of the Rays of the Solar Spectrum on Vegetable Colours, and on some new Photographic Processes' was accepted for publication in the *Philosophical Transactions of the Royal Society*. Part of this paper was read before the Society on 16 June, but it was not to appear in print until September. It will be convenient to refer to this seminal work as 'the 1842 Paper'.<sup>44</sup> It was here that Herschel first publicly described the making of prints in Prussian blue from potassium ferricyanide alone, as follows:

202. ... A beautiful example of such deoxidising action on a non-argentine compound has lately occurred to me in the examination of that interesting salt, the ferrosesquicyanuret of potassium, described by Mr. Smee in the *Philosophical magazine*, No. 109, September 1840, and which he has shown how to manufacture in abundance and purity by voltaic action on the common, or yellow ferrocyanuret. ...

203. Paper simply washed with a solution of this salt is highly sensitive to the action of light. Prussian blue is deposited ... After half an hour or an hour's exposure to sunshine, a very beautiful negative photograph is the result ...<sup>45</sup>

The relatively lengthy exposure needed here should be noted (indeed, Herschel's 'half an hour' tends towards an optimistic underestimate); it contrasts with the very short exposures, of a few minutes only, which are all that is required when ammonium ferric citrate is employed.

It is clear from the 1842 Paper that, by June, Herschel had also made cyanotypes (but not yet named them thus) by exposing a mixture of ammonium ferric citrate and potassium ferricyanide — the recipe that has endured as the standard practice until the present day:

206. If in lieu of the perchloride of iron, we substitute a solution of that curious salt the ammonio-citrate of iron, the photographic effects are among the most various and remarkable that have yet offered themselves to our notice in this novel and fertile field of inquiry. The two solutions<sup>46</sup> mix without causing any precipitate, and produce a liquid of a brown colour, which washed over paper is green (being strongly dichromatic). If this be done under the prism, the action of the spectrum is almost instantaneous, and most intense. A copious and richly coloured deposit of Prussian blue is formed over the blue, violet and extra-spectral rays ...<sup>47</sup>

Here the chronology of Herschel's experimental Memoranda is once again anomalous, in that they do not record such a test being made until 10 August 1842. This may indicate another lapse brought on by the excitement of the work in hand, for there can be no doubt that Herschel had already made the first 'standard cyanotypes' in June.<sup>48</sup> By this time, the serendipitous discovery had matured into a spirit of calculated invention using the ferric processes. Herschel had



proved that the greater part of the light sensitivity could be attributed to the ammonium ferric citrate, rather than the potassium ferricyanide, and his understanding of the photochemical basis for its 'deoxidizing' behaviour enabled him to make reasoned applications of this chemical knowledge in several different ways, such as the reduction of noble metal salts, as exemplified by his chrysotype process.

The Memoranda reveal that Prussian blue printing was totally eclipsed during the intervening month of July by Herschel's endeavours — again employing the marvellously versatile ammonium ferric citrate — to make pictures in mercury and gold, whose striking beauty captivated his undivided attention. His account in the 1842 Paper reveals a glimpse of the seductive delights of mercury prints:

229. ... affords pictures of such force and depth of colour, such velvety richness of material, and such perfection of detail and preservation of the relative intensities of the light, as infinitely to surpass any photographic production I have yet seen, and which indeed it seems impossible to go beyond.<sup>49</sup>

Lest the reader should feel tempted by this eulogy to throw all aside in favour of a search for mercury salts, it would be prudent to take note of Herschel's next sentence: 'Most unfortunately, they cannot be preserved'.<sup>50</sup>

The following week in August, however, saw Herschel's return to printing in Prussian blue, with fresh endeavours to refine and perfect the processes. His chemical logic suggested that a complementary, positive-working system could be achieved by employing not the ferricyanide but the commonplace ferrocyanide of potassium, in conjunction with ammonium ferric citrate. On 16 August 1842 he wrote the name 'cyanotype' in his Memoranda for the first time, to describe such a positive-working process, but the results that it yielded, as he later admitted in his paper of 1843, usually fell far short of giving satisfaction:

232. The positive cyanotype process described in Arts. 219, 220 of my papers, though beautiful in its effect (especially during the first few minutes of the appearance of the picture), is very precarious in its ultimate success ... this process, though exceedingly *easy* in its manipulations, could not be recommended as practically useful.<sup>51</sup>

By the end of August he had accumulated sufficient new results to justify adding a substantial postscript to his 1842 Paper, which was still awaiting publication by the Royal Society. It is in this postscript, dated 29 August 1842, that the name 'cyanotype' appears in print for the first time, but by then Herschel expressed a preference for it to be understood as a name embracing all the processes, both positive- and negative-working, which resulted in an image of Prussian blue:

219. *Cyanotype*. — If a nomenclature of this kind be admitted (and it has some recommendations), the whole class of processes in which cyanogen in its combinations with iron performs a leading part, and in which the resulting pictures are blue, may be designated by this epithet.<sup>52</sup>

We can do no better than respect Herschel's preference in our nomenclature today (contrary to the view of some bibliographers who take 'cyanotype' to mean only the positive-working process),<sup>53</sup> but the epithet should be qualified when necessary to make distinction between the differ-

ent variations of cyanotype process. Herschel then goes on to make an excusable overstatement: 'The varieties of cyanotype processes seem to be innumerable'.

From the observations in the 1842 Paper together with the notes in the Memoranda, we can distinguish no less than fifteen methods that Herschel had devised for making images in Prussian blue. Smee provides an illuminating postscript to this highly innovative episode, in a letter dated 29 September 1842, which was evidently his reply to a letter from Herschel which is lost:

The salts of iron to which you allude are neither children of mine by birth nor by adoption and the only circumstance which induced me to recommend them to your notice was their deep colour as perhaps you may recollect that a long time since you asked for specimens of any high coloured metallic salts not commonly met with. I know nothing about the salts further and had not the slightest idea that they could be used for Photographic purposes and did not even know the purpose for which you were likely to want dark coloured salts.<sup>54</sup>

This response implies that Herschel, ever scrupulous in acknowledging the priority of fellow scientists' discoveries, must have enquired whether Smee was the discoverer of ammonium ferric citrate and ammonium ferric tartrate, to determine if he should be accorded a 'proprietary acknowledgement' or wished to make use of them photographically himself. Smee's disavowal of any priority has a self-effacing tone, but he deserves great credit for directing Herschel's footsteps down such a fruitful path. Herschel's original search for 'dark coloured salts' had been founded, of course, on his hope that some of them might be susceptible to bleaching by light, and thus provide direct positive processes. In the event, the successful photochemistry proved to be quite the converse, but it is a mark of Herschel's great qualities as a scientist that he was able to turn these serendipitous discoveries into good inventions.

To take a contrary view, for a moment, from our present vantage point of chemical hindsight, we might have expected a man of Herschel's knowledge to have anticipated the photographic value of 'salts of iron with the vegetable acids', like ammonium ferric citrate, long before Smee pressed them upon him. Ten years earlier, while in Hamburg, Herschel became aware of the aforementioned researches just published by Döbereiner in 1831 on the decomposition by light of ferric oxalate (a compound similar to the citrate).<sup>55</sup> It is a remarkable omission on Herschel's part never to have made use of, nor ever referred to, the photosensitivity of this substance, or to its discoverer, Döbereiner. Very much later, in 1864, on an occasion when Herschel was obliged to defend his priority over the invention of cyanotype, he showed by his retrospective comments on 'these ferruginous combinations with vegetable acids', that he was well acquainted with the ferric oxalate possibility, but contented himself with the dismissive observation that it 'differs only from the processes described in §218 of the paper above cited ... by the substitution of the oxalic for the citric and tartaric acids, which, from the habitudes of that acid in general, might have been predicted'.<sup>56</sup>

It is nevertheless surprising that an avid experimentalist

like Herschel should never have tested the properties of ferric oxalate, of which he must have been aware at the time of his 1842 discovery. Even if his sense of propriety forbade him from taking up the work of another scientist, we might at least have expected some citation or comment from him concerning the relevance of Döbereiner's discovery. This photochemistry was familiar to Robert Hunt (1807–87), the author of the first manual on photographic processes, who was moved to comment tactfully in his 1844 edition on Herschel's omission:

So extensive have been the researches of the distinguished philosopher, whose labours I have so frequently quoted, particularly into the action of the sun's rays on the salts of iron, that little can be added to his published information. It may not, however, be uninteresting to add a few brief remarks on some of the salts of iron, to which Sir John Herschel has not extended his observations, or at least which have not been recommended by him as photographic agents.<sup>57</sup>

Hunt offers no explanation for the lacuna in Herschel's research, but goes on to describe his own experiments with ferric oxalate, which was to prove a very popular photosensitive salt, destined to be used successfully by several other photographic innovators in the years to come.<sup>58</sup> Herschel's total silence on this subject may have resulted from his highly developed code of scientific ethics being offended by much earlier actions on the part of Döbereiner. In the 'pre-photographic' year of 1831, Herschel had discovered that a particular platinum salt solution was sensitive to light, and threw down a white precipitate of 'platinate of lime' when irradiated.<sup>59</sup> Upon hearing about Döbereiner's parallel researches on iron salts, Herschel hastily had his platinum work published, to establish his priority in having observed these photochemical phenomena nearly two years previously, and to announce his intention of continuing with a chemical analysis to identify the products.<sup>60</sup> Herschel's result was quickly confirmed in Germany by repeating the experiment, and acknowledged with a published declaration that there was no intention of further trespassing on Herschel's field.<sup>61</sup> Despite this disavowal, Döbereiner subsequently initiated and supervised a research project into the analysis of Herschel's 'platinate of lime', in order to determine a formula for the photoproduct, which Döbereiner published in 1835, during Herschel's sojourn in the Cape of Good Hope from 1834 to 1838.<sup>62</sup> While it was not in Herschel's nature to harbour resentment, this action may have left him with a natural antipathy that he expressed only by completely shunning the work of his rival in photochemistry.

Without a close examination of Herschel's experimental records in the Memoranda, no one can fully appreciate the multiplicity of intertwining threads of investigation that he was following simultaneously in 1842–43. Multitudes of domestic plants had been pressed into service for their coloured juices, and even dog's urine and an 'extract' from his pet boa-constrictor! Salts of platinum, iridium, gold, mercury, iron, lead, silver and chromium all fell within the orbit of his experiments. Many of these led him up blind alleys; for instance, three pages of his cyanotype Memoranda, which describe experiments following up the apparently promising results of adding ferric iodide to the cyanotype

mixture, are struck through, endorsed with the later revocation in Herschel's hand: 'Hunting on a wrong scent'. Fruitless attempts to render permanent those exquisite prints in mercury also accounted for a large portion of his efforts at this time, and in a letter to Talbot we can hear a hint of exasperation in his complaint about their evanescence: 'It has led me such a dance as I never before was led by any physical enquiry and I have not yet succeeded in reducing it to a definite and certainly successful process'.<sup>63</sup>

Herschel directed more endeavour towards perfecting a positive-working cyanotype process than to the negative-working counterpart. The latter had simply fallen into his hands with a minimum of experimentation, but the former was always his preferred objective, probably because he saw it as providing a blue primary for a direct colour photographic process.<sup>64</sup> Yet it proved so variable in quality, and so difficult to fix, that he pronounced it 'could not be recommended as practically useful'. In an attempt to inhibit the spreading of the image substance, Herschel tried adding gum Arabic to his potassium ferrocyanide developer. Had he added it to the sensitizer, he might have met with greater success.<sup>65</sup> Later, in order to achieve fixation without degrading the image, he enlisted the dangerous poison 'corrosive sublimate' (mercuric chloride), but both toxicity and cost militate against this as a practical process. It is remarkable that some surprisingly fine specimens of Herschel's positive cyanotype still survive from 1842, especially in the collection of the National Museum of Photography Film & Television.

It seems appropriate to end this tale of discovery and invention with a sobering reflection on the fickle nature of Herschel's scientific muse. By the autumn of 1842, he had performed more than one thousand photographic experiments, most of which proved ultimately fruitless. Herschel's greatest and most enduring success, which was to give rise to a major industry lasting a century after his death, was the negative-working cyanotype process — and this he actually accomplished with just *three* test-papers.<sup>66</sup>

Cyanotype has always been an undervalued process which the standard texts on photography usually dismiss in a paragraph, or less. Despite its marginalized status this medium deserves to be more widely appreciated for the added light that it sheds upon the early development of photography — a light which is reflected in just one facet of the researches of a great polymath. Herschel's cyanotype serves us as a paradigm for the extraordinary interactions between chance, intuition and inductive logic, as they blended within an outstanding scientific mind of the nineteenth century.

## Notes

The author's book, *Cyanotype: the history, science and art of photographic printing in Prussian blue*, is published by the Science Museum, London, for the National Museum of Photography, Film & Television, 1998.

1. Helmut and Alison Gernsheim, *The History of Photography from the Camera Obscura to the Beginning of the Modern Era*, New York: McGraw-Hill 1969; Beaumont Newhall, *The History of Photography, 1839 to the Present Day*, New York: Museum of Modern Art 1949; J. M. Eder, *History of Photography*, trans. Edward Epstean, New York: Dover Publications 1978. The recognition of photosensitivity in silver halides can be traced back to Schultze in 1727.



2. R. Taylor and I. J. Schaaf, 'The Talbot Collection at Bradford', in *Henry Fox Talbot: Selected Texts and Bibliography*, ed. Mike Weaver, Oxford: Clarendon Press 1992, 131.
  3. Sir J. F. W. Herschel, *MS Notebook vol III* (3 March 1840), 427, Science Museum Library, London.
  4. Mike Ware, *Cyanotype: the history, science, and art of photographic printing in Prussian blue*, London: Science Museum and National Museum of Photography, Film & Television 1998.
  5. I. M. Eder, *History of Photography*, trans. Edward Efstean, New York: Dover Publications 1978, 86, 101.
  6. I. F. Dobereiner, 'Chemische Thätigkeit des Lichts und Erzeugung des (neutralen) Humboldts auf chemischem Wege', *Jahrbuch für Chemie und Physik von Schweigger Seidel* 62 (1831), 86–90.
  7. Ware, *Cyanotype*.
  8. I. Parnell, *The Life and Labours of John Mercer*, London: Longmans, Green & Co., 1886. I am indebted to Owain Davies for bringing this quotation to my attention, and to the late Harry Miligan for first acquainting me in 1984 with Mercer's researches. Although ferric nitrate is not an organic salt of iron, it was doubtless the cellulose of the cloth that provided the oxidizable material.
  9. His later contributions are summarised in Parnell, *The Life and Labours of John Mercer*, and in Dr Stella Butler's lecture, *Colouring Material: John Mercer (1791–1866) and his Photographs on Cloth*, delivered to the Historical Section of the Royal Society of Chemistry, in June 1987 at the Liverpool Maritime Museum.
  10. Larry J. Schaaf, *Out of the Shadows: Herschel, Talbot and the Invention of Photography*, New Haven & London: Yale University Press 1992. The history of this quest, and the fascinating story of the interaction between these two gifted men and their peers, is unfolded with clarity and scholarship in Dr Schaaf's book, which provides a complete historical background to this episode.
  11. I am grateful to the staff of the Harry Ransom Humanities Research Center, University of Texas at Austin, for supplying photocopies of the Memoranda and for permission to quote from this material.
  12. I am indebted to A. V. Simcock of the Museum of the History of Science, Oxford, for access to this archive, and for his valuable observations upon it.
  13. I acknowledge the sponsorship of the National Museum of Photography, Film & Television at Bradford in carrying out this work, and am grateful to the curatorial staff for their cooperation and help in affording me access to the Collection.
  14. I thank the Librarian of the Royal Society for making this archive available, and for permission to quote from it.
  15. Sir J. F. W. Herschel, *MS Notebook vol. III*, Science Museum Library, London.
  16. The sun was, of course, the only practicable light source available to the early pioneers in photography, and all experiments were at the mercy of the vagaries of the weather.
  17. Letter, Herschel to Talbot, 21 April 1842, NMPFT 1937–4900. See *Selected correspondence of William Henry Fox Talbot 1823–1874*, ed. L. J. Schaaf, London: Science Museum and National Museum of Photography, Film & Television 1994, 36, and Schaaf, *Out of the Shadows*, 126.
  18. 'Letter from Sir John F W Herschel, dated July 31, 1841', *Report of the Meeting of the British Association for the Advancement of Science, Transactions of the Sections*, Plymouth: 1841, 40.
  19. Sir J. F. W. Herschel, 'On the Action of the Rays of the Solar Spectrum on Vegetable Colours, and on some new Photographic Processes', *Philosophical Transactions of the Royal Society* (1842), 181–215.
  20. Schaaf, *Out of the Shadows*, 127.
  21. A. Smee, *Elements of Electro-metallurgy*, see also: A. Smee, 'The Principle, Construction and Use of Smee's Battery' (transcribed from a paper read at the Society of Arts, 1 June 1840), Appendix V in E. M. Smee-Odling, *Memoir of the Late Alfred Smee, FRS*, London: George Bell and Sons 1878.
  22. G. Gore, 'Electro-Metallurgy' in *The Circle of the Sciences*, VII, *Practical Chemistry*, London: Griffin, Bohn, and Co., 1856, 4, 7–100.
  23. The prefix 'sesqui-' in the first of these names arose through a misconception at the time of the chemical formulation of this salt.
  24. The name 'potassium ferricyanide' does not conform to the most recent recommendations for chemical nomenclature (by the International Union of Pure and Applied Chemistry), but it probably has wider currency than the approved form 'potassium hexacyanoferrate(III)'. It also trips more easily off the tongue. It is regrettable that the important difference between this substance and potassium ferrocyanide should reside entirely in a single vowel. The IUPAC nomenclature is no better, because the latter becomes potassium hexacyanoferrate(II).
- Numerous errors have resulted from misreading this fine distinction. *Carrot lecter!*
25. A. Smee, 'On the Ferrosesquicyanuret of Potassium', *Philosophical Magazine*, series 3 17: 109 (September 1840), 193–201.
  26. I. Gmelin, *Schweigger's Journal* 34 (1822), 325.
  27. 'F3/20 P' is the personal abbreviation that Herschel commonly used in his notes for 'ferrosesquicyanuret of potassium', i.e. potassium ferricyanide.
  28. Sir J. F. W. Herschel, *Photographic Memoranda*, HRHRC, cat. no. W0268.
  29. Sir J. F. W. Herschel, *Diary 1833 to 1864*, Transcript in the Library of the Royal Society, London, MS583–85.
  30. The pathways of photochemical decomposition of potassium ferricyanide are complex, and have not been fully mapped out even today.
  31. Sir J. F. W. Herschel, *Photographic Memoranda*, HRHRC, cat. no. W0268.
  32. The identification of the engravings that Herschel used for his experimental prints and their published sources are described in Ware, *Cyanotype*.
  33. Letter, Smee to Herschel, 25 April 1842, Royal Society Library.
  34. Letter, Smee to Herschel, 10 May 1842, Royal Society Library.
  35. A. Smee, 'Photogenic Drawing', *Literary Gazette* (18 May 1839), 314–16.
  36. Herschel was soon to abandon this simple method in favour of a 'faster' formula, but it continued to be recommended for several years by writers such as Golding Bird, *The Elements of Natural Philosophy*, London: John Churchill 1854, fourth edn, 576.
  37. The extraordinary account of this nostrum, which was 'blended in light' may be found in Eder, *History of Photography*, 159.
  38. R. Christison, *A Dispensatory, or Commentary on the Pharmacopoeias of Great Britain*, Edinburgh: Adam and Charles Black 1848, 975.
  39. M. Taniguchi, H. Imamura, T. Shiota, H. Okamatsu, Y. Fujii, M. Toba, and F. Hashimoto, 'Improvement in Iron-Deficiency Anemia through Therapy with Ferric Ammonium Citrate and Vitamin-C and the Effects of Aerobic Exercise', *Journal of Nutritional Science and Vitaminology* 37: 2 (1991), 161–71.
  40. Smee's biography by his daughter, which is otherwise fulsome in cataloguing his achievements, (which were indeed considerable) makes no mention of this correspondence and collaboration with Sir John Herschel. See: Elizabeth Mary Smee Odling, *Memoir of the Late Alfred Smee, FRS*, London: George Bell and Sons 1878.
  41. Draft of a letter, Herschel to Smee, 15 June 1842, Royal Society Library.
  42. See, for example: J. M. Eder, *Ausführliches Handbuch der Photographie*, Part 13, 'Die Lichtpausverfahren, die Platinotypie und verschiedene Copirverfahren ohne Silbersalze', Halle: Wilhelm Knapp 1899, 203–04; G. Pizzighelli, and Baron A. von Hübl, *Platinotype*, trans J. F. Iselin, London: Harrison and Sons 1886, 35; Capt. W. de W. Abney and L. Clark, *Platinotype, its Preparation and Manipulation*, London: Sampson Low, Marston & Co. 1895, 156; Chapman Jones, *The Science and Practice of Photography*, London: Iliffe & Sons 1904.
  43. The application of some modern chemistry, 150 years on, has enabled me to devise a latter-day chrysotype process that is less profligate in its consumption of gold, and provides images as fine and permanent even as platinotypes, but of a greatly extended range of colours. See: M. J. Ware, 'Prints of Gold: The Chrysotype Process Re-invented', *Scottish Photography Bulletin* 1 (1991), 6–8; *idem*, 'Photographic Printing in Colloidal Gold', *Journal of Photographic Science* 42: 5 (1994), 157–61.
  44. Herschel wrote four papers on photographic processes, of which three were published in the *Philosophical Transactions of the Royal Society* in 1840, 1842, and 1843. His first paper, written in 1839, was withdrawn before publication, and was long thought lost until the MS copy was discovered by Schaaf. See: L. J. Schaaf, 'Sir John Herschel's 1839 Royal Society paper on photography', *History of Photography* 3:1 (1979), 47–60. For ease of future reference, Herschel numbered his 'articles' throughout these three published papers: the 1840 paper comprises §1 to §148; the 1842 paper comprises §149 to §216, and its postscript §217 to §230; the 1843 paper comprises §231 to §241.
  45. Sir J. F. W. Herschel, 'On the Action of the Rays of the Solar Spectrum on Vegetable Colours, and on some new Photographic Processes', *Philosophical Transactions of the Royal Society* (1842), 181–215.
  46. The other solution referred to here by Herschel is the subject of his preceding articles §202 to §205, namely Smee's potassium ferricyanide.
  47. Herschel, 'On the Action of the Rays of the Solar Spectrum', 203.
  48. The first use of ammonium ferric citrate (coated, by itself, on prepared paper number 724) is recorded in the Memoranda on 22 July, but the entry also carries Herschel's parenthetical remark '(omitted before)'; moreover, a later note on 26 August states that paper 724 was 'prepared



- two months ago  $\pm$ . It seems likely that Herschel forgot to allocate a prepared paper number to it at the time.
49. Herschel, 'On the Action of the Rays of the Solar Spectrum', 214.
  50. Herschel made strenuous efforts in trying to secure a viable mercury-printing process, which he had christened 'kelenotype' or 'celanotype'. At Talbot's suggestion this was temporarily renamed 'amphitype'. Although that same title was later re-adopted for other processes. But ultimately Herschel was unsuccessful, and the mercury process came to nothing, probably because the metal of the image is sufficiently volatile to evaporate completely within a few days. The amphitypes that can be identified among the forty-two indexed Herschel specimens at HRHRC are completely blank.
  51. Sir J. F. W. Herschel, 'On certain improvements on Photographic Processes described in a former Communication, and on the Parathermic Rays of the Solar Spectrum', *Philosophical Transactions of the Royal Society* (1843).
  52. Herschel, 'On the Action of the Rays of the Solar Spectrum', 210.
  53. L. Nadeau, *Encyclopedia of Printing, Photographic, and Photomechanical Processes*, Fredericton: Atelier Luis Nadeau 1989, 80.
  54. Letter, Smee to Herschel, 29 September 1842, Royal Society Library.
  55. J. W. Döbereiner, 'Chemische Thätigkeit des Lichts und Erzeugung des (neutralen) Humboldtits auf Chemischem Wege', *Schweigger's Jahrbuch* 62 (1831), 86, 90–96. An abstract of this paper was published in *Pharmaceutisches Central Blatt* 2 (August 1831), 383–85. It was subsequently translated into French as 'Influence chimique de la lumière et formation de la humboldtite neutre par un moyen photométrique' [sic], *Journal de Pharmacie et des Sciences Accessoires* 18: 3 (March, 1832), 117–123.
  56. Sir J. F. W. Herschel, *The Photographic News* 8:278 (12 February 1864), 82.
  57. Robert Hunt, *Researches on Light*, London: Longman, Brown, Green & Longmans 1844, 147.
  58. Most importantly, it formed the basis for Willis's Platinotype (1873) and Nicol's Kallotype (1889) processes.
  59. The circumstances of this discovery and its potential significance have been described by Schaaf, *Out of the Shadows*, 33–34. The substance is now more correctly described as calcium hexahydroxyplatinate(IV).
  60. Herschel saw a copy of Döbereiner's paper while he was visiting Hamburg; it stimulated him to write on 12 June 1832 to Daubeny, who agreed to read Herschel's paper on the photosensitivity of platinum(IV) chloride in solution to the Oxford meeting of the British Association for the Advancement of Science on 22 June 1832. This was subsequently published as: 'On the Action of Light in determining the Precipitation of Muriate of Platinum by Lime-water; being an Extract from a Letter of Sir John F. W. Herschel, K. H. F. R. S. &c. to Dr. Daubeny', *London, Edinburgh, and Dublin Philosophical Magazine* 1 (July 1832), 58–60.
  61. Herschel's paper (note 60) was translated and published in German: John F. W. Herschel, 'Ueber die Wirkung des Lichts als Ursache der Präcipitation des salzauren Platins durch Kalkwasser', *Annalen der Pharmacie*, 3: 3 (1832), 337–41. This transcript carries a long editorial footnote (signed only 'Br.') describing Döbereiner's work, part of which can be translated from the German thus: 'Following this communication from Döbereiner we further note that we have repeated Herschel's experiment and found it to be confirmed ... Thus a compound of platinum oxide with calcium oxide has been formed through the action of light. We have not made any analysis of this compound, however, in order not to anticipate Herr Herschel, and content ourselves by confirming the facts.'
  62. J. W. Döbereiner, 'Chemische Eigenschaften und physische Natur des auf nassem Wege reducirten Platins', *Annalen der Pharmacie* 14 (1835), 10–21.
  63. Letter, Herschel to Talbot, 31 March 1843, National Museum of Photography, Film & Television.
  64. This application was finally accomplished in 1898 in a tri-colour printing process due to Brewerton.
  65. The positive-working process using gum Arabic was eventually exploited by Pellet's patent in 1877.
  66. The 'prepared paper numbers' in the Memoranda that refer to the standard negative-working cyanotype process are 780, 784, and 793 — three out of a total of twenty-six prepared papers devoted to cyanotype processes of all kinds. It is estimated that Herschel probably made from these three papers no more than thirty-four specimens *in toto* of negative-working cyanotype prints; see Ware, *Cyanotype*.