Cyanomicon

History, Science and Art of Cyanotype: photographic printing in Prussian blue

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Table of Contents

Preface

The first monograph on *Cyanotype* was published by the Science Museum of London in 1999, but has long been totally out of print, and only accessible as a partially digitized version online at Google Books. My book was devoted to the study of photographic printing in Prussian blue, engaging with its history, aesthetics, practice, conservation and chemistry. Now, in response to kind requests, I have substantially restructured this text in a revised and extended edition that I intend to make freely available as a download from the World Wide Web:

For the time being, it will remain largely unillustrated. With its 700+ references to the literature and the WWW, I hope it may serve occasionally as a useful resource for historians, curators and conservators of photographs and students of iron-based analogue imaging – should any of these good folk ever find themselves as castaways upon the strange blue shores of cyanotype. For those other shipwrecked mariners – photographic artists exploring cyanotype printmaking as an expressive medium – I have included full practical instruction in the modern process.

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1 An Introduction in Monochrome

"Blue, darkly, deeply, beautifully blue"
Robert Southey (1774-1843)
Poet Laureate

Out of the whole gamut of printing techniques left to us by the earliest pioneers of photography, only one process survives unchanged to the present day: cyanotype. Yet its images still seem unnatural to many viewers; the intensity of Prussian blue invests them with an incongruity that has curbed the scope of this process ever since it first saw light in the dawn of photography. Cyanotype endures nonetheless, and is still practised in just the same way as 172 years ago. With the advancing sophistication of our photographic vision, its strange blue aesthetic is gaining a wider acceptance than hitherto; so the time now seems ripe for a review of cyanotype as an alternative medium of photographic practice.

1.1 The legacy of John Herschel

Photography in Prussian blue was discovered on 23rd April, 1842 by Sir John Frederick William Herschel (1792-1871), just over three years after Louis Jacques Mandé Daguerre (1789-1851) and William Henry Fox Talbot (1800-1877) had announced their independent inventions of photography in silver, using substrates of metal and paper, respectively. The successes of these pioneers in finally securing photographs in silver was the fruition of an idea that had been gestating for more than a century in the minds and laboratories of several leading natural philosophers.[1] In contrast, the birth of the silverless cyanotype was totally unexpected; it came, literally and metaphorically ‘out of the blue’, to a ‘single parent’. Why should the circumstances of these two major photographic innovations have been so different? An attempt to answer this question will be offered in the next chapter.

While Talbot was creating several thousand silver images and assembling them into a creative *oeuvre* that is now recognised as the richest vision in early photographic art,[2] his fellow-scientist Herschel, rather than making new pictures, was experimenting widely with the processes of photography, for he was motivated by a preoccupation with the medium rather than the message. As one of the leading physical scientists of his day, Herschel was driven by a desire to understand photochemical phenomena, and to enlist them as tools for probing the electromagnetic spectrum outside the narrow optical limits imposed by human vision. He sought to venture beyond the shortwave end of the visible spectrum, into the region of the ultra-violet or 'actinic' rays that had been discovered in 1801 by Johann Ritter. At the other end of the optical spectrum, he explored beyond the longwave visible limit, into the region of the infra-red or 'thermic' rays, which had been discovered in 1800 by his own father, the celebrated astronomer 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" [3]

As a practical objective, Herschel also clearly 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 to multiply his photographic images in printers' ink was ultimately realised in his method of 'photoglyphic engraving'. It is therefore a happy irony that it was Herschel who became the inventor of the first process for reprographic photocopying.

Over the years since his death in 1871, Sir John Herschel's original writings, unpublished personal memoranda, experimental notes, and specimen images have become somewhat dispersed globally; but the following chapters will attempt to re-unite those fragments of his scientific legacy that are concerned with the cyanotype process, and to interpret them in the light of a modern understanding of the properties of the image substance, Prussian blue. The reader will find that every text on 'alternative' photographic processes quotes a formula for the cyanotype which is claimed to be 'Herschel's original', but references are never cited in support, because his publications are not explicit on the exact formula. I have now resolved this issue by reference to Herschel's own experimental notes of 1842 (from the manuscript archive at the Harry Ransom Humanities Research Center of the University of Texas, at Austin) which reveal how he explored at least fifteen chemically distinct ways of making images in Prussian blue. It will become clear that limitations in the chemical knowledge of Herschel's day pre-conditioned his achievements to a significant extent, and that he owed much to a young scientist, Dr Alfred Smee (1818-1877), whose chemical expertise provided Herschel with information and actual samples of newly-synthesised substances that would prove crucial to his success.

1.2 Equivocal blue images

The history of the cyanotype has a rather periodic character; within its 172 years (as of 2014) we can distinguish three main phases of use. At first Herschel's invention was taken up only by a small élite of amateur botanists for the purposes of plant illustration. The most notable achievement was that of Anna Atkins who, during two decades from 1843, produced her now celebrated and highly-treasured albums of botanical photograms.[4] Nonetheless, in the Great Exhibition of 1851, the cyanotype process was represented by just one minor specimen, among a multitude of exhibits illustrating the burgeoning art-science of photography.[5] This lack of practice is an indication of the insignificant status accorded to cyanotype at the time, which may be attributable, at least in part, to inadequate published descriptions of the best methods (see §2.9). The process continued its sojourn in disuse for a further twenty years. Following Herschel's death in 1871, cyanotype was appropriated by entrepreneurs of a more commercial turn of mind than its true inventor, and exploited as a reprographic medium, although Herschel himself had previously demonstrated its use for copying text and images. The re-branded 'ferroprussiate' process also found some use by photographers as a cheap and easy option for proofing negatives, but its major market was for copying the plans in every drawing office of the world.

By the turn of the century, the acceptibility of cyanotype as a pictorial medium had been seriously inhibited, at least in Britain, by the intolerant response of critics to its powerful colour. The arbiters of contemporary taste in 'the art of photography' were at the time habituated to an aesthetic of monochrome images that were mostly brown, so they declared the unremitting blue of the cyanotype to be anathema. Foremost among these critics was Peter Henry Emerson, always characteristically vituperative in his condemnations:

> " … no one but a vandal would print a landscape in red, or in cyanotype." [6]

Even R Child Bayley expressed his disdain for the process in this sneering, but witty, observation from *The Complete Photographer* :

> "…as to printing methods, there is the simple "blue print", which survives, as the Darwinians tell us some of the lower forms of life survive, from the extreme simplicity of its structure. The blue print needs nothing but a good washing in water to reveal its full vigour (such as it is). … There are certain subjects which the colour is said

> to suit, and I live in the hope that one day I may see such a subject.” [7]

As late as 1922, the prevailing view that cyanotype was fit only for proofing negatives was reflected in E J Wall’s dismissal:

> “One rarely wants to print from an ordinary negative in the vivid blue of cyanotype, for the color is not suitable for ordinary views, except possibly ice and glacier scenes, and these can be much more effectively dealt with by the cyanotype toning of a bromide or development print.” [8]

But one writer who did not join the general chorus of condemnation in Britain was the noted professional photographer, Frank Sutcliffe:

> “An amateur of my acquaintance prints everything he does in cyanotype blue, and I must confess that looking through his prints from time to time gives me more pleasure than I get from looking at any other workers prints. They never give me neuralgia in the eyes.” [9]

Despite this interesting claim for their therapeutic value, cyanotypes were held in low esteem by the British photographic establishment, which deemed them both unacceptable for exhibition and unworthy of acquisition. The prevalence of this prejudicial view is apparent from historical evidence of a negative kind. If one searches the major British collections of photographic art for examples of the process, cyanotypes are found to be conspicuously absent. For instance, the Royal Photographic Society’s collection, which is an outstanding representation of nineteenth-century work, had not admitted a single cyanotype, as of 1999.[10] The Scottish National Portrait Gallery holds a magnificent photographic collection, restricted neither to Scotland nor portraiture, but has acquired only one small cyanotype.[11] Even the Victoria & Albert Museum can only boast, in addition to its modest fascicle of Anna Atkins, a relatively small number of recently-acquired twentieth-century examples.[12] The National Museum of Photography, Film, & Television, now rebranded as the National Media Museum, naturally has important holdings of early cyanotypes by Herschel and Atkins, but otherwise the later use of the process in the history of photography is represented only by a few anonymous architectural studies of little consequence. A similar state of non-representation seems to prevail in other major British collections. It must also be considered significant that the (otherwise admirable) *Charts for the Recognition of Photographic Processes*, devised in 1976 by Messrs Coe, Collings and Gill for the Royal Photographic

Society, completely omitted the cyanotype process from their scheme of things.[13] The third phase of cyanotype – its rehabilitation as an art medium – came only in the last two decades of the 20th century, with the rise of the 'alternative photography' movement, as we shall see.

1.3 Acceptance of blue photographs

Early prejudice against the cyanotype process did not prevail universally. In Paris, the collections of the Musée d'Orsay and the Musée des Beaux Arts contain substantial holdings of beautiful cyanotypes by Paul Burty Haviland and Henri Le Secq. In the USA, the collection of the George Eastman House also has specimens of Le Secq's architectural studies, among many other significant cyanotypes. In Canada, the collection at the National Gallery in Ottawa contains many interesting cyanotypes, including a fine series of ethnographic studies of Native North Americans by Edward Curtis. Neither was the process despised among the amateur community in North America, as it largely was in Britain. One handbook published in the USA refers to the process as 'capable of such beautiful results',[14] and John Tennant, the editor of the influential American periodical *The Photo-Miniature*, conducted quite a spirited defence in one of his issues of 1900:

> "This prejudice against the blue print because of its color is, in itself, curiously interesting. In every-day life we are inclined to be enthusiastic about everything blue, from the deep blue of the sea or the deeper depths of blue in a woman's eyes, to the marvellous blue of old Delft ware or the Willow plates of years ago." [15]

But there was one North American photographer who did apparently find the process unacceptable: the young Alvin Langdon Coburn. According to Nancy Newhall,[16] he deemed the process 'villainous', a rather sophisticated judgement at the time – for an eight-year-old!

1.4 Commercial use of blueprint

In Britain, the cyanotype suffered an almost total aesthetic boycott by photographic artists, connoisseurs, and curators until the last two decades of the 20th century; but in contrast, one can point to huge archives of cyanotypes where the utility of the process was the paramount consideration. The commercial success of the cyanotype process was owed, not to its pictorial use, but its reprographic facility. These applications have endowed our language with a new word: *blueprint* – a word that endures long after the process it described became obsolete because it has now taken on the expanded and more abstract meaning of "master plan".[17] The era of the blueprint as a copying process was heralded by the manufacture of the cheap, sensitized paper in huge quantities, and by the beginning of the 20th century its use for copying engineering and architectural plans had become universal in drawing offices. In 1918, a 30 foot roll of cyanotype paper a yard wide could be purchased for as little as 1s. 6d.[18] This was just as well, because consumption must have been enormous: the plans for a battleship, for instance, required 11,000 square feet of the material![19] Although it faced two or three competing processes, the blueprint held sway for eighty years as the foremost industrial reprographic process, and was only finally displaced in the mid-1950's in the UK, first by the diazo print medium, then by the invention of electrophotography, which enabled photocopying by entirely dry methods.[20] It is interesting to note that commercial production and use of blueprint paper, though dwindling, was still significant in 1972 in the USA, and production of the paper survives there still, albeit on a very reduced scale.[21]

1.5 Artistic renaissance of cyanotype

Today we come full circle in witnessing a second revival of the cyanotype process among contemporary photographic artists who, like the very first users, are obliged to hand-coat their own paper or, in some instances, more unusual surfaces. There is a case to be made for the re-habilitation of cyanotype as a fine printing medium, despite – or perhaps even because of – its powerful colour. It is not generally acknowledged that, if it is carefully executed with a good formulation, cyanotype is capable of great delicacy in tonal gradation which can equal any other photographic printing process.[22] It combines the advantages of very low cost, low toxic hazard, simplicity in manipulation, applicability to many types of surface, in very large formats if desired and, thanks to Herschel's magnanimity, all this without restriction by patent or commercial secrecy. The well-known vulnerability of cyanotypes to light and alkali is not a serious problem, if they are treated with nothing more than 'benign neglect'. From a general observation of historic specimens of photography in major archives, I can justify the claim that most 150-year-old cyanotypes have survived better than their silver counterparts of a comparable age.

Nonetheless, the cyanotype is still relegated to the role of humble Cinderella among alternative printing processes. It is generally treated as a poor cousin to silver, carbon, and platinum printing – although it would be inappropriate to press this metaphor too far – I am not implying that these other processes are the ‘ugly sisters’! The rest of this introduction will be devoted to examining some possible explanations for this lowly status. One reason may be that the process is perceived by some as so facile, cheap, and unsophisticated, that they think it is only worth practising by the unskilled. A conspicuous proponent of alternative processes has stigmatized cyanotype as ‘photography for five-year-olds’.[23] A second reason may stem from a deep-seated aesthetic rejection evoked by the incongruity of the blue image, when the colour is so seldom to be seen in nature. A third more sophisticated motive may be that, by inevitably rendering all that it touches in an uncompromising blue, the cyanotype is felt to devalue the very colour that historically had always been reserved by artists to embody a sense of preciousness.

1.6 A rare colour in nature

It is an observable fact that blue pigments are very rare in the natural world.[24] Let us take a chromatic survey of the everyday hues in the landscape, viewed through a chemist’s spectroscopic eye. The plant kingdom is mainly characterised by the green photosynthetic pigment, chlorophyll, enlivened here and there by the yellow, orange, and red of carotenoids in flowers and the turning leaves of autumn. Tree trunks and boughs display the deep browns of complex oxidised organic macromolecules, lignins and tannins, and the soil is similarly coloured with humic acids. Many rocks are stained with the reddish-browns of iron oxides. Living creatures often display the dark tones of melanin in hair and hide, which contrasts with the crimson of myoglobin and haemoglobin, showing through in the pink and red of flesh and blood.[25] The reader can savour the rarity of blue among all these familiar colours of nature, by contemplating, for a moment, the unnatural prospect of a plateful of blue food.[26] Blue dye is used to mark condemned meat and hopefully ensure its non-consumption. It may also be significant in this context that blue was the colour conventionally chosen for the glass of poison bottles in Victorian times.

There is only one obvious source of blueness in the world which accustoms us to our everyday familiarity with the colour: the light that comes from the vast hemisphere of a clear sky. The presence of this ubiquitous blue source does not contradict the rarity of blue as a pigment because the colour of the sky is not due to absorption, but to a selective scattering of light, an optical phenomenon first elucidated by John

Tyndall in 1869, and quantified mathematically by Lord Rayleigh in 1871.[27] Expanses of water often reflect the blue of the sky, and if the optical path length through the water is very long it does appear blue in transmission owing to a very weak absorption band in the red end of the visible spectrum.[28]

Even the other, rare occurrences of blue in nature prove often to be examples, not of pigmentation, but of 'structural colour'; that is, chromatic phenomena generated by optical physics rather than chemistry.[29] The blues to be seen in some birds' plumage, for instance, are not caused by pigment but by selective light-scattering from the feathers; the striking blue colour of some species of Morpho butterfly[30] and the iridescent blue carapaces of some beetles are likewise due, not to the absorption of light, but to optical interference effects, akin to those in an opal, a soap bubble, or an oil film on a water surface.[31] The one important exception that 'proves' the rule of rarity is the occurrence of blue organic pigments – certain members of the family of anthocyanine dyes – in some common flowers such as bluebells and cornflowers. These we particularly admire for the vivid chromatic accents that they bring to contrasts in the natural landscape. It is possible that this botanical coloration has evolved as an adaptive characteristic, endowing the plants with survival advantages by attracting pollinating insects, which see them standing out against a common green background. Bees, for example, are blind to red light but can see into the ultraviolet; a blue flower may be even more conspicuous to them than to us.

It is therefore comprehensible that the scarcity of blue dyestuffs among naturally-occurring materials has always conferred high status or ritual significance on the use of the colour in many early cultures. Indigo has been valued since 2500 BC. The best natural source is the *Indigofera* plant that occurs in India, as its name implies, although the woad obtained by the Picts from *Isatis* is the same dyestuff.[32] In the early Mesoamerican cultures *ca.* 800 AD, indigo from *Indigofera Suffruticosa* (the *Anil* plant) was incorporated into a clay, palygorskite, to provide the remarkably stable pigment, Maya blue.

A close chemical relative of indigo is Tyrian purple,[33] famously reserved as the dye for emperor's robes of Imperial Rome, and as the biblical dye *argaman* for rabbinical vestments in the Judaic tradition. Tyrian purple was first extracted by the Phoenicians from a Mediterranean mollusc, *Murex Brandaris*,[34] but can be sourced from several other species and, because it is formed photochemically in sunlight, it has even been employed for photographic printing.[35] It is curious to reflect that when Julius Caesar's invading legions fought the Picts in 58 BC, both the Emperor's robes and the tribesmen's skins were coloured with chemically similar dyestuffs, but of rather different cultural origins. With the common availability of synthetic blue dyes in modern times, the distinction conferred by blue clothing has become socially inverted, so we now have the *bleu de travail* of the French *ouvrier*, the 'blue collar worker' of British class culture, and the ubiquitous and commonplace 'blue jeans' of denim.[36]

1.7 Symbolic blue in art and religion

Given the universal scarcity of blue pigmentation in the natural world, we can understand why the cyanotype image might have been considered 'unnatural'. Its low status in photographic art, however, still remains somewhat paradoxical when we contrast it with the elevated role of blue in the traditions of painting. Of all the colours in the spectrum, blue held the place of honour among the pigments on the artist's palette. Patrons of great paintings were inclined to limit their expenses by stipulating how much ultramarine the artist might use in the work; for this was the finest, most costly blue then available, 'the queen of all the pigments', and it was made by grinding up the gem-stone lapis lazuli, which was mined only in Afghanistan, and therefore came from 'over the sea', hence *ultra mare*. In the history of painting, therefore, blue was always reserved for a noble role. The baby pharoahs of ancient Egypt were swaddled in clothing dyed with Egyptian blue – the first synthetic pigment, the recipe for which was lost in the 9th century, and only rediscoved in recent times.[37] Blue was also a prized pigment for the decoration of fine ceramics, as exemplified by the blue and white porcelain adopted in China, traded by Marco Polo, with some specimens dated 1351 finally ending up as the celebrated 'David Vases' in the British Museum collection.

The association with the colour of the celestial hemisphere adds an extra dimension to the symbolism of blue. Because it appears in the sky after the obscuring clouds are dispelled, blue is said to be the 'colour of truth'. C J Jung conjectured that:

> "…blue, standing for the vertical, means height and depth (the blue sky above, the blue sea below)." [38]

Jolan de Jacobi, in her study of Jungian psychology, says:

> “…blue, the colour of the rarefied atmosphere, of the clear sky, stands for thinking.” [39]

In a religious context, blue is the colour symbolising some of the loftiest sentiments: spiritual devotion, heavenly love, and innocence. In the traditions of Western religious art, for instance, the Virgin Mary’s mantle is invariably rendered in blue, and so is that of Christ during his ministry on earth.[40] In some of the most notable altarpieces of Christian art, the entire court of heaven is clad in blue.[41] In Byzantine art, the haloes of the principal figures are golden if they are mere mortal emperors and prophets, but sky-blue is used for the haloes of the spiritual beings. Blue is also the predominant colour used to decorate the churches of the Greek Orthodox tradition. In Indian religious painting, Krishna, one of the incarnations of Vishnu the Preserver, is always represented with blue skin:

> “Since the infinite empty space appears as deep blue in colour, it is but proper that Vishnu, the all-pervading cosmic power, be depicted as blue in colour.” [42]

J E Cirlot, in his work on symbols, notes that: ‘About the various shades of blue, ranging from near black to clear sapphire, there has been a great deal of speculation.’[43] He points out that there is not one perception of blue, but many. There is also an antithesis here between darkness and light: ‘Blue is darkness made visible.’ Cirlot reminds us that colour symbolism derives from several sources, and we should distinguish the mystical and esoteric from those associations forged by primitive logic and intuition, on which modern psychology would put more weight. The diurnal life of early humankind was dictated by the cycle of night and day; and night was when action had to cease. According to Lüscher, the dark blue of the night sky is therefore the colour associated with quiescence and passivity.[44] He goes on to claim that prolonged contemplation of pure dark blue has calming physiological effects on the central nervous system, reducing blood pressure and lowering the rates of pulse and respiration. Lüscher’s colour categories list the affective aspects of dark blue as tranquility, contentment, tenderness, love and affection.

Although there is a high degree of subjectivity in making all these associations between colour and human feelings, there seems to be a broad measure of agreement emerging from different sources on the significances of blue, especially when the depth of the colour is also taken into account. The first great antithesis of colour, according to the aesthetic theories of the painter, Wassily Kandinsky, lies between yellow and blue, between warmth and coolness, between advance and retreat, between overflowing the boundaries and contracting within them. Concerning blue, he observed:

> “Depth is found in blue...The deeper its tone, the more intense and characteristic the effect. We feel a call to the infinite, a desire for purity and transcendence. Blue is the typical heavenly colour; the ultimate feeling it creates is one of rest. When it sinks almost to black, it echoes a grief that is hardly human. It becomes an infinite engrossment in solemn moods. As it grows lighter it becomes more indifferent and affects us in a remote and neutral fashion, like a high cerulean sky.” [45]

1.8 Liberation from blue preciousness

In 1706 the discovery of the new pigment, Prussian blue, by an artists' colour-maker, began the liberation of painting from its inhibitions concerning the expense of the colour blue – a liberation that was completed in 1821 by the discovery of a recipe for synthesising ultramarine itself.[46] Thereafter, the history of painting is witness to a spectacular influx of blue; for instance, in the work of the French Impressionists, especially the landscapes and figure studies of Paul Cézanne, and in the powerful work of Picasso's ‘blue period’. The Expressionist school of Munich painters – the so-called Blaue Reiter – is epitomised by Kandinsky's ‘Blue Rider’, and the blue horses of Franz Marc are later manifestations of their devotion to this colour and its significance in the artistic portrayal of the spiritual side of life.

A turning point in the significance of the colour blue came when monochrome painter, Yves Klein, told French artists' colourmaker, Edouard Adam, of his search for the perfect blue. Adam faced Klein with a choice: *bleu de Prusse or bleu d'outremer*.[47] “There was,” said Adam, “no contest, and you can see why. Prussian Blue is sombre, good for shadows. Even in this windowless room, ultramarine glows.” But the real advance came when the *marchand de couleur* replaced the traditional binder of rabbit glue, which dulled the vibrancy of the colour, with a polyvinyl acetate resin called Rhodopas M, (from manufacturing chemists, Rhône-Poulenc). Mixed with ultramarine, Rhodopas allows the powdered ultramarine to retain its granular look, its matt depth. In 1960, Klein patented the new pigment under the number 63471 and the name, *International Klein Blue*.

The colour continues to exert a fascination, as may be read in the lyrical *Rhapsody in Blue* of Alexander Theroux, with its wide-ranging free associations of the artistic, historical, linguistic and sociological connotations of blue,[48] and in John Gage's art-historically oriented appraisal of a recent exhibition of modern paintings on a blue theme.[49]

To return to the aesthetic difficulties with the cyanotype: John Wood, in his essay, *The Art of the Cyanotype,* has been the first to try to discover a reason for the sense of unnaturalness or incongruity that appears to pervade this type of image.[50] Wood puts forward two antithetical interpretations of the colour blue, which have some affinities with those I have cited above. On the one hand, he asserts that blue is 'celebratory, affirmative and joyous'; on the other, that it has a 'dark side' which is 'sad, depressed, and disturbing'.[51] Wood is then able to propose this dichotomy of a 'joyous-ominous' colour as the reason for the 'peculiar magic' of the cyanotype, although it might be said that no objective evidence is offered to support these personal interpretations of the significances of the colour. Perhaps this idea is also encapsulated in the German concept *Schadenfreude* – taking pleasure in the sorrow of others.

Blue has recently been declared as the world's favourite colour. In recent surveys of randomly-chosen sample populations from several nations, the colour blue has emerged at the top of every poll. These surveys are part of the work of two post-modernist artists in the USA, Vitaly Komar and Alexander Melamid. Their method is to use telephone opinion polls to furnish sets of average aesthetic parameters for statistically 'ideal' paintings, according to the common taste of each national group. Their objective is to paint for each public exactly what it wants, which turns out in every case to be predominantly blue landscapes.[52]

1.9 Colour language and coordinates

In describing the various processes of cyanotype and the resulting images, it will be convenient to have a means of referring to colour in a way that can be conveyed unambiguously to the reader.[53] I propose to adopt here a simple notation that indicates the approximate location of the colour in a compact colour atlas, published as *The Methuen Handbook of Colour*,[54] where hue, tone and intensity are the three colour coordinates. The first number in this compilation, running from 1 to 30, corresponds to a page denoting the hue. Each double page spread presents six columns of colour patches, labelled A to F, which contain an increasing admixture of black, shading the tone from light towards dark. Within each column there are eight colour tablets, numbered 1 to 8 to indicate the increasing intensity or saturation of the colour, i.e. its relative brilliance or dullness. Some of the conventional names for the more saturated colours of blue are represented on this scale as follows:

17A8 Violet
18B8 Indigo
19C7 Royal blue
19D8 International Klein blue (French patent 63471)
20A8 Ultramarine (artificial)
20E8 Lapis Lazuli
21C8 Ultramarine (genuine)
21F7 Prussian blue (also called Berlin, Milori or Paris blue)
22B7 Cobalt blue
23A7 Cyan (azure blue)
23C7 Cerulean blue
23D7 Sapphire blue
24A8 Turquoise blue

Blue is the colour we see least efficiently, a fact that is quantified in the expression for the contributions of red, blue and green colours to the overall luminance of an image:

$$\text{RGB Luminance} = 0.3\text{R} + 0.59\text{G} + 0.11\text{B}$$

To conclude this chromatic introduction, it is my reluctant duty to record an etymological irony that completely undermines the very name of the cyanotype process and, in consequence, the title of this book. The prefix ‘cyano-’ derives from the Greek root ‘kyaneos’ (κυανεος), which is usually translated as ‘dark blue’; and the suffix ‘-type’ comes from ‘tupos’ (τυπος) meaning ‘strike’, *i.e.* ‘print’. However, in the development of language, it was commonly the case that blue was the last of the primary colours to receive a name; even today some primitive languages lack any expression for this colour concept.[55] Recent classical scholarship points to the likelihood that, in ancient Greek, ‘kyaneos’ simply meant ‘dark’, and the language of Homer therefore had no word for blue.[56]

2 The Invention of Cyanotype

"… sie macht sich nur durch Blut und Eisen."
("…It can only be carried out through blood and iron.")
Prince Otto Edward Leopold von Bismarck
Prussian House of Deputies, 28 January 1886. [57]

Cyanotype images are composed of the intensely-coloured substance Prussian blue, as it is known generally, except in the German-speaking world, where its preferred, and politically-correct name is *Berliner Blau* after the place of its discovery. This celebrated pigment deserves to be placed in its historical context because, fully a century before photography was invented, Prussian blue was already an important colour for artists,[58] and during that century it proved also to be a key substance for science, in opening up an entirely new area of chemistry.[59] Experiments on Prussian blue led to the discovery of a whole class of new compounds – the cyanides – which hover tantalisingly on the borderline dividing organic and inorganic matter, and which were therefore central to the debate surrounding the nineteenth-century doctrine of vitalism.[60] The political connotations of the name, Prussian blue, are purely accidental,[61] which makes even more remarkable the coincidence that it was indeed prepared traditionally from the raw materials of blood and iron.

2.1 A brief history of Prussian blue

Prussian blue has never been found in nature. There was no knowledge of it before the eighteenth century,[62] but this substance still qualifies as one of the earliest synthetic pigments,[63] dating from its first preparation probably in 1706, by a stroke of serendipity that befell an artists' colour-maker in Berlin, a Swiss immigrant called Johann Jacob Diesbach.[64] The chance occurrence of such a spectacular hue would have instantly attracted the attention of any colour-maker, for at the time there was a keen awareness of the limitations of existing blue pigments.[65] These were mainly provided by four substances, each suffering some disadvantage: ultramarine was very expensive – it had to be ground from the precious mineral, *lapis lazuli*, which was mined only in Afghanistan;[66] smalt, a cobalt blue glass used in ceramics, is rather weak in its covering power; azurite, a basic copper carbonate mineral, is unstable to heat and acids, turning into green malachite; and indigo, an organic dyestuff obtained from a plant native to India, is susceptible to fading.[67]

Diesbach identified the source of his accidental blue colour, and the manufacture of Prussian blue by Berlin chemist Johann Frisch began in 1708, and proved very profitable.[68] Diesbach announced its merits as a pigment in 1710;[69] but, no doubt in the pursuit of gain, he succeeded in concealing the method of its preparation until 1724, when it was finally disclosed in a publication by John Woodward.[70] Accounts of the original discovery therefore tend to be conjectural; the earliest, by G E Stahl, did not appear until 1731,[71] but one version has it that Diesbach was wanting to prepare a crimson lake by adding potash to a solution of cochineal, alum and iron(II) sulphate. Lacking any potash, he purchased some from a disreputable alchemist called Johann Konrad Dippel,[72] who had set up a laboratory in the same building. Dippel supplied Diesbach with an impure sample of potash that happened to be contaminated with a malodorous distillate of animal residues known as ‘Dippel’s oil’,[73] which provided the essential element - nitrogen - for Diesbach’s serendipitous reaction. Thus, the first preparation of Prussian blue, like several other notable chemical discoveries, can ultimately be attributed to the duplicity of an unscrupulous alchemist.[74]

There was no comprehension whatsoever of this reaction chemistry at the time, because nitrogen had yet to be identified as an element. It turned out that any nitrogenous animal matter (e.g. protein) could be used as a source for Prussian blue: hide, hair, feathers, horn, hooves or flesh. Dried ox blood, especially, proved a popular starting material. The recipes of the day were varied and complex, often entailing superfluous ingredients, and all were without doubt strikingly obnoxious in their manipulation, of which the following is a short and colourful example:

> “Six pounds of clippings of leather, six pounds of hoofs and horns, and ten pounds of common potash, are boiled together in an iron pot to dryness; the residue is then mixed with two pounds of crude tartar, and, by means of a strong fire, is brought into fusion. The lixiviation is conducted in the usual way, and a solution of five pounds of sulphate of iron, and fifteen of alum being added, a precipitate takes place, which is Prussian blue.” [75]

Prussian blue came rapidly to the notice of chemists. Pierre-Joseph Macquer, author of the first chemical dictionary, was attracted to the substance by his interests as government supervisor of the French dyeing industry, and he showed that it could indeed provide a fast dye for silk and wool.[76] His investigation in 1752 of the chief weakness of the pigment, the destruction of its colour by alkalies, had an important accidental outcome in the discovery of that useful salt ‘yellow prussiate of potash’ (potassium ferrocyanide),[77] prepared from the reaction of Prussian blue with potash (potassium carbonate).[78] Macquer, and other chemists of the time, also recognised that a volatile, colourless, inflammable substance, which they named ‘the colouring principle’, could be driven out of Prussian blue by heat, leaving a residue that contained iron. A result of great significance to chemical theory was later provided in 1782 by Scheele’s preparation of a solution of this ‘colouring principle’ from the action of sulphuric acid on Prussian blue, and his re-naming it as ‘prussic acid’. It is an unwitting testimony to Scheele’s manipulative skills, that he achieved this preparation without also making the uncomfortable discovery that prussic acid is a speedy, lethal poison.[79] Pure prussic acid was finally isolated in 1811 by Gay-Lussac, who determined its composition to be a simple compound of hydrogen, carbon and nitrogen,[80] formula HCN, later to be called hydrocyanic acid.[81] The German name for this colourless substance was *Blausäure* – ‘blue acid’ – in acknowledgement of its source. At this time, Gay-Lussac also coined the name that has become the common currency in this area of chemistry, a name that forms part of the title of this book. He called the –CN radical *cyanogène*, using the Greek roots κυανος χενναο (*kyanos gennao*) for ‘blue-generate’.[82] This acknowledgement of its colourful historical origins established the name for a whole class of important new compounds – the cyanides – which are, ironically, very often colourless.

So, a century after its discovery, Prussian blue, which is actually one of the most complex of these cyanides (ferric ferrocyanide), had furnished the means for isolating the simplest members of a new class of substance, whose name derives from its colour.[83] Thereafter, a rational basis for the chemistry of cyanides began to emerge, and in 1814 Gay-Lussac isolated the parent of them all, the gas cyanogen, having the simple formula $(CN)_2$. With the understanding that the fundamental unit in all this chemistry was just a simple radical consisting of carbon bonded to nitrogen,[84] the possibility was recognised of synthesising cyanides from purely inorganic materials, thereby making the use of organic animal residues unnecessary – most mercifully, in view of the ‘foetid vapours’ to which they gave rise. As a mark of approval for this achievement, the Society of Arts in 1837 conferred a medal upon Lewis Thompson for introducing a method of making potassium ferrocyanide by roasting charcoal with potash and iron filings at red heat, exposed to the atmosphere which provided the nitrogen.[85] Prussian blue could then be prepared from this product by reacting it with inorganic salts of iron.

By the 1780's Prussian blue was being widely manufactured in several places in Europe, including in Glasgow by the firm of Turnbull & Ramsay, Chemists,[86] consequently the pigment also came to be known as Turnbull's blue. Another Scottish user was raincoat inventor, Charles Macintosh, who established a manufactury in the alum-works at Lennoxtown in 1808 for dyeing wool, silk, and cotton with Prussian blue.[87] By the beginning of the nineteenth century, Prussian blue had become a popular artists' pigment; it was then widely used in European papermaking as an alternative to indigo for the colouring agent in the popular blue-toned papers,[88] and it was also a constituent of that everyday blue commodity, Stephen's Ink. In the USA it was used as a laundry whitener – 'Mrs Stewart's Blue'.

2.2 Light-sensitivity of iron salts

The cyanotype process is founded on a chemical reaction brought about by light acting on certain salts of iron. The notion that light can promote chemical transformations is, of course, central to the invention of photography, and its history has been described at length by Eder, and others.[89] We shall not concern ourselves here with the long-established sensitivity of silver halides to light, which provides the mainstream of the technical history of photography, but rather confine our attention to the less widely-known phenomenon of photosensitivity in iron compounds, which is of more recent discovery. The light-induced decomposition of an organic salt of iron was first recorded in 1831 by Johann Wolfgang Döbereiner (1780-1849), who observed that irradiation of an aqueous solution of ferric oxalate by sunlight forms a precipitate of ferrous oxalate (which was shown to be identical with the mineral Humboldtite) and evolves a gas, which proved to be carbon dioxide.[90] 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 well-known properties of Prussian blue. Such a connection could have hinted at the formation of the pigment as another means for making images photographically. But there is one little-known, pre-photographic observation in this respect. It was made by John Mercer (1791–1866), a Mancunian calico-dyer and printer, who became a self-taught colour chemist and finished as a Fellow of the Royal Society. In 1828 he 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 from his experimental notebooks:

> "I spotted a piece of white cloth with a solution of pernitrate 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." [91]

The pressure of maintaining his business deprived Mercer of the opportunity to pursue this pioneering observation any further until the 1840s, by which time photography had become well-established at the hands of other, more leisured, pioneers. The chance to be counted among the 'pre-inventors' of photography thus passed him by, owing to the unfortunate necessity for earning his living – a disadvantage not suffered by financially independent Victorian gentlemen-scientists, such as Talbot and Herschel. Mercer later made significant inventions of toning procedures for cyanotypes, as we shall see in §4.4.2 and §8.3, but these were only published in an insubstantial form, and subsequently re-invented by others. If we are seeking to identify an unsung hero of early photography, a worthy candidate might well be John Mercer.[92]

2.3 The first silver photographs on paper

In 1834, William Henry Fox Talbot, the inventor of photography on paper, began his experiments with silver salts as light-sensitive imaging materials. He evinced no particular interest in Prussian blue in his notebooks, although he did once record its formation, chemically rather than photochemically, on a sheet of paper treated with hydrochloric acid and potassium ferrocyanide, owing to ferric iron impurity in the acid.[93] It is significant that even after the invention of the cyanotype process, Talbot himself made no use of it; but, much later, he commented approvingly on its permanence in regard to the botanical prints of Anna Atkins (see §5.4), who had presented him with a copy of her cyanotype part-work, *British Algae: Cyanotype Impressions*.[94]

In January of 1839, stimulated by Talbot's announcement of his discoveries, Sir John Frederick William Herschel (1792–1871) took up the study of photographic phenomena. Within one week he had solved the problem of silver fixation. In contrast to Talbot's single-minded pursuit of the silver image, Herschel soon began to widen his investigations in the search for other viable photographic processes. The history of this quest, and the fascinating story of the interaction betweeen these two gifted men and their peers, has been unfolded with clarity and scholarship by Dr Larry Schaaf in his beautiful voume, *Out of the Shadows*, which provides a complete historical background to this episode, and is essential reading for anyone with an interest in the history of photography.[95] I will therefore confine this account chiefly to the discovery of the cyanotype process, and to those aspects of it which have not already been described in detail.

2.4 Herschel's research records

The primary sources for this account are Herschel's handwritten memoranda, experimental notes and test prints, and his published scientific papers that sprang from them. The original loose-leaf documents covering the crucial period of 1841-3 are held in the Herschel Collection of the manuscript archive of the Harry Ransom Humanities Research Center, in the University of Texas at Austin.[96] For brevity, these documents will be referred to henceforth as the '*Memoranda'*. The HRC also has 43 of Herschel's specimen prints which he consigned to the Royal Society to accompany the manuscript of his 1842 paper; the rest of the experimental prints and tests described in the *Memoranda* are still on this side of the Atlantic, divided between the Museum of the History of Science at Oxford, the National Museum of Photography, Film & Television (now the National Media Museum) at Bradford, and the Library of the Royal Society of London.

By February of 1840, Herschel's *Memoranda* reveal that he had carried out nearly seven hundred photochemical experiments, using silver salts almost exclusively. There is a chronological list of 'prepared papers' in the *Memoranda*, in which each preparation of chemicals coated on paper that Herschel tested for light-sensitive behaviour, was allocated a sequential number. It will be convenient to refer to this as his 'prepared paper number'. Most of these coated sheets were divided up into smaller pieces, and thereby sufficed for several different tests.

2.5 Anthotype and phytotype

In his quest for more colourful images, Herschel soon took leave of the brown pictures provided by silver, and in 1839 began working with juices from the flowers of his own garden, such as red stock or poppy. He crushed their petals in alcohol, extracting the dyestuffs (anthocyanins) into solutions to be painted on paper.[97] These dyed coatings would slowly bleach in sunlight, so exposure in contact with printed engravings directly yielded positive images in plant pigments which Herschel hoped would supply the primaries for a full colour printing system. He called this process anthotype (Greek: ανθος = 'flower') or sometimes phytotype (Greek: φυτον = 'plant'). But the printing was very slow, demanding protracted contact exposures lasting for days or even weeks. Worse, the images proved ephemeral: there was – and still is – no means of 'fixation', because subsequent exposure to strong light inexorably bleaches them. It is remarkable that some of Herschel's specimens still survive today.[98] Impermanence notwithstanding, the anthotype process was taken further by that gifted Scotswoman, Mary Somerville (née Fairfax, 1780–1872),[99] and there is still a lively constituency of practitioners today in this environmentally-friendly print medium.[100]

The spring weather of 1840 was remarkably brilliant, to the enduring benefit of the embryonic science of photography. Herschel had already initiated a new series of exposure tests of 'vegetable colours', but this work was interrupted in March by the relocation of the family home from Slough in Buckinghamshire to Hawkhurst in Kent. Once resettled at Collingwood, 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.[101] He pursued them nonetheless, during the very poor summer of 1841 that followed.[102] 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,[103] 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." [104]

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, which was further evidence for the Grotthuss law of photochemical absorption (§3.6).

2.6 Discovery of cyanotype

In the early spring of 1842, Herschel discontinued his rather unsatisfactory tests of plant dyes in favour of further broadening his search for new photosensitive substances for his 'non argentine photography'; 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." [105]

His awareness of these 'lax' inorganic compounds had been informed by earlier consultations with Dr Alfred Smee (1818–1877). The important role played by this talented young physician and scientist in enabling the discoveries that were to follow has been brought to our attention by Larry Schaaf.[106] Smee was well-grounded in chemistry, and his interests at the time lay in the exciting new sub-science of electrochemistry, which was then enjoying its golden era, following the invention in 1800 of the electric battery by Alessandro Volta (1745–1827), and the thrilling use made of it in 1807 by Sir Humphry Davy (1778–1829), who harnessed its electric power to "tear their elements asunder" and isolate the amazingly reactive 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 construction of a large battery for his own electrochemical researches.[107] 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 - so it was referred to at the time as 'the sister art of heliography'.[108]

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',[109] but we can now identify it by the modern name of potassium ferricyanide.[110] 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*.[111] The chief outcome of this research was to make this interesting, bright-red, soluble, crystalline 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,[112] 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.[113] 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, early in 1842, Smee responded by sending Herschel a specimen of potassium ferricyanide. On 23 April 1842, Herschel made the following entry in his *Memoranda*:

> "Photography. Photochromy.
>
> Non Argentine, Mineral substances ($F^{3}/_{2}CP$) [114]
>
> 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 Guiacum … 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." [115]

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 (Greek: κυανεος = 'deep blue') was not coined by Herschel until four months later.[116] The significance of this observation impressed Herschel sufficiently to include it also in his general diary entry for 23 April 1842:

> "Discovered the Photographic property of the Red Ferro sesquicyanuret of Potass^{m}." [117]

'Discovery' certainly seems a more appropriate word than 'invention' to describe this moment of photographic innovation.[118] 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. $F^{3}/_{2}CP$
>
> April 24/42. Various modes of improving colour & increasing action tried.
>
> 1. Pure water destroys the Dove col^{r} first & washes away the yellowish pink border. It also darkens the impression to a good blue
>
> 2. Dilute Sul^{c} 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 <u>negative</u> 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." [119]
> (Underlining in original)

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 photographic copies of 'positive' images, usually engravings, by means of positive-working processes such as the bleaching of dyes. 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 realised that this would entail a loss of definition. 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.

2.7 Invention of siderotype

The 'list of prepared papers' in the *Memoranda* shows that Herschel received a further sample of potassium ferricyanide from Smee on 27 April,[120] and promptly employed it to make more Prussian blue '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." [121]
> (italics in original)

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.[122] 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 useful in the camera was unfounded. Had matters rested here, it is unlikely that Herschel's discovery of the 'proto-cyanotype' process 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. 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." [123]

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 realise 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 quite 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'. 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 after 1841.[124] Then they were promoted by druggists as 'chalybeate remedies'[125] and, indeed, they are still valued as iron tonics today.[126]

Finding the chemical 'ammonio citrate of iron' already on the pharmacy shelves, Herschel soon followed Smee's recommendation to try it - photographically, rather than medicinally[127] - and immediately discovered that it was highly sensitive to light. He successfully sun-printed with it in a variety of ways, but his tests of the substances that he abbreviated as 'ACI' and 'ATI' are of uncertain date, 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,[128] 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." [129] (Underlining in original)

Thanks to Smee, Herschel had been able to devise a faster cyanotype recipe, which has come down essentially unchanged to the present day. Moreover, his astute chemical reasoning quickly suggested ways of making images in noble metals, such as silver, gold, and mercury using the same iron salt.[130] Thus in 1842, just three years after the first public announcements of silver photography, came Herschel's novel processes based on light-sensitive salts of iron, see Table 2.1. His collective name for these was *siderotype*, (Greek: σιδηρος = 'iron'; τυπος = 'wrought').[131]

Year	Inventor	Process name	Image Substance
1842	Herschel	Cyanotype	Prussian blue
1842	Herschel	Argentotype	Silver
1842	Herschel	Chrysotype[132]	Gold
1842	Herschel	Kelainotype	Mercury
1859	Poitevin	Ferrogallate	Iron-gall ink
1873	Willis	Platinotype[133]	Platinum
1877	Pellet	Pellet print	Prussian blue
1889	Nicol	Kallitype[134]	Silver
1889	Arndt	Van Dyke	Silver
1917	Willis	Palladiotype	Palladium

Table 2.1. Early Siderotype processes

The chrysotype process which so enthused Herschel, although strikingly coloured, never took its promised place in the photographic repertoire; far from rivalling Talbot’s Calotype in general practice, as Herschel had hoped, it was destined to be dismissed by all the major photographic authorities of the nineteenth century as impractical, unsatisfactory and obsolete.[135] However, Herschel’s original conviction concerning the excellence of printing in gold has finally been vindicated by the writer in recent years.[136] The light-sensitivity of all the siderotype processes proved to be little greater than Talbot's first silver process of 'photogenic drawing', so they were not seriously entertained as useful means for securing images in the camera, once the much faster calotype process discovered by Talbot in 1840 was in general use. Of all the sun's light scattered by a photographic subject, only a small fraction (*ca.* one hundredth to one thousandth) is captured by a camera lens and projected onto the photographically sensitized surface. It follows from the law of reciprocity that direct exposure of the same sensitized surface to the incident rays of the sun will take only about one hundredth to one thousandth of the camera exposure time, to provide a clear outline of any object placed upon it. Such 'photograms' are therefore much easier to make by direct contact than are camera photographs.[137]

2.8 Publication of siderotype

Herschel submitted details of his new photographic discoveries in a second, long and important paper to the Royal Society,[138] accompanied by 43 specimen sun-prints, all made from engravings.[139] His paper was entitled ‘On the Action of the Rays of the Solar Spectrum on Vegetable Colours, and on some new Photographic Processes’ and was accepted on the 15th of June 1842 for publication in the *Philosophical Transactions of the Royal Society*. Part of this paper was read by Herschel before the Society on the 16th of June, but it did not appear in print until September; it will be convenient to refer to this seminal work as ‘the 1842 Paper’.[140] 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" [141]

The relatively lengthy exposure needed here should be noted (indeed, Herschel's 'half an hour or 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 for a contact print when ammonium ferric citrate is employed.

It can be inferred 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[[142]] 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." [143]
> (Italics in original)

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.[144] By this time, the serendipitous discovery had matured into a spirit of calculated invention using the ferric processes. Herschel made a simple experiment to show which of the two components was the more light-sensitive: by deliberately isolating the ammonium ferric citrate and exposing it alone, followed by development in a bath of potassium ferricyanide, Herschel proved that by far the greater part of the light-sensitivity could be attributed to the former iron salt, not the latter.

> "210. It seems at first sight natural to refer these curious and complex changes to the instability of the cyanic compounds, and that this opinion is to a certain extent correct, is proved by the photographic impressions described in Arts. 204 and 209, where no iron is added beyond what exists in the ferrocyanic salts themselves. Nevertheless the following experiments abundantly

> prove that in several of the changes above described, the *immediate action* of the solar rays is not exerted on these salts, but on the iron contained in the ferruginous solution added to them, which it deoxidizes or otherwise alters, thereby presenting it to the ferrocyanic salts in such a form as to precipitate the acids in combination with the peroxide or protoxide of iron, as the case may be. To make this evident all that is necessary is *simply to leave out the ferrocyanate* in the preparation of the paper, which thus becomes reduced to a simple washing over with the ammonio-citric solution." [Herschel's italics]

Herschel's understanding of the photochemical basis for the 'deoxidising' behaviour of ammonium ferric citrate enabled him to make reasoned applications of this chemical knowledge in several different ways, as exemplified by his chrysotype, argentotype and kelainotype processes. Herschel's important observation of high sensitivity to light in ammonium ferric citrate (his "ferruginous solution" of Article 210) led to the invention of these new photographic processes (Articles 212 and 226). The *Memoranda* reveal that Prussian blue printing was totally eclipsed during the intervening month of July 1842 by Herschel's endeavours - again employing the marvellously versatile ammonium ferric citrate - to make pictures in mercury and gold, whose striking beauty captured his undivided attention. His account in the 1842 Paper reveals a glimpse of the seductive delights of mercury prints which he called kelainotypes[145]:

> "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." [146]

Lest the reader should feel tempted by this eulogy to cast this book 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." [147]

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 should be possible 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, read to the Royal Society on 17th November 1842, 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." [148]
> [Italics in original]

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 29th August 1842, that the word 'cyanotype' appears in print for the first time, but by then Herschel expressed a preference for the name to be understood as 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." [149]

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[150]) but the epithet should be qualified when necessary to make distinction between the different 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. These will be considered more closely in §4.1.

Smee provides an illuminating postscript to this highly innovative episode in a letter dated 29th 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." [151]

The implication of this response is that Herschel, who was scrupulous in acknowledging the priority of fellow scientists' discoveries, must have enquired if Smee was the discoverer of ammonium ferric citrate and ammonium ferric tartrate, to determine if he should be accorded a 'proprietorial acknowledgement' or wished to make use of them photographically himself. Smee's disavowal of any priority has a self-effacing tone, but one wonders if, perhaps, he knew more than he admitted there. Whatever the case, Smee 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 unexpected serendipitous discoveries into good inventions.

2.9 Misapprehension of Herschel's processes

Following the Royal Society's publication of Herschel's discoveries with iron-based photography, several early textbooks on the new photography republished their own accounts of his processes because the ordinary reader did not have ready access to the *Philosophical Transactions.* But, in the course of so doing, most of them misrepresented the relative significance of his different cyanotype methods because, as we have seen, Herschel was not entirely explicit in his 1842 Paper. Thus, George Fisher's important early manual *Photogenic Manipulation* of 1843 makes no mention of the negative-working process, but only describes the rather unsuccessful positive-working process (see §4.1.4):

> "Brush the paper with a solution of the ammonio-citrate of iron. This solution should be sufficiently strong to resemble sherry-wine in colour. Expose the paper in the usual way, and pass over it very sparingly and evenly, a wash of the common yellow ferro-cyanate of potass. As soon as the liquid is applied, the negative picture vanishes, and is replaced by a positive one…" [152]

The same procedure is the only one described for cyanotype by W.H. Thornthwaite in his *Photographic Manipulation* of 1843.[153] Robert Hunt, in the 5th edition of his *Manual of Photography* of 1857 likewise confined his description of cyanotype to the positive-working process using potassium ferrocyanide,[154] whereas in the 3rd and 4th editions of 1853 and 1854 he had quoted all of Herschel's writings *in extenso*. The *Practical Manual of Photography* of 1845 by "a practical chemist and photographist" does mention the negative process, but then goes on to complicate it by bleaching with mercury salts, as in the 'hydrargyrocyanotype'.[155] As late as 1852, in his widely-referenced work, *Photogenic Manipulation,* Robert J. Bingham foregrounds only the positive cyanotype process.[156] Publications from the USA erred in a similar way: Henry H. Snelling's well-known *History and Practice of Photography* of 1845 only mentions the positive process,[157] and S.D. Humphrey's *System of Photography* of 1849 gives precedence to it over the other,[158] while John Towler's *Silver Sunbeam* of 1864 surprisingly prescribes ferric chloride as the sensitizer for negative-working cyanotype.[159] Even the second edition of the authoritative *Dictionary of Photography* by Thomas Sutton and George Dawson in 1867 only describes three fallible cyanotype processes: the very slow 'proto-cyanotype'; the unreliable positive process; and the so-called 'hydrargyrocyanotype' using a mercury salt bleach.[160] These many unfortunate instances of misdirected practical instruction may well be responsible for the notable lack of take-up of Herschel's best cyanotype process – the neglected negative-working one – over the three decades following his discovery.

Similar misinterpretations of the 1842 Paper persist even today: in 2005, an account of Herschel's experiments was published in the popular photographic press to foster the impression that Herschel's preferred *modus operandi* for his negative-working cyanotype process consisted in coating the paper with ammonium ferric citrate solution alone, exposing it, then subsequently "developing" the image with a solution of potassium ferricyanide.[161] To support this claim, the last sentence only of Herschel's text in article 210 (see §2.8 above) was selectively quoted thus:

> "…all that is necessary is *simply to leave out the ferrocyanate* in the preparation of the paper, which thus becomes reduced to a simple washing over with the ammonio-citric solution."

The quoter then goes on disparagingly to allege that:

> "This critical statement, which Herschel takes the trouble to italicise, is the one either overlooked or dismissed by later historians." [162]

On the contrary, "later historians" have considered all of Herschel's statements very carefully: Article 210 does indeed report a rare occasion when he did not pre-mix the two ingredients, ammonium ferric citrate and potassium ferricyanide. Herschel's true intention becomes plain when one reads the text that the selective quotation was careful to omit - the beginning of Article 210, above. There he clearly states that he intended this as an *experiment* to show which of the two components contributes most to the photosensitivity of the mixture. He already knew that potassium ferricyanide was light-sensitive by itself (Articles 203 and 204), and that its admixture with ammonium ferric citrate was very sensitive (Articles 206 and 207). But by exposing ammonium ferric citrate first, then "developing" the result with potassium ferricyanide, he demonstrated that the former was by far the more light-sensitive of the two.

In fact, Herschel clearly describes his favoured practical method elsewhere in the same 1842 paper - in the Articles 206, 207 and 223:

> “223. If paper be washed with a mixture of the solutions of ammonio-citrate of iron and ferrosesquicyanate of potash, so as to contain the two salts in about equal proportions, and being then impressed with a picture, be thrown into water and dried, a negative blue picture will be produced agreeably to what is stated in Art. 154.”

The same formulation is given in his personal experimental *Memoranda* noting his formulae for cyanotype 'prepared papers', nos. 780, 784, and 793 (MSs at HRHRC, University of Texas at Austin), which he coated two months *after* writing the 1842 paper. From these sources it is plain that, to make his negative-working cyanotype papers, Herschel always preferred to pre-mix his solutions of ammonium ferric citrate and potassium ferricyanide, before coating his paper with the mixture, and exposing it. The economy of this procedure is obvious, and it results in a better quality of print.

This issue has been further obfuscated by authors citing the fact that Herschel adopted the procedure of separate exposure of ammonium ferric citrate alone, followed by "development", in the cases of his positive-working cyanotype process and his chrysotype process. The former, which was never entirely successful, required development with potassium ferrocyanide solution; the latter with neutralised gold chloride (sodium tetrachloroaurate), which was very costly. In both these cases, pre-mixing the two chemicals was ruled out by the speedy decomposition of the mixed sensitizer before the paper could be coated and exposed. These processes should not be conflated with the negative-working cyanotype, which became the commercially successful blueprint process, and the version of cyanotype still popular today.

A proper study of all Herschel's photographic writings – rather than a single, misleading and selective quotation – brings one to the unsurprising conclusion that the negative-working cyanotype procedure which he personally preferred was the same as that used ever since by almost everyone, including his own son Alexander. There is no case here for re-writing this episode of photographic history, but regrettably this misrepresentation of what is misleadingly called ‘the Herschel process’ is now becoming embedded in some of the popular literature on cyanotype.[163]

2.10 An unaccountable omission

From our present vantage-point of chemical hindsight, we might, on the other hand, take the uncharitable view that a man of Herschel’s knowledge should 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 had become aware of researches just published by Döbereiner,[164] who had demonstrated in 1831 the decomposition by light of ferric oxalate, a compound similar to the citrate. It is a remarkable omission by Herschel at the time, nowhere to have made any 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.” [165]

It is nevertheless very surprising that an avid experimentalist like Herschel should not have tested the properties of ferric oxalate, of which he must have been aware at the time. Had he done so, he might have discovered the platinotype process thirty years before it was developed by William Willis in 1873.

Even if Herschel's sense of propriety forbade him from taking up the discovery of another scientist, we might at least have expected some citation or comment from him concerning the relevance of Döbereiner's work on ferric oxalate. The author of the first manual on photographic processes, Robert Hunt (1807–1887), was well-acquainted with this photochemistry and 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." [166]

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 photographic innovators in the years to come (see §4.4.4).[167]

A possible explanation for Herschel's total silence on this subject may be that his highly-developed code of scientific ethics had been offended by 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.[168] Upon hearing about Döbereiner's parallel photochemical researches on iron salts, Herschel hastily had his platinum work published, to establish his priority in this area of photochemistry, and to announce his intention of continuing with an analysis to identify the product.[169] Herschel's result was quickly confirmed in Germany by repeating the experiment, and acknowledged with a declaration that there was no intention of further trespassing on Herschel's field.[170] 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.[171] While it was not in Herschel's nature to harbour resentment, this action may have left him with a natural feeling of 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 1842-3. Multitudes of domestic plants had been pressed into service for their coloured juices, and even dog's urine and an 'extract' from a 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 kelainotype 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…" [172]

Herschel directed much more of his endeavour towards perfecting a positive-working cyanotype process than he did 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;[173] yet it proved so variable in quality and so difficult to fix, that he reached the verdict that 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. 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 Media Museum (previously the National Museum of Photography Film & Television) at Bradford.

It seems appropriate to end this tale of discovery and invention with a sobering reflection on the fickle character of Herschel's scientific muse.

By the autumn of 1842, he had performed more than a thousand photographic experiments, most of which proved ultimately fruitless; Herschel's greatest and most enduring success, the negative-working cyanotype process, was actually accomplished with just *three* test-papers.[174]

2.11 Pursuit of photographic permanence

Following Anna Atkins' monumental achievement to be described in §5.4, and the more modest endeavours of her peers during the 1850s, the cyanotype process fell into desuetude for about twenty years. During these two decades, photographic technology made enormous strides, but one of the most hotly debated issues was the impermanence of some images. Silver had revealed its chemical vulnerability early on, to the chagrin of Talbot, Henneman, and others who printed extensively in the medium. In 1855 the Royal Photographic Society set up its aptly-named 'Fading Committee' to investigate the deterioration of silver images.[175] The Committee's recommendation of gold toning as a partial remedy did much to extend the longevity of silver photographs made thereafter, but this measure was not universally successful in its application. The 'Achilles' Heel' of silver images lies in their susceptibility to sulphiding. The necessity for using sodium thiosulphate as the fixing agent (another of Herschel's discoveries) in order to dissolve and remove the excess silver halide, could, if the thiosulphate was not fully washed out of the paper, lead to the eventual transformation of the silver image into silver sulphide. This greatly weakened the density of colour, especially in the early salted-paper process, which contained relatively small amounts of silver.[176]

Alternatives to printing in silver were therefore keenly sought, and photographic innovation was spurred on in 1856 by the Duc de Luynes' offer of substantial prizes for the invention of methods for making permanent prints. The Duke's gold medal was awarded in 1859 to Alphonse Poitevin for his process of print-making by the photo-hardening of pigmented colloids such as gelatin.[177] Here the maker is free to choose the most permanent pigments for the substance of the image, such as those known to painters for a millennium. One of these, lampblack, bestowed its identity on this *carbon* process, as it was called. Following further refinement by Swan in 1864, it is still practised today. The process is labour-intensive and demands considerable skill in manipulating and transferring the pigmented gelatin tissues, but it still provides the only means for making truly permanent photographs in colour.

An alternative route to permanent monochrome prints lies in seeking for the image a metal more ‘noble’ – that is to say, more chemically resistant – than silver. Gold and platinum share the metallic summit of the hierarchy of elemental chemical stability. Gold was tried with some success by Herschel, as has already been described, but his beautiful chrysotype process of 1842 proved too expensive and uncontrollable for general practice.[178] Platinum printing remained intractable chemically until 1873, when William Willis began to work towards his goal of a viable platinotype process. With further refinement over the next twenty years, this was to become the premier medium for ‘fine-art photography’. By the turn of the century, the walls of the photographic salons exhibited more platinotypes than any other process.[179]

2.12 Marion’s reappropriation

It is still surprising today to see what little application the cyanotype process found in the thirty years following its invention; it has been argued in §2.9 that Herschel’s achievement was not well served by his bibliographers, most of whom only reported his unsatisfactory attempt at a positive-working process. It is interesting to note that Herschel himself had demonstrated the usefulness of the negative-working medium for photocopying text, in view of its enormous commercial importance later on for reprography. In his literary work he made a translation in 1867 of a Schiller poem from German into Latin, and copied his manuscript in cyanotype. His son, Alexander, also used the process for copying his astronomical notes. The only other persons to have made significant use of the process over three decades appear to have been Anna Atkins and her circle of amateur lady botanists, as will be described in §5.4. Despite their historic, but relatively private endeavours, the process became largely forgotten. Perhaps for this reason, we witness more than one instance of its spontaneous re-invention by others. In 1864, *The Photographic News* carried a report of “A process for obtaining proofs in Turnbull’s blue … by Professor Schwarz, of Breslau”,[180] who thought that calico printers might avail themselves of it as a dyestuff, evidently unaware that Mercer had already done so two decades before. This brought forth a letter from Herschel himself in the following issue of *The Photographic News*, which the editor entitled “Sir J F W Herschel’s Cyanotype Process. – A Reclamation”. Herschel firmly pointed out that

Schwarz's process was essentially identical with the one described in his 1842 paper.

Notwithstanding such sporadic revivals, and the endeavours of a few experimentalists such as Mercer and Carey Lea (see §4.4), there followed a period of disuse so prolonged that the readers of Herschel's obituary in the *British Journal of Photography* of 19 May 1871 had to be reminded of these photographic achievements:

> "In the course of his experiments he discovered several elegant processes possessing much interest, which, although lying dormant to a great extent at present, may yet be resuscitated..." [181]

And resuscitated they were but in a new guise: out of the rich legacy of unpatented processes left by Herschel, the cyanotype was seized upon commercially by Marion and Company of Paris, who launched the so-called 'Marion's Ferro-prussiate Paper' on the market in 1872.[182] No doubt for proprietory business reasons they chose to re-brand the cyanotype, and the publicity heralding the appearance of this product made no hint of an acknowledgement to Herschel, nor intimated that there might have been any 'prior art'.[183] Unsurprisingly, no patent was granted, nor apparently even applied for; instead, the formula was kept a secret which appears never to have been disclosed, so it is still impossible to tell if "the ferro-prussiate method of M. Marion" actually contributed anything by way of an improvement on Herschel's original formula. This commercial usurping of an invention of thirty years standing, one that had originally been given freely to the world by its creator, excited indignation at the time in at least one commentator, the editor of *The Photographic News*. His remarks in the issue of 24 August 1877 merit quotation as a polemic which is still full of relevance today for those who practice 're-inventing' the processes due to others:

> "The Cyanotype Process.
> It is not unusual, as every photographer knows, for a process to remain *perdu* for some years, and then to get made known again with some mystery and circumstance. We see old friends revived in this way from time to time, and, like somebody whom we meet for the first time in a quaintly shaped hat or a different-coloured coat than usual, we fail to recognise him at the first moment of our rencontre. But it is only for an instant that the deception holds good, and the well known features are as apparent as ever as soon as we get on close terms again. The cyanotype process, as Sir John Herschel used to call it, is the latest attempt at "fraudulent enlistment," and the circumstance that we have here to do with a genuine article, and not a spurious one, does not make the

> deception the less barefaced. The cyanotype process as practiced by Sir John Herschel is a very simple affair, and one that is found extremely useful for copying outline sketches or multiplying tracings, instead of using tracing-paper. Sir John Herschel employed it, as does Professor Herschel, of Newcastle, to the present day, for making copies of their calculations of astronomical tables, the characters or figures being produced in white upon a blue ground. The paper, ready prepared for use by draughtsmen or others, is to be purchased in Paris; and also, we believe, in this country, of Messrs. Marion, of Soho Square; but those who desire to make it for themselves can easily do so. Good, smooth paper is treated with
>
> Citrate of iron (or ammonio-citrate) ... 140 grains
> Red prussiate of potash ....120 grains
>
> Dissolved together in two fluid ounces of water." [184]

Having thus exposed Marion's 'secret', the article then went on to describe its use. This little polemic is actually of great value in providing us with one of the earliest specifications of Herschel's formula, other than those in his own *Memoranda*, and its implications will be discussed in §4.1 on the varieties of the process.

The advent of commercial blueprint paper, marketed by Marion and others, enabled the widespread use of the process for expedient copying of engineering drawings. In the USA, for instance, students of mechanical engineering at Massachusetts Institute of Technology were instructed in the use of the process as early as 1875, and they caused its introduction into many drawing offices. The first commercial blueprint machine, made by a Swiss company, was introduced into the USA at the Philadelphia Centennial Exposition of 1876. The American teachers of the process only acknowledged that it had been 'originally introduced from France by Mr A L Holley'.[185] The name of Herschel, by then, had been totally eclipsed.

3 The Molecular Basis of Blueprinting

"Stone walls do not a prison make,
Nor iron bars a cage"
Richard Lovelace 1649

The processes of cyanotype show a surprising range of behaviour that cannot be understood without some appreciation of the underlying chemistry. This need not make deeply technical demands on the reader nor require a formal scientific background – the sterner approach is confined to Appendices II and III, which are intended only for those readers who are comfortably fluent in the language and symbols of chemistry. In this short chapter, I shall try to provide an account that is accessible to the majority of nonspecialist readers, who may have only a slight acquaintance with chemical science, but are prepared to endure a little of its jargon – in return for one or two anecdotes.

3.1 Introduction to the chemistry of Prussian blue

The chemical identity of Prussian blue is ferric ferrocyanide.[186] Among the many compounds of iron known to chemistry, Prussian blue is quite unusual in containing the element combined in two different states of oxidation: both as 'ferric' iron and 'ferrous' iron.[187] Intense colour is a quintessential property of this mixed state of oxidation, and it is seen in a number of other such iron compounds.[188] The deep-blue colour is directly attributable to the absorption of energy, in the form of red light, by electrons 'hopping' easily from the ferrous to the ferric iron.[189] The removal of red from the spectrum of white light leaves us with a sensation of the complementary colour, blue, generally called 'cyan' in modern colour language.

The simple experiment of preparing Prussian blue in a test-tube is visually astonishing, and has long been the basis for tricks of parlour magic and 'sympathetic inks' for secret writing. Two dilute water solutions are required, each of them unremarkable in appearance: one, of a ferric salt (it matters not whether it is the sulphate, nitrate, or chloride) is pale yellow; the other, of potassium ferrocyanide, is colourless. On mixing the two solutions, an inky liquid of the deepest blue is instantantly formed, from which a dark blue precipitate slowly separates:

ferric cation + ferrocyanide anion → ferric ferrocyanide

Performance of this dramatic reaction was part of the stock-in-trade for the public lecture-demonstrations of celebrated nineteenth-century chemists such as Michael Faraday. The wonder of carrying out this experiment has been beautifully captured in a fine, but anonymous nineteenth-century painting in the collection of Alfred Bader,[190] who identifies the demonstrator of the reaction as William Thomas Brande (1788–1866), while a youthful Michael Faraday looks on. Bader points out that, in the copy of Brande's seminal *Manual of Chemistry* once owned by Faraday, there are extensive annotations in Faraday's hand on the subject of Prussian blue, which evidently engaged his attention for some years.[191]

The compounds of the Prussian blue family all have a similar structure in which there are two different types of environment for the iron atoms; one of them is distinguished by cyanide groups strongly-bound through their carbon atoms. Since there are also two possible oxidation states for the iron in each type of environment, we therefore have a total of four possibilities when combining ferric or ferrous salts with a ferricyanide or a ferrocyanide, and the properties of the resulting substances are summarised in Table 3.1.[192] Note how the other three compounds are all readily transformed into Prussian blue, which is by far the most stable product of the four.

Reactant	Ferricyanides	Ferrocyanides
Ferric salts	**Ferric ferricyanide** Prussian yellow (or Berlin brown) Soluble; a powerful oxidant, easily oxidises water, and paper etc., being reduced via green intermediates (Berlin green) to Prussian blue	**Ferric ferrocyanide** Prussian blue (or Berlin blue) Highly insoluble; most intensely coloured, and most stable of all four possible products in this table, to which the others revert
Ferrous salts	**Ferrous ferricyanide** A highly unstable substance that instantly reverts by electron transfer to ferric ferrocyanide, Prussian blue which, formed this way, is often called Turnbull's blue after its manufacturer	**Ferrous ferrocyanide** Prussian white (also Everitt's salt[193] or Williamson's salt[194] or Berlin white) Insoluble and colourless, but readily oxidised by air (and other oxidants) to Prussian blue

Table 3.1. Varieties of complex iron cyanides

Because negative-working cyanotypes are usually formed by the reaction of a ferrous salt (resulting from the decomposition of ferric salts by light) with a ferricyanide, a common error in all older published accounts of the cyanotype process is to describe the resulting pigment, Turnbull's blue, as ferrous ferricyanide, and this misconception even persists among some antagonists today.[195] Modern chemical research of the last 30 years has conclusively shown this to be wrong (see Appendix II.4); when formed, ferrous ferricyanide rearranges 'instantly' by transferring an electron between its two types of iron to give ferric ferrocyanide, Prussian blue:

ferrous cation + ferricyanide anion → [ferrous ferricyanide -unstable]
→ ferric ferrocyanide (Prussian blue)

However, the early experimentalists may be forgiven for thinking that Turnbull's blue was different from Prussian blue, because the appearance of its hue often suggests so, for reasons to be described below.

The colourless substance, ferrous ferrocyanide, or Prussian white, will be important to our considerations later, because it is formed directly in one variant of commercial blueprint paper. Prussian white is also the product of the fading of Prussian blue by light; its formation accounts for the tonal reversal that the cyanotype image undergoes upon extended exposure, where the paling of the shadow areas is called 'solarisation' by photographers. However, it should be understood that this fading transformation is not brought about solely by light; the chemical reduction of Prussian blue to Prussian white must be accompanied by a corresponding oxidation of something else:

light + Prussian blue + reductant → Prussian white + oxidation products

but what reductant exactly is oxidised is an open, and very important question, which will be addressed later. Prussian white is unstable in air and is slowly oxidized by oxygen back to Prussian blue:

Prussian white + oxygen + water → Prussian blue + hydroxide ions

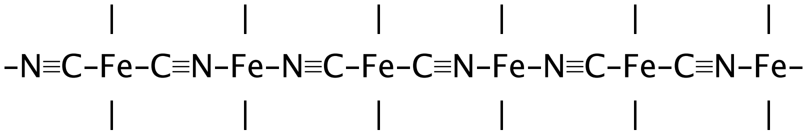
If this were all that there is to say about the chemistry of Prussian blue, my task would have been simple. But nature at the molecular level is seldom unsophisticated, and sometimes 'imperfect'. In fact, there exist several 'Prussian blues', all of them in essence ferric ferrocyanide, but each having an individual composition depending on its precise method of preparation.[196] The analytical complexity and intractability of this 'substance' has engaged - and frustrated - chemists for no less than two centuries,[197] but only in the last two decades has a clear understanding begun to emerge, thanks to the powerful instrumental techniques of modern chemical research. The structural details are set out in Appendix II, but it will serve the purposes of a general discussion to summarise them as follows.

The formulae for Prussian Blue are usually stated to range from an ‘insoluble’ Prussian blue,[198] to the so-called ‘soluble’ Prussian blue,[199] which also contains potassium ions.[200] The latter is a serious misnomer: in fact, *all* forms of Prussian blue are highly insoluble in water. The apparent ‘solubility’ in the latter case is an illusion created by the ease with which this solid may be dispersed in water as minute particles, called nanoparticles, which form a blue suspension giving the appearance of a true solution. Chemists call this process *peptization,*[201] and the resulting suspension of the nanoparticles or *colloid* is known as a *sol* which is small enough to pass through a filter paper.[202] The ease of peptizing ‘soluble’ Prussian blue is responsible for some of the problems that beset the making and conservation of cyanotypes.

The Prussian blue pigment of commerce, which is manufactured globally on a scale of 50,000 tonnes per year, is now prepared via Prussian white by a method which ensures that a substance is obtained in which ammonium ions replace potassium.[203] This variety has a brighter colour, and is more resistant to peptization and destruction by alkalies.[204]

3.2 Molecular structure of Prussian blue

Many of the remarkable properties and present-day uses of Prussian blue can be understood in terms of the three-dimensional structure of the solid at the atomic level – its “molecular architecture”. This structure is so simple and (ideally) regular, that visualizing it should present no difficulty even to non-chemists. Imagine a cubic scaffolding: iron atoms are located at the joints, alternately ferric and ferrous, the cyanide groups ($-\mathrm{C{\equiv}N}$) form the rods that connect them, with their carbon atoms adjacent to the ferrous ions, and nitrogen atoms to the ferric ions. In one direction, the structure runs like this:


$$\mathrm{-N{\equiv}C-\overset{|}{\underset{|}{Fe}}-C{\equiv}N-\overset{|}{\underset{|}{Fe}}-N{\equiv}C-\overset{|}{\underset{|}{Fe}}-C{\equiv}N-\overset{|}{\underset{|}{Fe}}-N{\equiv}C-\overset{|}{\underset{|}{Fe}}-C{\equiv}N-\overset{|}{\underset{|}{Fe}}-}$$

and likewise in two other mutually perpendicular directions. For a representation of the three-dimensional structure, see Figure 3.1. Note how spacious this arrangement is: not close-packed as are many simple crystalline solids.

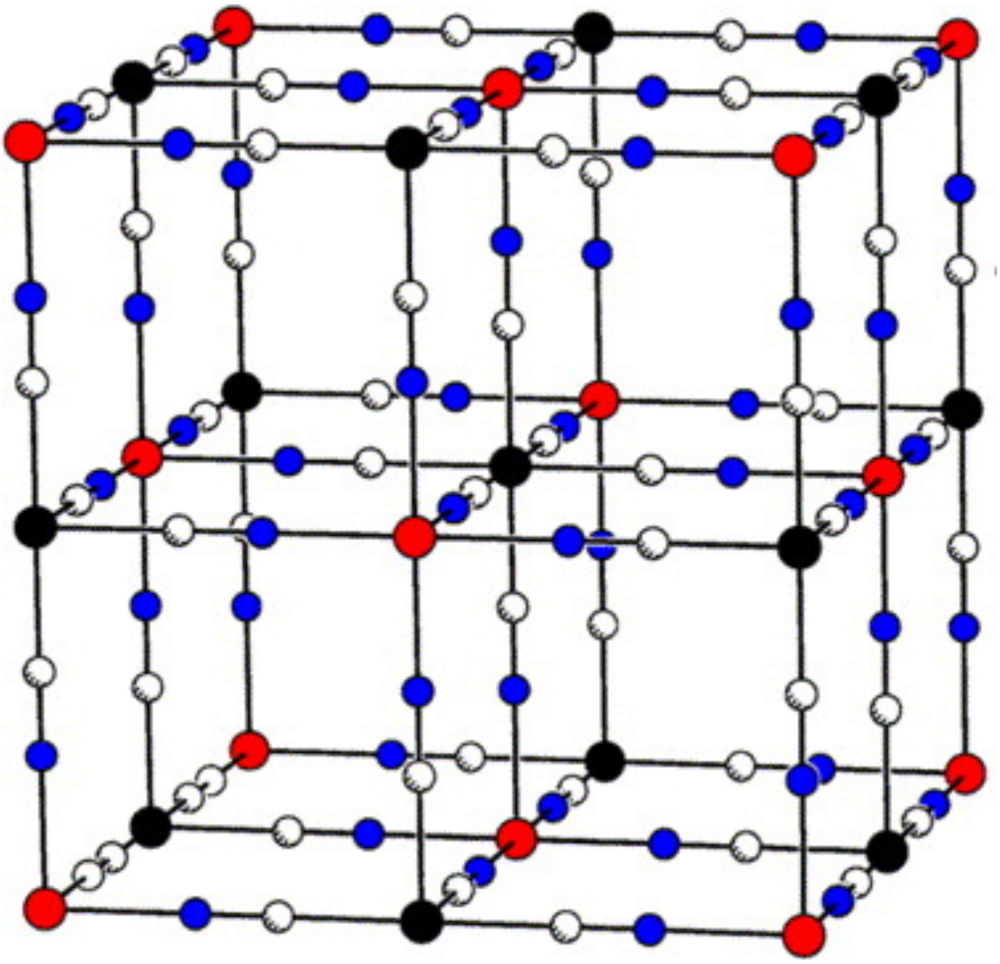


Fig. 3.1 The crystal lattice of Prussian blue

Throughout this open lattice we can see tunnels running in three perpendicular directions, and a large void within each cube, which can accommodate molecules of water, for example, or metal ions, and which allow Prussian blue to act as a kind of chemical host. In the case of 'soluble' Prussian blue, half of these spaces are occupied by potassium ions. The incorporation of varying amounts of water and other ions into the voids in this lattice accounts for some of the variations observed in the formulae, and the puzzlement of early analytical chemists.

The other cause of variability in the composition of Prussian blue is the presence of defects in the lattice; that is, departures from symmetrical regularity due to the absence of a proportion of the ferrocyanide groups. The formula of the 'insoluble' variety is explained by a lattice that has one quarter of its ferrocyanide groups missing, and water molecules in their place. In the language of the crystallographer, the lattice is said to have ‘systematic vacancies’. The formula recently found for Turnbull’s blue implies that in its lattice one third of the ferrocyanide groups are missing, and replaced by water molecules and anions. This is nominally, at least, the form of Prussian blue formed in the cyanotype process; it will be seen later that the possibility of a defect lattice which can act as host to anions is of great significance to its light-stability.

3.3 Prussian blue for ion exchange

The open structure of the Prussian blue lattice gives it a porous quality that explains why the substance is a very useful ‘chemical sponge’ for soaking up and trapping cations similar to potassium, such as those of the metals caesium and thallium.[205] Prussian blue itself is non-toxic, unreactive and tasteless, and can be safely eaten in gram quantities without harmful effects,[206] and its insolubility ensures it is excreted easily, making it a valuable antidote to poisoning by these heavy metals, and it has been used successfully to detoxify both animals and humans.

As an example of the ability of the microporous Prussian blue lattice to act as host for relatively large amounts of impurity ions, it was put to good use for ‘locking up’ some of the radioactive fallout, in the form of the radioisotope caesium-137, that was deposited on the uplands of North Wales, Cumbria and Scotland following the disastrous Chernobyl reactor explosion of April 1986.[207] Tests were conducted to see if this contamination could be countered by spreading Prussian blue on the contaminated soil of the pastures, thus inhibiting the uptake of caesium by growing grass which, in turn, would prevent its ingestion by the animals grazing the slopes, but it was found more effective to feed the Prussian blue directly to the affected sheep, and thus avoid turning the green hills of Britain to navy blue![208] The effects of Chernobyl lingered on. In 1992, it was discovered that migrant herds of reindeer in Norway had also absorbed Caesium-137 from this disaster, because they graze on lichens and are particularly partial to mushrooms, which both concentrate the caesium. The livelihood of their Sámi herders was in jeopardy,[209] so Prussian blue was added to the ‘salt licks’ that these nomadic animals are so fond of, with beneficial effects for the migrant herds.[210] Prussian blue continues to be used to detoxify the livestock in the Chernobyl-contaminated regions of Belarus, Russia and Ukraine, and has saved their agricultural industries of milk and meat production from enormous losses.

In Germany, appropriately, the benefits of feeding Prussian blue to radioactively-contaminated pigs has also been amply demonstrated in a recent scientific study.[211] Caesium-137 is also used in radiotherapy to treat certain cancers, so there are substantial quantities of this radioisotope in specialist medical facilities worldwide. Acknowledging the risk that these stocks could be abused by terrorists to make a radiological “dirty bomb”, the Federal Drug Administration in the USA has recently licensed the use of Prussian blue as a safe antidote to Cs^{137} contamination in humans.[212]

Poisoning of humans by salts of the scarce heavy-metal, thallium (which resembles lead), is fortunately not frequent, but In the mid-20th Century, it enjoyed a spell of notoriety as a subtle toxin: its unusual symptoms could be mistaken for diseases such as encephalitis or epilepsy, but incidentally the victim’s hair dropped out, so sudden alopecia offered a clue.[213] (Its use as a depilatory, however, declined in the 1930s.) This highly toxic metal is a favourite of poisoners who happen to be both chemically erudite and homicidally inclined; their hope is that its unfamiliar toxicology may help them evade detection. Thallium(I) sulphate is colourless, odourless, tasteless, and sufficiently water-soluble to be administered easily to an unsuspecting victim. The symptoms do not appear for several days, but a dose of a gram or so is usually fatal, because the body cannot get rid of the element, which mimics potassium but blocks its vital enzymic action, especially in the brain.

Thallium was used quite extensively by the secret police of the late Saddam Hussein’s regime in Iraq for disposing of senior political dissidents. A useful trick was to administer the dose just before the victim was allowed to leave the country, so he died abroad. The substance was readily available in the Middle East, where it was commonly employed to destroy rats and cockroaches, so accidental poisoning was also common. Fortunately – if the cause of the poisoning is correctly diagnosed – there is an antidote which has saved many lives: Prussian blue.[214] The thallium(I) cation can enter the Prussian blue lattice in place of potassium. There it becomes trapped, and can be safely excreted by the body. Prussian blue was therefore put forward by German pharmacologist, Horst Heydlauf of Karlsruhe, as the preferred antidote for thallium poisoning, and its value has since been amply confirmed.[215]

These two instances of the ability of Prussian blue to act as a ‘prison’ for chemical poisons are not just irrelevant digressions to the present work. Later in §8, we shall consider methods of toning the cyanotype image, among which are processes using salts of lead and thallium. Lead resembles thallium quite closely, and its ability to cause a shift in the colour of Prussian blue may probably be attributed to its incorporation within the lattice, as just described. As we shall see in §9 on the vulnerability of cyanotypes and in Appendix III, the fading of Prussian blue in the light may also be greatly promoted by the presence of impurities trapped within it.

3.4 Prussian blue for electrochromic displays

Over the last decade, Prussian blue has attracted an enormous amount of research interest from electrochemists because it can be commercially exploited as an electrochromic display; that is, a solid-state device whose colour can be changed by varying the electric potential applied to it. As the voltage across a Prussian white electrode is raised, and negatively-charged electrons are abstracted from it, the colour passes through a spectacular, reversible sequence: white, blue, green, and finally yellow:

ferrous ferrocyanide → ferric ferrocyanide → ferric ferricyanide

white blue (green) yellow

a beautiful visual demonstration of the increasing oxidation states of the two types of iron atom that are summarised in Table 3.1.[216]

3.5 Chemical history of siderotype

The cyanotype process is just one member of a whole class of alternative photographic printing processes which all share a common type of light-sensitive component: the ferric salts of certain organic substances, which were appropriately called ‘vegetable acids’ by Herschel, owing to their widespread natural occurrence within the plant kingdom. However, the discovery of this light-sensitivity in organic iron salts considerably pre-dates its photographic uses. The first such observation, albeit a rather indirect one, is attributed to Count Bestuscheff (1693-1766), the Lord High Chancellor of Russia. This worthy is said to have devised, in 1725, a nostrum called *Tinctura tonico-nervina*, of a secret formulation, but reputed to contain gold - presumably in order to justify its exhorbitant price.[217] Bestuscheff claimed that the agency of sunlight was employed in its production - a further alchemical reference to gold. When the secret of the tincture’s composition was finally revealed by the Empress Catherine the Great, who purchased it from Bestuscheff’s heirs, it turned out to be no more precious than a solution of ferric chloride in alcohol, which had been decolourised by exposure to sunlight.[218]

Despite the unmasking of its commonplace nature, the tonic continued to enjoy a long-lived commercial success as ‘Bestuscheff’s Nervine Tincture’, although we do not know whether it was the iron, or the alcohol, that conferred the greater benefit. As late as 1853, the tincture can still be found listed in the pharmacopoeias as *Spiritus Sulphurico Etherus Martiatus*, or as *Ferruginated Sulphuric Ether*,[219] having undergone in 1782 a modification due to Martin Klaproth, who replaced the ethyl alcohol with diethyl ether – making an altogether more heady mixture – but the tincture was still said to be ‘blended in light’. In 1813, a scientific investigation of the light-induced bleaching of ferric chloride in ether solution by Henri August Vogel, found it to be very sensitive.[220] These early observations have no probable bearing on the actual invention of cyanotype, but they may be responsible for some of the more misleading and unhistorical statements that have been made concerning the process, such as:

> “The principles involved in sensitizing blueprint paper were discovered in France in about 1725 and perfected by Sir John Herschel in England in 1842.” [221]

The action of light on ferric salts of organic acids produces ferrous salts by promoting an internal oxidation-reduction reaction.[222] All the iron imaging systems have this same basis; the key compound is usually a ferric salt of citric, tartaric, or oxalic acid.[223] For simplicity in our brief excursion into the chemical formulae, we will take the last-named as our example: ferric oxalate, which contains iron(III), Fe^{3+}, and oxalate, $C_2O_4^{2-}$, chemically bound together. Under the influence of ultra-violet light, this salt undergoes the reaction first observed by Döbereiner in 1831, as described in §2.2. Iron(III) reacts with oxalate ions to form iron(II) and carbon dioxide gas – a process which is expressed symbolically by the following chemical equation (the only equation that readers will encounter, unless they venture into the depths of Appendices II and III):

$$\text{UV light} + 2Fe^{3+} + C_2O_4^{2-} \rightarrow 2Fe^{2+} + 2CO_2$$

$$\text{UV light + ferric ions + oxalate ions} \rightarrow \text{ferrous ions + carbon dioxide}$$

Note how two negative charges (which are carried by electrons) have been transferred from oxalate to iron(III), *reducing* it to iron(II).

This light-induced change occurs in the dry, solid ferric oxalate, and in related compounds such as ammonium ferric oxalate and ammonium ferric citrate; but it is only accompanied by a slight colour change from pale yellow-green to pale yellow-brown; moreover this change is temporary, because the iron(II) is slowly re-oxidised back to iron(III) by oxygen in the air. In order to make a permanent photograph, the iron(II) which is formed by the action of light must be immediately reacted to produce a more visible and enduring substance for the image. Chemically, iron(II) is a reducing agent, because it readily gives up an electron and reverts to iron(III); so one option is to use it to reduce the compounds of a 'noble' metal, such as platinum, palladium, silver or gold, to the metallic state:

ferrous ions + platinum salts → ferric ions + platinum black

Reactions of this type provide the basis for the well-known platinotype, palladiotype, argyrotype and chrysotype processes.[224]

3.6 Introduction to photochemical principles

Photochemical theory had its beginnings in 1818 with the Grotthuss-Draper Law: ***only light absorbed by a substance can induce a chemical change within it***. Light is energy. Across the visible spectrum, going from red to blue, the intrinsic energy of light nearly doubles. When a molecule absorbs visible light, which is the cause of colour, its internal energy is increased, and it is said to be lifted into an 'excited' state. Sooner or later, this excess energy is transformed and lost, so that the molecule returns to its normal or 'ground' state. This process is appropriately called 'relaxation'. The manner of the transformation of the absorbed energy, however, can be various, and it depends on the lifetime of the excited state and other factors. The least interesting, and most common, process is 'thermal relaxation', that is the dissipation of the excess energy as heat - embodied in more agitated motion of the molecules. In some spectacular instances, part of the excess energy may be re-emitted as light, giving us the attractive and useful luminescent phenomena, called fluorescence and phosphorescence, depending on whether the excited state is short- or long-lived, respectively. Most importantly for our purposes, the excess energy may be directed to bring about a chemical reaction if the molecular circumstances are favourable. It should come as no surprise that a molecule in an excited state is capable of more vigorous chemical reactions than when it is in its ground state. Ultra-violet light is often required to supply sufficient energy for such chemical transformations.

There is an equivalence between the quantity of light absorbed and the amount of substance that is chemically transformed, both of which are measurable, and may be related by an elementary principle of quantum theory, as it applies to photochemical changes.[225] This principle, which constitutes the second law of photochemistry, dates from *ca* 1912 and is usually referred to as the Stark-Einstein Law.[226] It is easily appreciated without invoking much jargon, and the non-technical reader should readily see that it amounts to nothing more than a statement of ‘good book-keeping’ at the molecular level. The Stark-Einstein Law effectively requires that: ***for each molecule of the substance to be transformed, one photon must be absorbed***.[227] (A photon is the fundamental, indivisible particle or ‘quantum’ of light.)

From this basis, a calculation may be performed assuming the most favourable circumstances (see Appendix III), which yields an estimate for the maximum light sensitivity of any ‘print-out’ photographic material – no matter what its detailed photochemistry.[228] This limiting sensitivity is a maximum in the near ultraviolet and blue regions of the spectrum, over a wavelength range of about 300-400 nm (known as UVA). Unsurprisingly, the sensitivity turns out to be very low, requiring a radiant energy density of about 34 J/m^2 (Joules per square meter) to form a perceptible image. On a scale familiar to photographers, the ‘speed’ of such a material can be rated approximately at 10^{-5} ISO (arithmetic);[229] that is, one ten-millionth of the speed of an ordinary camera film of 100 ISO (arithmetic).

3.7 Chemistry of blueprinting

In the negative-working cyanotype process, the iron(II) photo-product is reacted with ferricyanide to yield Prussian (alias Turnbull’s) blue:

ferrous ions + ferricyanide ions → Prussian blue

This reaction entails a switch in the oxidation states of the two types of iron, as indicated in Table 3.1: the intermediate ferrous ferricyanide is highly unstable and transforms very rapidly to ferric ferrocyanide.

If the light-sensitive iron(III) salt is present in excess, and the exposure is prolonged sufficiently, the photochemistry proceeds one stage further: some of the Prussian blue (ferric ferrocyanide) is further reduced to Prussian white (ferrous ferrocyanide), and the deep blue image begins to pale in its regions of greatest exposure.

light + Prussian blue + ferrous ions → Prussian white + ferric ions

This tonal reversal is the phenomenon of ‘solarisation’ first observed and named by Herschel. It is actually desirable for making a print-out image, because it can ultimately yield a higher maximum density: the self-masking action by the Prussian blue in the shadow regions of a printed-out image is diminished by the reversal to white, which allows the ingress of more light and formation of more (white) product. After the exposure, the Prussian white so formed is oxidised back to Prussian blue, either slowly by the oxygen of the air, or more rapidly by including a bath of an oxidising agent, such as hydrogen peroxide or a dichromate, in the wet-processing sequence:

Prussian white + hydrogen peroxide → Prussian blue + hydroxide ions

When pure Prussian blue absorbs light, the excited state quickly loses its excess energy by thermal relaxation only, and returns to the ground state unaltered (apart from a slight warming of the substance). However, if there is an oxidisable impurity in intimate contact with the Prussian blue – for instance, trapped in its lattice – then the excited state may have time to accept an electron and undergo chemical reduction to Prussian white. This photoreduction underlies Herschel’s observation of bleaching Prussian blue (§4.1.6) and is the reason why cyanotypes tend to fade in the light; the phenomenon is central to the problems of conserving cyanotypes, and will be fully discussed in §9.1 and Appendix III.9.

4 Historical Variations on Cyanotype

"The Artists go on boldly,
and are not afraid to be Chemists,
the Chemists gain courage
and long to be Artists."
The Athenæum 1858 [230]

This chapter reviews some of the historical variations on the cyanotype theme which have been used to arrive at images in Prussian blue, including the employment of glass, plastic and fabrics as alternatives to paper for the substrate of the cyanotype. The application of practical chemistry retrospectively to convert the Prussian blue image into different coloured substances will be largely deferred until §8, which is devoted to describing the practices of 'toning' cyanotypes.

4.1 Herschel's formulae

From Herschel's observations in his 1842 paper together with the notes in his *Memoranda*, we can distinguish at least fifteen variations on his photochemical theme for making images in Prussian blue. Subsequent experimenters have re-invented several of these, or played further variations upon them.

4.1.1 'Proto-cyanotype'

This name is newly coined here to distinguish the method of cyanotype that has emerged from the historical evidence presented in §2.6 as the very *first* method discovered by Herschel to provide prints in Prussian blue. This was simply the exposure of a coating of potassium ferricyanide alone. The concentration of the solution to be spread on the paper should be lower than saturation (which is 33% w/v at room temperature), say 10% to 16%, otherwise undesirable crystallization may occur on the surface before the solution is absorbed by the fibres. This is the simplest cyanotype method of all, and is capable of producing a well-graduated, clean, negative-working print of a somewhat greenish-blue (23C7 to 23E7), but of rather low maximum density, because it does not undergo tonal reversal ('solarisation'), and is therefore self-masking during exposure. The chief disadvantage of this simple method is the very long exposure required – in the order of one or two hours to bright sunlight – because potassium ferricyanide is intrinsically not very sensitive to light. Experimenters are also advised that perceptible amounts of deadly poisonous hydrogen cyanide and cyanogen gases are released during the exposure of this substance, which should not, therefore, be carried out in a confined space.[231]

Herschel noted that much greater 'speed' and higher densities can be obtained by developing the image in a bath of ferric chloride or nitrate solution, but this invariably causes blue fog in the highlights.[232] These are probably the reasons why Herschel appears to have abandoned the method soon after he discovered it, in favour of the much 'faster' sensitizer which also incorporated ammonium ferric citrate provided by Alfred Smee. However, the use of potassium ferricyanide by itself continued to be recommended for several years as 'one of the best methods', by authorities such as Robert Hunt[233] and Golding Bird:

> "This easily prepared paper affords a ready and excellent means for copying ferns, sea-weeds, lace-work, engravings, &c., but is not sufficiently delicate for the camera." [234]

Bird's popular text, *The Elements of Natural Philosophy*, in its second and later editions, is thought to have provided an accessible instruction manual for many early practitioners of the cyanotype process.[235] There is at least one important album containing cyanotypes and their original botanical specimens, dating from 1843, which may have been printed by this simple means, as will be described in §5.6. The 'proto-cyanotype' method was still published in the 1867 edition of the influential *Dictionary of Photography,*[236] but by the time of the first 'revival' of cyanotype towards the end of the nineteenth century, the method of using potassium ferricyanide alone had disappeared entirely from the manuals and encyclopedias. A similar procedure was, however, briefly 're-discovered' by a Professor Gintl of Prague in 1872, who used potassium ferricyanide in conjunction with gelatin to achieve selective photohardening of the colloid, before the Prussian blue image was developed by means of a bath of ferric chloride.[237]

4.1.2 Negative-working cyanotype

In Herschel's 'standard' negative-working cyanotype process, iron(II) is generated photochemically from ammonium ferric citrate, and reacts with the potassium ferricyanide in the sensitizer to form Prussian blue in proportion to the light that has fallen; *i.e.* it is a Turnbull's blue process (§3.1) and the potassium ferricyanide is usually in excess over the iron(II), so the product may be of the so-called 'soluble' variety. A recipe for this negative-working cyanotype process can be found in every photographic text that touches on alternative processes, and many of these claim to be quoting Herschel's original formula, but they never support this by citing any reference. The reason for their omission is simple: nowhere in Herschel's published work does he specify the concentrations and relative proportions of the solutions of potassium ferricyanide and ammonium ferric citrate that he used for this cyanotype process. This information can only be found in the *Memoranda*, as is clear in the following entry:

> "Photography
>
> FerroSesquiCyan. P Cyanogen Iron
>
> Aug 13/42. Mixed sol of $F^{3}/_{2}CP$ and Amm^{o} Citr of Iron as in Paper 780 ie. equal parts of sat^{d} sol of $F^{3}/_{2}CP$ and ACI $^{1}/_{11}$ (1 salt + 10 water). The properties of this paper are singularly complex & interesting." [238] [underlining in original]

Herschel's use of a saturated solution of potassium ferricyanide (*ca.* 33% *w/v*) and the rather dilute solution of ammonium ferric citrate (*ca.* 9% *w/v*) are surprising. He goes on to describe in detail his observations of the effects of exposing this sensitizer to light; in particular, his attention was caught by the tonal reversal of the image as the exposure progressed – a phenomenon for which he promptly coined the term 'solarising':[239]

> "**A.** It first darkens to a dull bluish grey the original hue of the paper being green-yellow. The darkening reaches a maximum in about 30 or 40 seconds in good sun (the paper is very sensitive), – It then whitens again – to a pale greenish-grey. Hence a picture withdrawn at various stages of exposure presents several aspects.
>
> 1st If not long exposed the margin is dark and the picture negative in a bluish or lead grey.
>
> 2d If very long exposed the picture is positive the parts where the light has acted being actually paler than the original formed tint. This I call over-sunning or solarising.
>
> 3d If the exposure be not so prolonged as to "solarise" it the picture is very remarkable. It is positive, but in 3 tints the ground being the original greenish-yellow. – the full lights being the aforesaid solarised white – a very pale greenish-grey. – The half lights are darker than the ground but contrast sufficiently with it in colour to relieve the lights on the one hand and to stand off from the ground on the other.
>
> **B.** When the picture so produced is thrown into whater [*sic*] it gradually changes to a fine Prussian Blue Negative Photograph, & the process of the change is highly curious as to Pictorial effect. Especially if a solarised Photogr be used.– The white faces take by degrees a leaden hue & the change is like the effect of the "dissolving views"." [240] [Underlining in original]

It is clear from his 1842 paper that Herschel had a correct chemical understanding of the cause of his ‘solarisation’; a footnote to §207 reads:

> “The whitening is very obviously due to the deoxidation of the precipitated Prussian blue and the formation of the proto-ferrocyanuret of iron; the resumption of colour in the shade, to the re-oxidisement of the compound, which is well known to absorb oxygen from the air with avidity. Simple Prussian blue, however, is not whitened by the violet rays. Its state must be peculiar.” [241]

On 16 August 1842, Herschel modified the proportions of mixing his solutions of ammonium ferric citrate to potassium ferricyanide from 1 : 1 to 5 : 3, respectively, but there is no record of his making further changes after that. It is puzzling that the proportions and concentrations he had then arrived at still differ considerably from those that were subsequently recalled and publicised by his son, Professor Alexander Stewart Herschel (1836-1907), in the 1870s as representing his father’s working recipe.[242] The concentrations resulting in the final working sensitizer from these various formulations are summarised in Table 4.1.

Formulation	**Ammonium Ferric Citrate % w/v**	**Potassium Ferricyanide % w/v**
Herschel ‘proto’	None	*ca* 16
Herschel original	4.7	16.6
Herschel modified	6.6	12.4
Alexander Herschel	14.7	12.8
Later C19th average	*ca* 10 (brown salt)	*ca* 8
Usual C20th average	*ca* 13 (green salt)	*ca* 6

Table 4.1 Early cyanotype formulations (final concentrations)

The processing of an exposed cyanotype could not be simpler: ‘fixation’ of the image is most easily accomplished by washing in water, because the excess sensitizer and other photoproducts are entirely soluble. This is one of the strongest recommendations for the cyanotype, since it meets an ideal that Herschel had always sought in his processes; it offers a considerable advantage over the practice necessary in silver photography, where the insoluble silver halide requires a fixing agent, sodium thiosulphate, for its removal, and residues of thiosulphate can lead to deterioration of the silver image, as many early photographers, including Talbot, found to their cost.[243]

4.1.3 Hydrargyro-cyanotype

This cumbersome name appears only in Herschel's *Memoranda*, but the 1842 Paper carries an account of the phenomenon in Article 223, which was republished by Hunt and others,[244] and goes as follows. A cyanotype is made and processed in the usual way from ammonium ferric citrate and potassium ferricyanide by Herschel's 'Method (a)'. This is then coated with a solution of mercurous nitrate;[245] within a period of a few hours the blue image disappears and the blank paper is washed and dried. On heating strongly with a flat-iron – but not so much as to cause scorching of the paper – a brown image becomes visible. This tends to fade slowly in the dark over a matter of days, but may be regenerated again by further heating. We can only conjecture what chemistry may be involved here, for the observations deserve further scientific investigation; the reversibility of the phenomenon may be a consequence of the mercury(I) being trapped in the Prussian blue lattice in the same way as thallium(I) is known to be, and then reducing the substance to Prussian white. The effect of heat may be to cause decomposition of the mercury ions to mercury metal, which in a finely divided state would appear brown. I have repeated and confirmed this curious process, but cannot recommend it generally owing to the high toxic hazard presented by the mercury salts, especially when heated.

4.1.4 Positive-working cyanotype

In the positive-working cyanotype process, the Prussian blue image is meant to be formed in inverse proportion to the illumination, by the ferric ions derived from the *unchanged* ammonium ferric citrate sensitizer reacting with potassium ferrocyanide, which is applied in solution after the exposure. This procedure introduces an inherent and rather intractable problem: the lighter regions of the image, which have received the most exposure, contain much ferrous iron that also reacts with the applied ferrocyanide to give the insoluble product, ferrous ferrocyanide or Prussian white. Now this substance does not remain white for very long, being readily oxidised by the air to Prussian blue, so it must be removed in order to fix the positive image. Any treatment intended to achieve this is likely also to remove the Prussian blue image itself, which explains why Herschel – and everyone who has followed him – found the positive-working version of the process so much more difficult to carry out satisfactorily, and virtually impossible to perfect. Herschel's first recourse was to include gum Arabic in the developer to increase its viscosity, but this did not fully answer the problem. Had he included it in the sensitizer, as Pellet subsequently did (see below) he would have met with more success. His second attempted solution was to include ‘corrosive sublimate’[246] in the sensitizer in order that the image, after development with a coating of gum and potassium ferrocyanide, would be fixed without any washing at all:

> “All the care that is required is, that the film of liquid be very thinly, evenly , and above all, quickly spread. Being then allowed to dry in the dark, it rarely fails to produce a good picture. And what is very remarkable, it is *ipso facto* fixed as soon as dry, so at least as not to be injured by exposure to common day-light, immediately; and after a few days’ keeping it becomes entirely so, and will bear strong lights uninjured.” [247]

In spite of Herschel’s claim for the success of this procedure it cannot be recommended, in view of the very high toxicity (and expense) of mercury(II) chloride. Even today this chemistry is somewhat obscure. Herschel offered no rationalization, but it is known that mercury(II) has an enormous affinity for cyanide, forming a very stable complex; it is likely that its effect is to destroy the Prussian white in the highlight areas, which cannot then revert to blue.

4.1.5 Anachronistic ‘Herschelotype’

A curious inversion of the foregoing process was proposed in 2007 as a practical alternative method for negative-working cyanotype: to expose ammonium ferric citrate alone, then develop it in potassium ferrocyanide to form an invisible negative image in Prussian white, which then slowly re-oxidizes in air to Prussian blue, so providing a negative-working process overall. This procedure may sound plausible but, as we have just seen in §4.1.4, it has an obvious problem: a strong positive-working image in Prussian blue is also formed immediately by the ferrocyanide reacting with residual iron(III) in the unreduced sensitizer, and this initial blue image must be completely and quickly dispersed – by scrubbing it away, according to the author – before the Prussian white negative image becomes oxidized by air to Prussian blue. It seems very improbable that this procedure could be successfully employed for making prints of any size and quality. The author goes on to announce, rather stridently:

> "This new process, as the inventor, I'm attributing to Herschel and call it the "Herschelotype"." [248]

Retrospectively to enlist the name of Sir John Herschel for this unworkable and falsely-claimed "new process” is a clumsy misappropriation that insults his memory. It is presumptuous of the author to assume this 'right of naming' because Herschel never attempted to use this process, nor did he employ potassium ferrocyanide in the negative-working/reoxidation manner. He did, of course, attempt to use ferrocyanide development in the contrary sense, as a positive-working process, but rarely with much success (§4.1.4). Moreover, the process described is in no way new, and any modern claim to be its inventor is empty. The inclusion of potassium ferrocyanide in negative-working cyanotype was, in fact, widely patented in the USA and UK in the 1930s, and employed commercially for the production of blueprint papers of the ‘Blue Layer’ type as described in §4.8. The only difference was that the potassium ferrocyanide was more conveniently and economically incorporated in the sensitised coating, rather than used as a developer bath.

4.1.6 Light-bleaching of Prussian blue

Herschel discovered that there is yet another way of obtaining a positive-working image in Prussian blue; namely, to cause the image-forming light to bleach a uniform ground of prepared Prussian blue, by promoting its reduction to Prussian white in the presence of certain oxidisable substances (the function of which he may not have been aware). Unfortunately, such images cannot be fixed because there is no good way of removing the Prussian white without damaging the Prussian blue, as in the case above, so the picture quite rapidly reverts to its original uniform deep-blue ground under the effect of aerial reoxidation. Herschel was quite taken with this process, nonetheless, to the extent that he described it in a letter to the readers of *The Athenæum*, in preference to his negative-working process, as follows:

> “Mix together equal parts of the solution of the above-named salt [ammonio-citrate of iron], and of a saturated solution of, not the ferrosesquicyanate of potash (as stated in the *Athenæum*), but the common yellow ferrocyanate, or as it is called, prussiate of potash. The result is a very black ink, which, washed over paper, gives it a deep violet-purple colour, and is remarkably sensitive to light – whitening rapidly, and giving positive pictures – the only defect of which (and it is a fatal one for use) is their want of durability, as they fade with darkness in a few hours. And what is very singular, *the same paper* is again and again susceptible of receiving another and another picture, which die away in like manner without any possibility, so far as I have yet discovered, of arresting them.” [249] (italics in original)

The reported reversibility of this phenomenon is most striking, and it is given further consideration in Appendix III.9 and §9.1 on experiments on the fading of cyanotypes by light. This formulation is, in fact, a very early precursor of the ‘blue layer’ type of blueprint paper that was developed as late as the 1940s (see §4.8) using potassium ferrocyanide instead of ferricyanide. But the fact that Herschel was using brown ammonium ferric citrate meant that free ferric iron caused the formation of much Prussian blue immediately, which could not be removed and enable the use of the paper in a negative-working mode, through the intermediate formation of Prussian white, which reoxidised to Prussian blue. Herschel’s description implies that his chemicals must have been rather impure; when this combination is made with modern reagents, one does not get ‘a very black ink’, only a greenish coloration. Had Herschel’s chemical been of a higher purity (the green variety of ammonium ferric citrate rather than the brown), the benefits of using potassium ferrocyanide might have been discovered much earlier.

4.2 Pellet’s process

Twenty-five years had to elapse following Herschel’s experiments on the positive-working cyanotype process before it was commercially exploited and gained some acceptance in practice. It was promoted by the carbohydrate chemist Henri Pellet, who obtained an English patent in 1877 for a process that bears his name.[250] It was also patented in France in 1877,[251] and in the USA in 1881,[252] under the names of *Cyanofer* and *Papier Gommoferrique*. The new feature that Pellet introduced to solve the problem of fixing the positive-working process was based on earlier observations by Alphonse Poitevin in 1863, that ferric salts cause gum and similar colloids to harden and become insoluble in water, whereas ferrous salts do not.

Pellet included ferric chloride and gum Arabic in the sensitizer layer, in order to harden it and protect the Prussian blue image formed in the unexposed regions upon development. In the exposed regions, there were two consequences of the light-induced reduction of iron(III) to iron(II): the gum became re-solubilised and, on development in potassium ferrocyanide, insoluble Prussian white was formed, which could be readily wiped off, thus fixing the image without much disturbing the Prussian blue. Pellet’s successful positive cyanotypes were exhibited in the 1878 International Exhibition held in Paris, and apparently excited the admiration of J M Eder.[253] Pellet’s patents, however, are framed in such vague ‘catch-all’ language that it is not possible to extract from them a clear working method – doubtless, just as he intended. Solutions of many types and compositions are cited as examples. Lietze's Manual sets out an abridged version of Pellet's US Patent of 1881; the following brief quotation will convey a taste of its wholly ambiguous style:

> "After exposure, it is passed through a bath of yellow prussiate (ferrocyanide of potassium), the bath being concentrated, or dilute, neutral, slightly acid, or slightly alkaline, hot, or cold." [254]

Given information of this opacity, it comes as no surprise that, at the end of his transcription, Lietze is moved to observe:

> "The author has tried Pellet's process, several times ... without succeeding in producing good prints. The background was always more or less colored." [255]

Pellet is said to have received much benefit and distinction from his process at the time,[256] but his commercial paper met with varying approbation because the processing was quite complicated and not a little uncertain in its outcome. In addition to Lietze, other contemporary authors have reported on its unsatisfactory performance.[257] By 1943, the process was deemed to be defunct.[258]

In contrast to Pellet's obfuscated patent specification, two clearly-formulated, but slightly different, versions of Herschel's positive-working process were subsequently published in many manuals.[259] It should be noted that these recipes are given according to the 'old fashioned' method for making up solutions (see Appendix III), but are here converted into metric units.

The first was published by Giuseppe Pizzighelli and Ludwig von Itterheim in 1881. Three stock solutions are required:

A. Gum Arabic:	20 g in 100 cc of water
B. Ammonium ferric citrate:	50 g in 100 cc of water
C. Ferric chloride:	50 g in 100 cc of water.

These three solutions are mixed in order, in the volume ratios:

A : B : C = 20 : 8 : 5

Regarding the coating, the published accounts differ significantly in their advice: the mixture becomes very viscous after a few minutes, in which condition, one source says, it is suitable for coating the paper; however, some accounts assert the contrary and recommend immediate coating before it thickens. Yet another description states that the thick cloudy mixture eventually becomes clear and liquid again, and that this is the time when it is ready for use.

After exposure (which is markedly shorter than for the conventional cyanotype) the image is developed by a solution of potassium ferrocyanide: 20 g in 100 cc of water, which may be brushed on. It is next washed in water and the soluble gum is removed by a soft brush. Finally it is cleared in a solution of dilute hydrochloric acid, washed again and dried.[260]

The second process is often attributed to Colonel James Waterhouse,[261] but he, in turn, acknowledges that the method was recommended by Fisch.[262] According to Duchochois,[263] the formula is substantially that devised by Poitevin, with the addition of gum Arabic, according to Pellet's suggestion. Three stock solutions are again combined at the time of coating (the quantities below have been scaled to make them directly comparable with the method described above):

A. Gum Arabic:	26 g in 100 cc of water
B. Tartaric acid:	27 g in 100 cc of water
C. Ferric chloride:	100 g in 100 cc of water[264]

These three solutions are mixed in order, in the volume ratios:

A : B : C = 13 : 3 :2

The mixture is set aside in the dark for 24 hours then diluted with distilled water to a hydrometer reading of specific gravity 1.100, when it is ready for coating. The processing procedure is identical to that given above.

Under the direction of Waterhouse, both these procedures were tested and compared by a Mr Pope in the Survey of India Photographic Office, Calcutta, in 1887-8. In the climate of that country, they found that paper sensitized by the second method had the better keeping properties. The process was quite extensively used in Waterhouse's office for duplicating maps in the the Survey of India.[265] The process was much less common than blueprint, and since it called for greater skill, it tended to be confined to the hands of professional blueprinters.[266]

4.3 Survey of negative-working formulae

As was seen in Table 4.1, Herschel's two recipes for negative cyanotype in his *Memoranda* differ from the proportions that his son Alexander recalled in the 1870s, and these differ again from the proportions that are commonly claimed to be Herschel's by the principal manuals on the subject. In the absence of further information to resolve this disparity, I felt it necessary to investigate all four formulations in the experimental investigations described in §9.1.

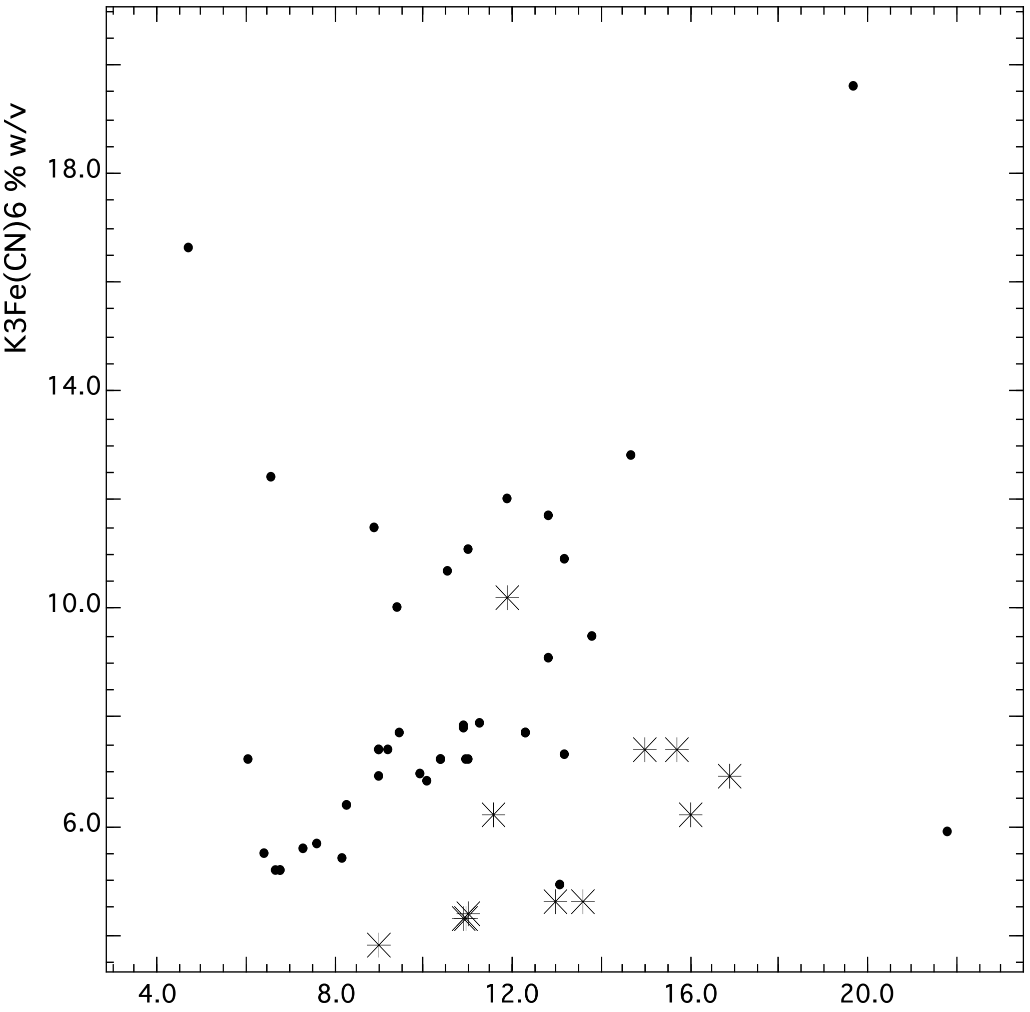
The only significant chemical advance in the entire history of the cyanotype process was brought about by the preparation of an alternative form of ammonium ferric citrate in 1897 by Eduard Valenta (1857–1937).[267] This new substance is green and somewhat acidic, in contrast to the brown, and basic form of ammonium ferric citrate which had been used hitherto; it was claimed that the green form provided a sensitizer eight times faster than the brown.[268] However, the apparent speed depends on the criterion for its assessment; there is less speed difference in the mid-tones than in the shadows where solarisation has an effect. A comparison of the two substances is summarized in Table 4.2.

Property	**Brown Salt**	**Green Salt**
First preparation	ca. 1840	Valenta 1897
Iron content	19% - 28%	14% - 18%
Nature of salt	Basic	Acidic
Speed of printing	Slow	*ca* 1 stop faster in midtones
Reversal or 'solarization'	Relatively slight	Stronger effect: higher Dmax
Edge etch effect	Distinctive	Absent
Colour of image	Dull blue	Brighter blue
Light fading of image	Fairly resistant	More susceptible

Table 4.2 Comparison of green and brown ammonium ferric citrate as cyanotype sensitizers

The sources of the green salt were limited at first to a few chemical manufacturers in Germany,[269] but it soon became available in the USA, and after 1900 the majority of cyanotypes were probably made by its means. The chemical implications of this discovery are examined in more detail in Appendix III. Most 20th century formulations of cyanotype recommend the green form of the salt in preference to the brown.[270]

I have compared the formulae in about sixty published recipes for the cyanotype process,[271] by converting the various archaic expressions for solution strengths into a single system of units: the concentrations of potassium ferricyanide and ammonium ferric citrate are expressed as 'weight per cent volume' (% w/v – see Appendix IV) *in the final, mixed sensitizer solution*, thereby avoiding the problem of comparing recipes where the two stock solutions are not mixed in equal amounts.[272] The results of this survey take account of the introduction of green ammonium ferric citrate in 1897, and are conveniently displayed in graphical form in the scatter chart, Figure 4.1, which conveys some impression of the range of different proportions that have been recommended over 150 years.



Ammonium ferric citrate % w/v ⁎ green salt; • brown salt

Fig 4.1 Composition of cyanotype sensitizers

Apart from three wild 'outliers', the recipes using brown ammonium ferric citrate are grouped around average final concentrations of 10% for the brown ammonium ferric citrate and 8% for the potassium ferricyanide. The recipes using the green salt are clustered around final averages of 13% for the green ammonium ferric citrate and 6% for the potassium ferricyanide.

As can be seen from the range of concentrations in the chart, the process appears to work satisfactorily almost regardless of the proportions chosen; presumably there is little difference to the visible outcome – at least so far as these many practitioners were able to judge. This is not particularly surprising when it is realised what a small proportion of the sensitizer originally applied to the paper actually remains as Prussian blue in the final image (see Appendix III).

The flexibility in the formulae using the brown ammonium ferric citrate is born out by the report of Channing Whitaker in 1883, who tested sensitizer solutions with a wide range of compositions, having the concentration ratio of ammonium ferric citrate to potassium ferricyanide varying from 2% : 20% to 20% : 2%, respectively. On the basis of his results, Whitaker settled on an optimum ratio of 15% : 10%. He remarks that ‘the same blue results with any good proportions of the chemicals named.’[273] According to Whitaker, excess of the citrate speeds printing but shortens the storage life of the coated paper; excess of the ferricyanide provides a finer quality but greatly lengthens the exposure time (due, as we now know, to the ‘internal filter effect’).

Anyone wishing to make use of this method today will find it convenient to mix equal volumes of the two stock solutions; the recommended average concentrations of these should therefore be made up approximately to the following:

20% w/v for brown ammonium ferric citrate, and
16% w/v for potassium ferricyanide;
or
26% w/v for green ammonium ferric citrate, and
12% w/v for potassium ferricyanide.

Further practical details are given in §7.1. The differing ratios of the two components reflect the different iron contents of brown and green forms of ammonium ferric citrate, which are further discussed in Appendix III.4.

4.4 Modifications of the cyanotype sensitizer

4.4.1 Robert Hunt’s ‘chromo-cyanotype’

In 1844, Robert Hunt (1807–1887) published a paper entitled ‘Chromo-Cyanotype, a new Photographic Process’.[274] Hunt had been studying the light sensitivity of potassium dichromate, and had already devised several photographic processes based upon it, such as the chromatype, in which it was mixed with copper sulphate. The chromo-cyanotype sensitizer was a mixture of potassium dichromate and potassium ferrocyanide; depending on the developing agent, which could be either ferrous sulphate or ferric sulphate, a positive- or a negative-working image, respectively, was obtained, the latter being of rather stronger quality. Hunt found this difficult to explain at the time, and it may be significant that he made no further mention of this process in his subsequent Manual of 1853.[275] It is now known that potassium dichromate rapidly oxidises potassium ferrocyanide to the ferricyanide;[276] if the effect of light is to cause the photoreduction of this back to the ferrocyanide, possibly assisted by a chromium(IV) or (V) species which would be present, the development phenomena reported by Hunt become comprehensible. A number of cyanotypes feature among Hunt's early photographic specimens which were re-examined in 1890, when his widow sent a parcel of them to John Spiller.[277]

4.4.2 John Mercer's 'chromatic photographs'

John Mercer (1791–1866) was a self-taught colour chemist and calico-printer of Manchester, and is remembered today for inventing in 1850 the process to which his name has been given – that of mercerization, the strengthening and shrinking of cotton by treatment with caustic alkali. I have already noted in §2.2 that he has the distinction of being the earliest observer (in 1828) of the photochemical formation of Prussian blue; but he did not follow up this discovery until 1847, when he evolved the following method for obtaining negative cyanotypes:

> "I found that if paper or cotton cloth is smeared with a solution of pernitrate or persulphate of iron with certain quantities of oxalic and tartaric acids, dried in the dark, then exposed to the light (solar), and immediately dipped in solution of red prussiate containing a little free sulphuric acid (preferably free from yellow prussiate), where the light has caused deoxidation, the blue is fixed, and where the peroxide remains unchanged there is no colour. The cloth or paper must be washed immediately in water containing a little sulphuric acid, and afterwards in pure water. The picture is a reverse blue print." [278]

Mercer's business commitments allowed him little time for progressing these experiments until 1854, when he began to produce striking, richly-coloured prints on paper, and cotton fabrics especially, which were exhibited at the annual meeting of the British Association for the Advancement of Science, in Leeds in 1858.[279] The short note in the *Transactions* describing this lecture seems to be the entire extent of Mercer's publication of his work,[280] but fortunately Parnell's biography of Mercer contains details of his formulae,[281] taken from Mercer's own notebooks and memoranda.

His preferred process was based on a cyanotype formulation of a singular kind, that seems not to have been previously employed by anyone else.[282] His sensitizer was a solution of ferric oxalate, prepared by the oxidation of freshly precipitated ferrous oxalate by nitric acid in the presence of excess oxalic acid. He does not explain his choice of this troublesome preparation, rather than using the universally available ammonium ferric citrate, but it must have been due to his particular interest in printing on textiles rather than on paper. He had already shown that ferric oxalate is a good mordant for dyeing wool and cotton and had introduced its use into his own dyeworks; whereas the citrate is ineffective in not being absorbed by the cellulose fibres. Following the light exposure, he would sometimes treat the product directly with potassium ferricyanide solution to obtain a cyanotype as described above; but Mercer also adopted another unique procedure: fixation in a bath of sodium arsenate. This disagreeably toxic substance does not appear to have caused him any problems (it was then commonly employed by calico-printers) but it can hardly be recommended for general use today. Its effect is to convert both iron(II) and iron(III) oxalates into the corresponding arsenates, which are insoluble in water and photoinactive, but soluble in acids; thus the image in iron(II) is 'fixed', and then it may finally be 'brought up' by treatment with an acidified solution of potassium ferricyanide, which dissolves the iron(III) arsenate and converts the iron(II) arsenate into Prussian blue. If this procedure seems convoluted, it cannot be denied that it yielded fine permanent cyanotype images on calico and mercerised cotton, which survive well from 1857 to the present in the Mercer archive.[283]

4.4.3 Charles Burnett's 'cobalt cyanotype'

Charles John Burnett (1820–1907) is an equivocal figure in the history of photographic processes. His publications attest an eclectic interest in photoactive substances of all kinds, but it is sometimes hard to discriminate in his writings between the results of genuine experiment and the speculations of an inventive mind. As far as contributing to the cyanotype process goes, there is clear evidence that he exhibited a 'Photograph of Sea-weed' in Glasgow in September, 1855; the catalogue carries this description, originally contained in a letter from Burnett to William Church:[284]

> "Printed in natural colour, by process discovered in March last; paper prepared by ferridcyanide[[285]] of potassium, development by nitrate of cobalt solution." [286]

Burnett describes his experiments in more detail in *Photographic Notes* of 1857,[287] but is obliged there to admit that the ‘cobalt process’ prints, although remarkably beautiful initially, suffered a ‘very marked deterioration’ within a few months.

Another innovation suggested by Burnett in this article is the use of sodium nitroprusside instead of potassium ferricyanide for forming the pigment. Despite the differing names these are very similar compounds as may be seen from the formulae.[288] Burnett states that this salt “by itself gives a blue and white picture” and when mixed with ammonium ferric oxalate the resulting sensitizer yields a “dull green” image. The present writer has confirmed these claims but my investigation found a number of disadvantages – such as crystallization and very slow printing – which do not recommend these as viable printing procedures, especially in view of the toxicity and expense of sodium nitroprusside. Apparently Burnett exhibited prints made by these methods in 1859 at the London Photographic Society.[289] However in 1899 a US patent claimed that soluble nitroprussides could be combined with ammonium ferric citrate to give sensitizers yielding brown or black images – a surprising colour.[290] This is still an area with potential for some experimentation.

4.4.4 Other iron(III) salts as sensitizers

Several alternatives to ammonium ferric citrate as the light-sensitive component of the cyanotype have been suggested over the years. Ammonium ferric tartrate was first tried by Herschel, and the corresponding potassium salt was re-introduced in 1892 by an author who admitted that he had not read Herschel’s work.[291] No particular benefit has been claimed to result from their use, and they are rather uncommon chemicals.

In 1900 the brothers Lumiére found that ferric sucrate, made from cane sugar, is light-sensitive and has good keeping properties; a paper coated with this salt and exposed in the usual manner could be developed as a negative or positive cyanotype in potassium ferricyanide or ferrocyanide solutions.[292] This process does not seem to have been followed up.

Valenta, in 1917, reported the preparation of ammonium ferric glycolate, and found that paper sensitized with a mixture of this and potassium ferricyanide yielded prints of a

> “...fine intense indigo-blue colour, such as are not yielded with ferric ammonium citrate. But unfortunately the sensitized paper has exceedingly poor keeping quality, fogging in the course of a day or

> two in the dark ... It was not found possible to avoid this drawback by addition of oxidising substances to the sensitizer." [293]

The likelihood is that the quality of paper at that time may well have been inferior, and impurities may have been responsible for the reported rapid degradation. In view of this possibility, this novel photosensitive salt, and the cyanotypes that it furnishes, would seem to deserve re-examination.

The use of ferric oxalate as a cyanotype sensitizer has already been mentioned in §4.4.2, and will arise again in §4.4.5, but this salt is highly variable in its properties and composition, and is troublesome to obtain; a better alternative is the well-characterised substance, ammonium ferric oxalate, which can be widely purchased and does offer some real advantages over the traditional citrate, as will be described separately in §7.5. The use of ammonium ferric oxalate for 'pictorial' quality cyanotype sensitizers had been proposed in the past (§2.9), but when mixed with potassium ferricyanide, the sparingly soluble salt, potassium ferrioxalate, tends to crystallise out, ruining the image. The only procedure suggested to counter this was the wasteful one in which the 'latent' image was formed in ammonium ferric oxalate by itself, and then developed after exposure in a separate bath of potassium ferricyanide solution. Hermann Halleur in *The Art of Photography* of 1854 described this negative-working cyanotype, and recommended exposing "oxalate of sesqui-oxide of iron and ammonia" (i.e. ammonium ferric oxalate) alone, then developing it by brushing over a solution of potassium ferricyanide.[294] Matthew Carey Lea used this method of making cyanotypes to avoid the crystallization problem, and described it to the Annual Meeting of the British Association in 1863.[295] Although this method was also advocated with enthusiasm in an annual editorial review by Traill-Taylor in 1889,[296] it never passed into general practice, probably because the development bath rapidly becomes contaminated in use with excess sensitizer and precipitated Prussian blue, which will stain the print – this is clearly uneconomic in view of the price of potassium ferricyanide. In 1921 the claims of a German patent that ammonium ferric oxalate could be employed in the sensitizer in place of the citrate were tested experimentally by Valenta, who came to the conclusion that the claims were unjustified and it was inferior because of the crystallization problem.[297] However, it will be shown in §7.3 how ammonium ferric oxalate *can* be used in a modern improved cyanotype process.

A related variant to this is the employment of the unusual cation in guanidinium ferrioxalate for the cyanotype sensitizer.[298] A US patent of 1941 claimed that this sensitizer had a better shelf life,[299] but it does not seem to have been taken up for cyanotype, although it has been employed recently for an iron-silver process.[300]

From time to time a number of additives have been suggested to improve the performance of the traditional sensitizer, but these proposals are rarely acccompanied by direct experimental comparisons to demonstrate their putative benefits. However, in 1955 Hnatek published a detailed investigation of the enhancement of the sensitivity of brown ammonium ferric citrate by the addition of carboxylic acids.[301] He found that oxalic or tartaric acids increased the sensitivity and printing range considerably, but that citric or acetic acids had no significant effect. Most acids will assist clearing because a low pH prevents hydrolysis of the iron(III) to its insoluble yellow hydrated oxide. Moreover the light sensitivity of ammonium ferric citrate has been found to pass through a maximum at pH 3 to 4. The presence of a small amount of dichromate assists sensitizer stability and shelf-life by preventing premature formation of Prussian blue. Many of these findings probably stem from endeavours to improve the characteristics of commercial blueprint papers which will be considered later in §4.8.

4.4.5 Terry King’s ‘cyanotype rex’

In 2004 Terry King, then chairman of the Historical Group of the Royal Photographic Society, announced his 'Cyanotype Rex' process for which he claimed "modern improvements" both on the traditional cyanotype and the new cyanotype.[302] The first “improvement” was the use of ferric oxalate, rather than ammonium ferric citrate, as the sensitizer. The author seemed unaware that ferric oxalate had been employed by Mercer in the 1850s (§4.4.2) and its use for negative-working cyanotype is clearly described in the *British Journal of Photography* of 1874;[303] eventually, ferric oxalate became a common ingredient in the many patented blueprint formulations of the 1930s (§4.8). However, the availability of ferric oxalate today is very limited: its preparation is beset with uncertainty over the nature and purity of the product and, owing to this variability of the substance's composition, few – if any – fine chemicals houses will stock it. Ferric oxalate is a polymorphic and notoriously 'ill-characterised' compound, reluctant to dissolve in water, unstable when persuaded to, and giving a solution that is limited in shelf-life and unreliable in practice.[304] Its present-day use for alternative printing processes is further disadvantaged by its monopolistic price, which is many times that of pure ammonium ferric oxalate, the preferred, commercially-available photosensitive salt.

The second “improvement” was the procedure discussed above in §2.9 of exposing the sensitizer coating alone, then applying the potassium ferricyanide in a separate development bath.[305] The serious print-maker will find this both expensive and wasteful, because the ferricyanide ‘developer’ bath soon accumulates a staining impurity of Prussian blue, causing a rapid fall-off in the quality of successive prints put through it, and it must therefore be frequently replaced. A litre of 10% potassium ferricyanide solution may cost over £5.

A third “improvement” states that:

> “Where traditional cyanotypes can prove difficult to tone, the Cyanotype Rex tones beautifully in alkaline solutions of varying strength…” [306]

It has long been known that the destruction of Prussian blue by alkalies is far from “difficult”, so there seems to be little novelty in this “improvement”. Historical toning procedures for cyanotypes are described further in §8.

The use of ‘separate development’ can, however, justly claim one advantage: an increase in printing speed. In a conventional mixed cyanotype sensitizer the ferricyanide ion inevitably absorbs some of the actinic UVA light non-productively, thereby lowering the sensitivity (Appendix III.2). By placing the ferricyanide entirely in a development bath, this ‘internal filter effect’, as it is called, is eliminated, with a consequent restoration of speed amounting to about two or three stops (4-8x) at most. This was hailed as a “huge improvement in speed” for the ‘Cyanotype Rex’ process, which was said to provide “viable camera-speed photography”. This claim calls for careful examination: where Maunder and King refer in their articles to:

> “…exposure times well down to a minute.” [307]
>
> “…exposures cut down to a few seconds or minutes.” [308]

they are being ‘economical with the truth’. They do not make it clear that these times refer to ***contact*** exposures, which require roughly a hundredth of the in-camera exposure time.[309] Contact exposure of “a minute” agrees with the theoretical calculations, and with the experience of anyone who has made a new cyanotype (§7), which takes about one or two minute's exposure to the sun for a photogram. An in-camera exposure of the same sensitizer requires a few hours at f/5.6, depending on the weather, as my own tests have shown.

Even with King's "fastest" camera exposures in the order of an hour at maximum lens aperture, there is actually little point in trying to produce cyanotype negatives in the camera,. An hour is hardly a useful exposure duration for portraiture, people, or subjects in motion, so the claim that these processes are "viable in-camera technologies" that will "revolutionise photography" is an absurd exaggeration.[310] Moreover, cyanotype negatives can only produce very dingy positive images when printed with the UVA-sensitive alternative printing processes; the lack of contrast is due to the fact that the negative is blue, and therefore has low optical density in the operative region of the spectrum. As an alternative to printing such cyanotype negatives, J.E. Piper has adopted the procedure of tonally inverting them in Photoshop, with the results that can be seen on the Alternative Photography website.[311]

Finally we note that King has recently progressed by announcing his discovery of the process 'Cyanotype Rex (2)',[312] which employs the advantages of using ammonium ferric oxalate, (first published by Hermann Halleur just 160 years ago, see §4.4.4).

4.4.6 Cyanotype using uranium salts

Among the many variations suggested for the cyanotype process, one which has receded into obsolescence, probably for safety reasons, is the addition of uranium(VI) salts to the sensitizer. This was claimed to enhance sensitivity, and to speed up printing by catalysing the photoreduction of iron(III) to iron(II). Tests by this author have shown that addition of uranyl nitrate at the 1% to 2% level to both ferrioxalate and ferricitrate sensitizers does indeed increase speed of printing by about one stop (a factor of 2x) but further increases in the uranium concentration bring little additional advantage.[313]

A form of so-called 'uranium cyanotype' (a serious misnomer) or, better, 'uranotype' should also be mentioned here, in which the sensitizer consists entirely of a uranium(VI) salt, which is transformed by light to uranium(IV). Treatment after exposure in a development bath of potassium ferricyanide yields an image in red uranyl ferrocyanide, a process which was originated by Burnett.[314] Examples of contemporary users in the 21st century include alternative process artists Robert W. Schramm,[315] Bob Kiss,[316] and the late Blake Ferris.[317] The rich mahogany red colour and relative stability of uranyl ferrocyanide have also suggested the use of this substance as a toner of silver-gelatin materials,[318] and of platinotypes, where the action is catalytic.[319] By treating an uncleared platinum print, which still contains iron(III), with this toner, the two pigments, one red and one blue, uranyl ferrocyanide and Prussian blue, are formed simultaneously, and the mixtures of them can therefore produce a whole gamut of unattractive false colours superimposed upon the long-suffering platinum image.[320]

4.5 Cyanotype diapositives on glass and film

From the end of the 19th century, when the 'magic lantern' enjoyed great popularity, it is not surprising to find published instructions for the means to make cyanotypes on glass slides. According to one account, the procedure is simply to coat a glass plate with gelatin and, when dry, immerse it in a conventional cyanotype sensitizer.[321] A more detailed procedure starts with old, unused (and probably fogged) silver-gelatin plates and describes how the silver salts are first removed by a thiosulphate fixer bath, and the gelatin layer then hardened by chrome alum. If the plates already have a silver image, they can be cleaned by a ferricyanide/thiosulphate bath ('Farmer's Reducer'). After washing, the hardened gelatin-coated plate is soaked in a conventional cyanotype sensitizer for several hours, then carefully wiped and dried. Exposure and processing is similar to that of a conventional paper cyanotype. The transparencies are said "to show remarkably fine detail when compared with an ordinary blueprint." [322] George Brown, in his treatise on *Ferric and Heliographic Processes*, also gives detailed instructions for making cyanotype transparencies on glass and translucent paper. He prefers iodine cyanide to Farmer's reducer for removing old silver images from spoiled lantern plates. He also provides a recipe for making transparencies using collodion, instead of gelatin, as the binder vehicle for the iron sensitizer.[323] The problem of coating glass to make it receptive to aqueous sensitizers has recently been addressed by Bill Winkler using some modern chemistry – an amino-alkoxysilane to bind to the glass surface, and mediate a coating of PVA and organic hydrophilic colloid such as starch which can absorb the sensitizer.[324] Winkler uses the method for platinum-palladium printing, but it should be adaptable to cyanotype.

If a flexible substrate (plastic film) is acceptable, rather than a rigid one (glass), then the transparency films intended for making digital negatives (e.g. from Pictorico or PermaJet) will be found to take aqueous iron-based sensitizer solutions very well, and the zeolyte coating holds the image nanoparticles without 'bleeding'. Diapositive contact prints have been made by the author on Pictorico OHP transparency film coated with new cyanotype sensitizer. Tonalities are very good, the only problem is in laying down the coat evenly: the usual glass rod coater is unsuitable, suffering intolerable friction on the ceramic-treated surface of the film. A squeegee or foam brush is better, and a straight Teflon (PTFE) rod makes an acceptable coating instrument for Pictorico – smooth and clean with no friction, although its hydrophobic nature is a disadvantage. [325]

There is one possibly important consequence of using plastic film as a substrate for alternative printing which remains to be tested: it is presumably much more dimensionally stable than cellulose paper under wet processing – so might prove useful to those who favour multiple coating and developing for their image-making. If it works for new cyanotype, there is no reason why it should not also work for platinum, palladium and other siderotype processes. It also has the advantage that this substrate can be used 'out of the box' with no pretreatment at all.

4.6 Cyanotypes on ceramics

The use of cyanotype on ceramic substrates suggests an attractive reminiscence of the celebrated blue Delftware, but regrettably it is limited by the fact that Prussian blue cannot be fired under a glaze because it decomposes thermally around 200 C, with the evolution of poisonous cyanogen and hydrogen cyanide gases, destroying the blue and leaving only weak brown 'iron earth' coloured images (iron oxides). However, the sensitizer is easily imbibed into a bisque-fired ceramic surface, such as possessed by unglazed tile bodies. This is still very absorbent and probably needs its porosity to be restricted with a sizing agent, such as gelatin. Dutch designer and artist Sarah van Gameren of Studio Glithero in North London has succeeded in making plant photograms in cyanotype on tiles and effectively clearing and sealing the image surface for permanence, possibly with an acrylic varnish.[326] The Studio has devised means to shape their botanical specimens onto the curved surfaces of earthenware, so can also offer uniquely decorated blueware vases and lampshades.[327]

It is worth warning that cyanotype does not work on plaster surfaces treated with 'gesso' which contains chalk – calcium carbonate – an alkaline substance very hostile to cyanotypes, which are destroyed by alkali (§9.2). The inappropriateness of this substrate for cyanotype is also the reason why Prussian blue pigment was not used by artists for fresco painting.

4.7 Cyanotypes on fabrics and textiles

One of the earliest commercial uses found for Prussian blue itself was for dyeing all kinds of traditional fabrics – cotton, silk and woollen – in a range of shades of blue, controlled by the details of the process. In the industrial practice of the nineteenth-century, two baths were generally used: the first was a solution of a ferric salt, usually the nitrate or chloride, which mordanted strongly to the fibres of the fabric, then, after rinsing, it was followed by an acidic bath of potassium ferrocyanide, which formed the Prussian blue pigment in situ.[328]

Of all the possible methods of printing photographic images, the iron-based processes would seem to be best-suited to delicate textiles, because they do not employ a sizing agent or binder medium, such as gelatin or gum, which would spoil the 'drape' of the fabric. I have already described how John Mercer discovered at an early stage that textiles can be impregnated with cyanotype sensitizers to enable them to receive decorative photographs or photograms. The process was popular,[329] and continues to be used successfully by present-day practitioners, such as the British textile artists Wendy Wilson and Barbara Jones, and the American artist and designer, Jan Arnow.[330] Wilson has found that the mordanting of sensitizer to cotton and silk fibres appears to be better with ferrioxalate, rather than with ferricitrate sensitizers.[331]

In the past, a bath of potassium dichromate was commonly recommended as part of the wet-processing of fabric cyanotypes, both for development (re-oxidation), and reputedly for improving the light-fastness of the image. Dichromate could act either by destroying potential reducing agents which would assist fading, or possibly by being itself incorporated into the Prussian blue. However, the toxic, allergenic and carcinogenic hazards now recognised in dichromates make this practice particularly inadvisable for prints on fabrics, which may come into contact with human skin. There is at least one well-documented case-history of an artist working with cyanotype on textiles who suffered considerable ill-health as a consequence of using dichromate baths.[332]

The process of making cyanotypes on fabrics to provide photographic decoration for quilt-covers and cushions became quite popular in North America in the period 1880–1920, and even built up to a minor industry, as is evidenced by at least one commercial catalogue, from the Nashua Pillow Company of New Hampshire, which offered for sale several cushion covers illustrated with cyanotype scenes of natural beauty or national and patriotic significance. The catalogue proudly declares that:

> "There is no happier combination of ornamentation and usefulness for the Home Beautiful, than a Blue Print Sofa Pillow Top." [333]

The Nashua Pillow Company also offered a service for transferring the customer's own negatives into cyanotype prints on prepared fabric. The assertion is made in this catalogue that, in terms of brilliance and permanence, the cyanotype prints on cloth were superior to those on paper, although it is hard to understand the basis of this claim. A fine specimen of this genre, which is probably one of the Nashua Pillow Company's products, can be seen in the collection of the National Gallery of Canada: a cushion cover bearing twelve cyanotypes of unidentified coastal landscapes.[334] The rediscovery of other specimens of the Nashua Pillow Company's products has been recently reported. The company also offered its sensitized blueprint cloth for sale in 1900, under the registered trade mark of 'Silkdown', at 75 cents per square yard.

The tradition of fabric printing in cyanotype was continued in the USA by Barbara Hewitt, a specialist supplier of sensitized textiles who founded with her husband, John Basye, the Californian company of *Blueprints-Printables* in 1983, and published an attractive craft handbook on the subject of *Blueprints on Fabric*.[335] On their retirement, the company was taken over by Linda Stemer of Vashon Island WA, as *Blueprints on Fabric* and continues to supply this market in the USA today.[336] In the UK, Ruth Brown was also inspired by Barbara Hewitt's artistic enterprise with textiles, and founded her own cyanotype fabric printing business, *Stone Creek Textiles,* at Sunk Island, Yorkshire,[337] publishing her own contemporary handbook on the subject.[338] The history of the use of cyanotype on fabrics has recently been reviewed in the Journal of the *Surface Design Association*.[339]

4.8 Gel lithography: 'true-to-scale' process

The invention of this photomechanical process for offset duplication of plans and drawings has been attributed to A. Tellkampf and A. Traube, who obtained a German patent in 1905.[340] However, Nadeau in his *Encyclopedia* cites evidence that the idea was conceived by Félix J. Dorel of England in 1900 who licensed the secret process in 1904,[341] and later re-patented it in the USA.[342] The explanation for its alternative name 'the true-to-scale process' is that no wet-baths were involved in processing the reprographic image, so there was no dimensional change in the paper substrate, and copies of exactly the original size were obtained – a characteristic of great importance for the accurate reproduction of scale drawings, without the necessity to annotate them with dimensions. Shrinkage of prints during wet processing had previously been one of the chief difficulties besetting the photo-printer.

Gel lithography was also variously known in its hey-day by several proprietory names: Lithoprint, Ferro-gelatine, Fotol, Ordoverax, Velograph or Fulgur printing. The method took an over-exposed, but unprocessed negative blueprint image as its source, which was lightly squeegeed into contact with a matrix of moist gelatine, known as a "graph", containing a ferrous salt. Diffusion of excess potassium ferricyanide out of the lightly-exposed and unexposed regions of the cyanotype (the image shadows) formed Prussian blue in the gelatin matrix, with the effect of hardening it locally, so making it receptive to a greasy lithographers' ink, which was still repelled by the moisture in the unhardened regions of the gelatin. After a minute or so, the cyanotype was peeled off and the jelly surface inked with a roller. About 25 positive copies of the original image could be 'pulled', using little pressure, from the jelly, which was re-inked between each.[343] There are a number of fine points of detail to observe in formulating the gelatine mass and the cyanotype paper if best results are to be obtained.[344] This first successful 'dry copying' process became the preferred method for reproducing engineering drawings and it was a major reprographic process until the 1950s,[345] but then rendered obsolete by the advent of diazo and electrostatic reprographic methods.

As it was originally formulated, the process is only suitable for line drawings and cannot adequately reproduce the continuous tonal gradation of a photograph, in the way the collotype process, for example, can. However, a number of modifications were introduced, using a half-tone screen to enable pictorial matter to be reproduced by either positive- or negative-working processes,[346] and most recently Roger Farnham of Glasgow has created very effective halftone gel-lithographic prints by adding a grain screen to the image in Photoshop.[347]

A similar principle of colloid hardening by the diffusion of ferric salts underlies the 'Iron-Ozobrome Process', which also takes a cyanotype as its starting point.[348] This is first hydrolysed by a dilute sodium hydroxide bath to ferric hydroxide, then squeegeed into contact with a carbon tissue which has been immersed in a bath of dilute sulphuric acid and formaldehyde. Over a period of about an hour the ferric ions in the cyanotype are rendered soluble by the acid and diffuse into and harden the gelatin of the carbon tissue in the shadow regions of the image, so providing a positive-working process. After separation, the carbon tissue can be developed in the usual way. Another variation is to coat the ferric hydroxide image with pigmented gelatin, and when dry, to immerse in the acid/formaldehyde bath. The print is then developed from the front with warm water.

4.9 Commercial blueprint papers

The great majority of commercial blueprint papers were made for plan-copying – i.e. 'line' work – which naturally calls for characteristics rather different from those desirable in papers intended for pictorial purposes. For this reason, commercial blueprint papers will not be very fully considered in this book, but insofar as they did find a limited pictorial use, it will be appropriate here to summarise the history of their development.[349]

The paramount considerations for blueprint copying were expediency in exposure and processing, high contrast, and good shelf-life. The properties of an ideal copying paper were described as follows:[350]

- It should be as sensitive as possible, being fast enough to print by electric arc light, or mercury vapour lamp, within a few seconds.
- The contrast should be high, 'line' images with an intense blue, and whites that clear rapidly in the wet processing, which was usually carried out in a continuously-operating machine.
- The blue colour should retain its quality even when over-exposed.
- There must be no 'bleeding' or running of colour from the exposed portions into the unexposed white lines, even when the paper is over-exposed.
- The paper should remain stable on long storage, for two or three months, without the unexposed portions developing blue pigment.

In practice, using the customary formulations, these requirements proved to be mutually conflicting. The ferricyanide component absorbs blue and ultra-violet light strongly, but contributes little itself to the light-sensitivity, and therefore acts as an 'internal filter', attenuating the printing light to no good effect. In order to achieve high speed (criterion 1) the ferricyanide concentration must be kept low, with the result that the maximum intensity of blue (criterion 2) is limited. Necessarily, it follows that the light-sensitive component, ferricitrate or ferrioxalate, will be present in great excess over the ferricyanide; with the undesirable consequence that even slight over-exposure will generate excess ferrous iron, which washes over into the unexposed portions causing ‘bleeding’ (criterion 4), and in the exposed regions it adversely affects the quality of the colour, giving it a greyish cast, called ‘burning out’ (criterion 3). In order to improve the keeping and washing properties of the paper (criterion 5), substances such as alkali metal oxalates, citrates and phosphates were added to the sensitizer mixture, but their presence diminished the sensitivity (criterion 1) and degraded the intensity and quality of the colour (criteria 2 and 3).

As a result, the sensitizers employed for early copying papers embodied a compromise between these conflicting requirements; they were only capable of relatively low maximum density – just a mid-blue sufficing for plan blueprints. In view of this lack of density and the high contrast, photography texts often warned the amateur against the use of commercial copying paper for pictorial purposes.

The formulations used by early manufacturers of blueprint paper were generally withheld as commercial secrets, and even today they are reluctant to release explicit recipes. Fortunately, there are at least two published accounts of early formulae that are readily accessible: by Robert E. Kwech, a chemist of the Huey Blue Printing Company of Chicago,[351] and by K Willcock.

The paper employed for coating had a high proportion of rag stock, usually between 50% and 100%, and was surface-sized with ‘animal glue’ or gelatin, but not highly calendered. Kwech describes manufacturers of the time (1924) adopting four varieties of blue-printing formulae, depending on the speed of the final product, which he designates as ‘Regular’, ‘X’, ‘XX’, and ‘XXX’, requiring relative exposures of 4 minutes, 2 minutes, 45 seconds and 15 seconds to bright sunlight. The sensitizers for these are summarised in Table 4.3 which gives both the proportions of the various stock solutions that were taken, and the resulting final concentrations (as %) of the ingredients in the mixed sensitizer. The ‘Regular’ solution was claimed to be Herschel’s, and deemed most satisfactory for photographic purposes. The faster papers were intended for continuous printing in arc-light machines, and were suitable only for line subjects. The recipes for these tend to be more dilute, (the concentration of ferricyanide has to be very low – about 1 to 2% – to minimise the internal filter effect) and to contain some ferric ammonium oxalate (which is more light-sensitive than the citrate), and even some ferric chloride.

Parts by volume (final % w/v)		Paper	Grade	
Solute concentration	**Regular**	**X**	**XX**	**XXX**
Ammonium ferric citrate 26%	4 parts (16)	4 parts (11.6)	–	3 parts (10.4)
Ammonium ferric citrate 16%	–	–	4 parts (6.4)	–
Sodium ferric oxalate 10%	–	3 parts (3.3)	4 parts (4)	1 part (1.3)
Ammonium ferric oxalate 10%	–	–	–	1 part (1.3)
Ferric chloride 7%	–	–	0.5part (0.35)	1 part (0.93)
Citric acid 10%	–	0.5part (0.6)	–	–
Oxalic acid 10%	–	–	0.5part (0.5)	1 part (1.3)
Potassium ferricyanide 16%	2.5parts (6.2)	1.5part (2.7)	1 part (1.6)	0.5part (1.1)
Exposure to bright sunlight	4 mins	2 mins	45 secs	15 secs

Table 4.3 Commercial blueprint sensitizers – Kwech's formulae
(Figures in parentheses are % w/v in final mixed sensitizer)

The complexity of these recipes is almost Byzantine, and it is hard to credit that the formulations have actually been optimized by testing all the variables. The use of citric acid as a 'clearing agent' will be noted; the implications of this for image fading will be discussed later. In 1935, K Willcock published three recipes for blueprint sensitizer solutions suitable for a commercial coating machine: 'Herschel's', a 'medium-rapid', and an 'ultra-rapid' formula;[352] these were reprinted by Neblette in the 4th edition of his treatise in 1942.[353] They differ in some respects from Kwech's formulae, in containing gum Arabic, and may be compared in

Table 4.4 where the concentrations have been converted to the percentages of the components present in the final mixed solutions.

Component	Herschel	Rapid	Ultra-rapid
Ammonium ferric citrate	10	7.5	4.4
Ammonium ferric oxalate	-	-	2.3
Sodium ferric oxalate	-	2.5	3.8
Ferric oxalate	-	0.16	0.6
Gum Arabic	1.9	1.9	1.9
Potassium ferricyanide	5	2.5	2.3

Table 4.4 Commercial blueprint sensitizers - Willcock's formulae
(Figures are % w/v in final mixed sensitizer)

The faster the blueprint paper, the worse were its keeping properties. There is an extensive patent literature, claiming a variety of improvements to blueprint papers, which has been summarised by Kosar, whose monograph should be consulted for a full list of references.[354] The criteria for such improvements were usually dictated by commercial factors, such as the shelf-life of the paper, speed of exposure, or expediency of wet-processing, rather than by consideration of its pictorial qualities.

Processing of commercial papers usually entailed 'development' in a dilute (ca. 7%) dichromate bath rather than just pure water,[355] to re-oxidise any solarized Prussian white rapidly back to Prussian blue, and possibly to improve the light-fastness of the image (see Chapter 7). A preferable oxidant, which was marketed under a proprietory name as a blueprint 'developer', was urea peroxide;[356] it has none of the toxic disadvantages of dichromate, and in solid form is more convenient to distribute than hydrogen peroxide solution, which may also be used, but there are serious safety reservations about the storage of such organic peroxides, which present an explosion hazard.

By 1930, the current patent specifications imply that ammonium ferric citrate had been almost entirely displaced from the commercial formulae by ammonium ferric oxalate, in the interests of faster printing. Around the mid 1930s, however, the manufacture of blueprint paper saw the introduction of a significantly different way of formulating the sensitizers, involving the addition of potassium ferrocyanide. This reacts with the ferrous iron generated by light to yield Prussian white, which can subsequently be readily oxidized to Prussian blue by the ‘developer’ in the wet processing sequence. For further discussion of the chemistry of this process see Appendix III.

It was noted earlier that potassium ferrocyanide had been first employed by Herschel (with ammonium ferric citrate), in the hope that it would furnish a positive-working process. Superficially this appeared to be the case, because Herschel’s chemicals were of low purity, and mixing them resulted in the formation of a significant amount of Prussian blue, which was at first bleached by light to give a positive image. However, the major portion of the reactants still constituted a negative-working sensitizer producing Prussian white which oxidised to the Blue, so prolonging the exposure led to the rather puzzling observation of a positive image gradually fading and being replaced by a more permanent negative one.

In modern times, the use of potassium ferrocyanide was first suggested by Kwech in 1931 as a ‘pre-development’ bath which followed the exposure, in order to eliminate ‘bleeding’.[357] Later it was found that potassium ferrocyanide could be successfully incorporated into the sensitizer itself.[358] The replacement of some or all of the potassium ferricyanide by ferrocyanide in the customary formulation brought benefits in printing speed and the suppression of ‘bleeding’, for reasons that are explained in Appendix III, but it also imparted a blue colour to the coating, which tended to leave a stain of Prussian blue in the unexposed highlight regions after processing, unless suitable agents were added to improve the ‘wash-out’.[359] One such agent, whose use was patented by Jahoda in 1950, is sodium hexametaphosphate, and the following is one of his formulations which made use of it:

In 120 cc of water at room temperature, dissolve, in order:
2.5 g sodium hexametaphosphate
4.5 g potassium oxalate
20 g ammonium ferric oxalate
5 g potassium ferrocyanide.

This provides a ‘B-Type’ layer of fast printing speed. Although the sensitizer solution as made appears dark blue, the concentration of Prussian blue is very low, and when spread on paper it leaves only a sky-blue layer. However, the presence of potassium ions in this sensitizer tends to cause crystallization in the coating even at these relatively low concentrations, and substitution of ammonium salts is recommended.

So, by the 1940s, the formulae for commercial blueprint papers had diverged into two main families, called 'yellow layer' and 'blue layer' papers, whose characteristics are summarized in Table 4.5.[360]

Property	**Yellow Layer paper**	**Blue layer paper**
Components	Ferrioxalate and Ferricyanide	Ferrioxalate + Ferrocyanide B Ferrooxalate + Ferricyanide C
Types	A	B, C, mixed AB, AC, BC
Colour (unexposed)	Yellow	Blue (B, C, BC) Green (AB, AC)
Speed	Variable to High	Very High (B, C) Variable (AB, AC)
Contrast	Very High No latitude	Medium to Low Wider latitude
Max Density	Low to medium	High
Bleeding	Susceptible	Absent
Burnout	Susceptible	Absent
Washout	Clear easily Good whites	Problematic Tend to blue highlights
Purpose	Line work	Mixed subjects, Pictorial
Printout	Negative, reversing shadow exposures	Positive, changing to negative in processing

Table 4.5 Characteristics of later commercial blueprint papers

The 'blue layer' types of paper were favoured for copying pencil and ink originals, or thick and thin lines, to register which a lower contrast was desirable. A paper of this type, the Huey Company's No. 347-6, was adopted by Heron as a medium suitable for printing continuous tone photographic negatives.[361] It provided an excellent rich blue with a very high D_{max} and a well-separated tonal scale similar to a Grade 1 silver-gelatin paper.[362]

Commercial manufacture of blueprint paper ceased in the UK in the 1960s, but production continued in the USA, where there had been much more widespread investment in commercial processing machines. In 1964, the Andrews Paper and Chemical Company, the principal suppliers of the raw materials and chemicals to the coating industry, listed 30 US companies as manufacturing blueprint paper.[363] But by the early 1970s the annual output figures had been showing a steady decline for several years, and 1972 was the last year that blueprint paper featured separately in the annual statistics of the reprographic industry products in the USA, at which time there were still 18 firms coating and marketing the product.[364] Surprisingly, a relatively small amount continues to be manufactured in the USA today,[365] and there is at least one retail supplier of ready-made blueprint paper and sensitized fabrics for recreational and educational purposes.[366]

5 Studies in Blue 1842–2013

"Quiénes gritaron de alegria
Cuando nació el color azul?"
("Who shouted with glee
when the colour blue was born?")
Pablo Neruda
Book of Quotations

The first cyanotypes in 1842 were not derived from camera negatives in any way – they were Herschel's cyanotype copies, sun-printed from steel engravings printed on paper. The next cyanotype *oeuvre* historically was the archive of botanical photograms by Anna Atkins. It was not until the 1870s that cyanotype began to find employment for images that were fully photographic in origin, in the sense that they were printed from silver negatives that had been made in the camera. This chapter will trace an outline history of the documentary and artistic uses of the process, from its beginnings up to the present day.

5.1 Herschel's use of engravings

Sir John Herschel produced relatively few photographs compared with his colleague in photographic innovation, Henry Talbot, and the images that Herschel did make were obtained by printing in contact with engravings rather than camera negatives.[367] The latter were still quite troublesome to prepare in 1842, notwithstanding the great advance in speed represented by Talbot's recently patented Calotype process.[368] Most (and possibly all) of the printed pictures that Herschel pressed into service, commencing in January 1839, were small, high-quality steel engravings supplied by his brother-in-law, Peter Stewart, who was a printer.[369] The craft of engraving on hardened steel plates was of relatively recent invention, having been patented in 1819. It rapidly gained commercial success because the long life of the steel plate meant that large editions of 10,000 or more could be pulled from it, unlike engravings on copper, which were limited to a hundred or two only, before the plate became too worn. Some artists responded with indignation at this extent of the proliferation of their work, feeling that it was cheapened thereby.[370]

From the very start of his photographic researches, Herschel had always displayed a preference for employing these ready-made positive images on paper; as early as 30 January 1839, his notebook records his first accomplishment of a 'transfer from a print' by a silver halide process.[371] But he immediately recognised the two disadvantages of this procedure: it gives rise to images that are always spatially reversed, because the image transfer has to be formed face-to-face; the picture is usually tonally reversed too, because the majority of useful photographic processes are intrinsically negative-working.[372] Herschel was thus obliged to carry out a second derivative printing, which he called a 're-transfer' or 're-reversal', in order to restore his reversed negative, to a correct positive image.[373] It might be noted, in passing, that Herschel was the first to apply the words *negative* and *positive* in the photographic context, presumably because his mathematically-trained mind immediately saw that their phenomenology parallels the behaviour of the integers -1 and +1, respectively, under the operation of multiplication.[374]

Herschel expressed a particular concern to achieve a high degree of definition and translucency in his 'first transfers' (which today we would call inter-negatives) so that positive prints made from them should not be too deficient in detail. In his unpublished 1839 paper he observed:

> "To operate a second transfer, or, by a double inversion to reproduce the original effect, is a matter of infinitely greater difficulty, and one in which I have only recently ascertained the cause of former failures and the remedy to be applied. In consequence, the specimens produced will be found somewhat inferior in points of sharpness, and are by no means to be taken as favourable instances." [375]

In his 1840 paper, Herschel set out the criteria that must be observed for achieving a good result in this respect; foremost among them was the application of sufficient pressure to ensure extremely close contact of the sensitized paper with the original, but the quality of the paper itself was also important, and he found that a double negative, carefully aligned, resulted in a better print.[376]

The alternative to this procedure of 're-transfer' was to devise direct positive-working processes, but these had the disadvantage of producing a spatially reversed, positive image, unless the chirality were corrected by printing through the *verso* of the original. From a paper diaphane this results in such a severe loss of definition that it was generally unacceptable.

The use of engravings as source images may also have imposed some limitations on Herschel's technical assessment of his process's quality, which he did not fully appreciate in those early days of photography.[377] It is true that ‘line’ originals provide a good test of spatial resolution but, having effectively only two densities, of ‘black’ and ‘white’, they are not capable of disclosing the ability of a process to reproduce continuous tonal gradation, because they lack the subtly-modulated optical densities of a photographic negative. A well-printed steel engraving provides a suitable source for making striking and attractive photographic copies, even via processes of very high contrast with no capability for rendering intermediate tones. This may be one reason why the cyanotype process, as developed by Herschel, later acquired a reputation for rather poor tonal separation, and was not highly regarded by most photographers as a satisfactory pictorial medium.

5.2 Identifying the sources of engravings

Herschel only selected engravings with no printing on the verso as diaphanes, and he often rendered them more translucent by treatment with wax, oil, or varnish. Included in the *Memoranda* is a document headed List of Engravings, & how rendered Transparent consisting of 24 numbered titles, often abbreviated, of the original pictures; a summary of this list, together with some additional titles mentioned by Herschel elsewhere in his *Memoranda*, is given in Table 5.1. The Herschel archive at the Museum of the History of Science in Oxford holds most (53) of the actual engravings that Herschel used as diaphanes; some of these show clear evidence of having been treated with substances to render them semi-transparent.

It is regrettable that, when preparing his diaphanes, Herschel invariably trimmed off the title together with the names of the engraver and the original artist, which were usually printed below the picture.[378] He did not annotate the resulting test prints with their appropriate titles, which to him would have seemed superfluous, but he did usually inscribe his ‘prepared paper number’ on the *verso*. At several places in his personal *Memoranda* he refers to pictorial test prints by their subject titles alone. Clearly, the purposes of photohistorical research would benefit from the identification of the pictures to which the titles refer; the assignment of an image to each title would provide a correlation between the actual specimen prints which have come down to us, and the *Memoranda* in which Herschel described their preparation and subsequent distribution to friends, colleagues and institutions.

This assignment is obscured by the rather non-specific, romantic nature of most of the titles quoted in Herschel’s ‘List of Engravings’, such as *Still in my Teens, Youth & Beauty,* and *The Countess*; none of which can be attributed with certainty to any particular image. The key to discovering the original source, in which many of these engravings were first published, was provided by just two of Herschel's titles, which refer to depictions of identifiable ladies of the time, namely, *Mrs. L. Stanhope* and *Mrs. Sheridan*.[379] An engraving entitled *The Honourable Mrs. Leicester Stanhope* is listed in the *Art Libraries Association Portrait Index*[380] as having been first published in the 1836 issue of *Friendship's Offering,*[381] which was one of the many Victorian presentation annuals, or illustrated 'gift books': anthologies of verses, stories, and essays.[382] The particular *raison d'être* of these publications was to provide a vehicle for the new craft of fine steel engraving, and they became very popular as Christmas presents with the genteel classes during the second quarter of the nineteenth century.

Mrs. Sheridan proved harder to identify uniquely, because engravings of several notable ladies of that name are on record. But in searching among these, Dr Sara Stevenson found that the *British Museum Catalogue of Engraved British Portraits*[383] lists an engraving of Lady Louisa Henrietta Wyatt (neé Sheridan) 'standing, playing the harp', and this too had been published as a plate in *Friendship's Offering* for 1838.[384] A standing lady harpist happens to be one of Herschel's best-known, but hitherto unidentified, test images; he reproduced it extensively in several processes, including cyanotype.[385] The dimensions quoted for the images agreed to within a millimeter with those of Herschel's test prints in the Oxford archive, and, on consulting copies of the annual *Friendship's Offering* for 1836 and 1838,[386] I found the original engravings and Herschel's cyanotypes to be perfect positive-negative pairs.

Friendship's Offering having been identified as the source of two of Herschel's diaphanes, the *List of Embellishments* in every issue of this annual between 1824 and 1844 was examined for other titles that might coincide with the titles in the 'List of Engravings'. Of the 30 titles used by Herschel, 19 were found to correspond with engravings from this publication, although in a few cases it transpired that Herschel had invented his own titles, quite different to those published for the image; this only became apparent, of course, when the images themselves were identified as described below. Table 5.1 summarises the titles and sources of these engravings. Herschel's numbered 'List of Engravings and how rendered Transparent' from his *Memoranda* in HRHRC constitute numbers 1 to 24 in the following Table, but his details of rendering them transparent have been omitted. The seven remaining unnumbered titles occur elsewhere in Herschel's *Memoranda*, especially in the 'Lists of Specimens' sent to various people.Titles in parentheses are alternative versions used by Herschel. Tentative identifications are prefaced with '?' The references refer to the year, plate number, and opposite page of *Friendship's Offering* where the engraving was originally published.

When the original engraving diaphane also exists in the Oxford Herschel archive it is denoted by *, which assists the attribution in spite of Herschel's changed titles. It is also significant that the publishers of *Friendship's Offering*, Smith, Elder and Company, of 65 Cornhill, London, had the same address as Peter Stewart, Herschel's brother-in-law printer, who had furnished him with a number of engravings in 1839. Stewart's working address is revealed in a note left by Herschel giving directions for the safe return of his prints via this person.[387] Since Peter Stewart would have been able to supply loose specimens of the engravings, there is no need for us to suppose that Herschel had descended to mutilating bound copies of these 'friendship books'!

All the engravings in *Friendships' Offering* from 1824 to 1844 were also compared for matches to the 53 cropped engravings in the Herschel archive at Oxford. Of these, 28 were so identified. Some of the remaining engravings were also used as diaphanes by Herschel, but were never explicitly referred to by him in the *Memoranda*; two have been identified by Simcock[388] as originating from a part-work of 1831 depicting Edinburgh: *Modern Athens! Displayed in a series of Views*.[389] These were used by Herschel for some of his earliest test prints that are still extant; one, an engraving of the Edinburgh Royal Exchange by W. Watkins, is the diaphane for what is believed to be Herschel's oldest surviving dated photograph, a hypo-fixed silver print dated 7 February 1839.

It is possible that the remaining Herschel diaphanes may be found in other gift books published by Smith, Elder and Company, who employed Peter Stewart's services. Of the remaining engravings in the Oxford archive, there are no specimen prints by Herschel known as yet.

No	Herschel's Title	Published Title	Year	Pl.	P.
1	Wise Men. Rembrandt	Halt of the Caravan* ?	1831	11	305
2	Mrs L. Stanhope	The Honourable Mrs Leicester Stanhope	1836	3	36
3	Bridal Morn	The Bridal Morn	1837	7	181
4	Still in my teens	Still in my Teens	1838	8	217
5	Early Morning	Early Morning*	1837	8	217
6	Orpheus	unidentified			
7	Infant Lyra	Lyra*	1830	2	
8	Lady with flowers	Mine Own* ?	1830	8	181
9	The Countess	The Countess*	1836	7	181
10	Royal Prisoner (Royal Captive)	The Royal Prisoner*	1839	9	325
11	Old barns &c.	unidentified			
12	Mrs. Sheridan	Miss Louisa H. Sheridan	1838	4	73
13	Opening the Chest	The Co-heiresses	1840	5	157
14	Scene in Italy (Italian Landscape)	A Scene in Italy*	1839	8	289
15	Torcello	Torcello	1838	5	121
16	Burghersh Family	The Children of Lady Burghersh	1840	7	252
17	Frescatura	The Festival* ?	1836	4	73
18	Youth & Beauty	Youth and Beauty	1838	7	181
19	Amazons Basso relievo	unidentified			
20	Hercules & Lion Basso R	unidentified			
21	Schooner	unidentified			
22	Roman Lady	[may be 'Donna Elena']	1837	3	28
23	Poetry	Poesie* ?	1831	13	373
24	Boy & Lyre	unidentified			
	Rosolia	Rosolia	1837	8	217
	Helena	Donna Elena*	1837	3	28
	Lady & Lute	The Lady of the Palace*	1830		
	Letter of Bad News (Reading the Letter)	Reading the News	1830		57
	Biancha	Bianca Vanezzi	1834		
	Italian Lady	The Gondola* ?	1834	11	325
	Square-rigged ship	unidentified			

Table 5.1 Herschel's titles for his diaphanes and where published

5.3 Herschel's cyanotype tests

Many cyanotypes still survive which were made by Herschel according to the procedures described in his 1842 Paper and the *Memoranda* at the HRHRC. The majority of these specimens is divided between the collections of the Museum of the History of Science, in Oxford,[390] and the National Museum of Photography, Film & Television, (now the National Media Museum) in Bradford; two are in the Library of the Royal Society, London; eleven are in the collection of HRHRC at Texas,[391] and isolated specimens exist in a number of other collections in the USA: the J Paul Getty Museum, the University of Princeton, and the Smithsonian Institute.

In 1965, the Oxford archive was given prominence by R S Schultze in a publication setting out the broad structure of the collection and making some specific points of interest in relation to the several processes that Herschel had tested in the early 1840s.[392] In his paper, Schultze raised some unanswered questions relating to the cyanotype processes designated (a) (b) and (c) by Herschel, which can now be resolved by reference to the *Memoranda*, which were not available to Schultze at the time of his research. In 1989, the year which was taken to mark the sesquicentenary of the announcement of the invention of photography, to celebrate Herschel's contribution to this discovery, an exhibition at Oxford was curated by A V Simcock, whose accompanying monograph nicely illustrates and elaborates the relationships between the processes that may be found in this archive.[393]

Among the HRHRC *Memoranda* there are several lists of titles of test specimens, with other details of process, which Herschel had sent to various interested friends and colleagues, including one addressed to Julia Margaret Cameron, which contained a number of cyanotypes as may be seen below in the transcript of Table 5.2. Herschel first met Mrs. Cameron in 1836 at the Cape of Good Hope, during his stay from 1834 to 1838 for the purposes of astronomical research. It was in a sense prophetic that he should subsequently send her specimens of the new photography in 1842, for this was a pursuit that she was destined to take up herself twenty-one years later, and then with most memorable effect. She first photographed her mentor Herschel in 1867. In her unfinished manuscript *Annals from my Glass House*, Mrs Cameron refers to him as follows:

> "...I photographed my illustrious and revered as well as beloved friend, Sir John Herschel. He was to me as a Teacher and High Priest. From my earliest girlhood I had loved and honoured him,

> and it was after a friendship of 31 years' duration that the high task of giving his portrait to the nation was allotted to me. He had corresponded with me when the art was in its first infancy in the days of Talbot-type and autotype. I was then residing in Calcutta, and scientific discoveries sent to that then benighted land were water to the parched lips of the starved, to say nothing of the blessing of friendship so faithfully evinced." [394]

Mrs. Cameron's reference to the 'autotype' is an error; the process was not Herschel's, nor was it introduced until 1864. She may possibly have meant amphitype, or even cyanotype.

List of Photographs sent to Mrs. Cameron. Aug 22/42

1	Burghersh Fam		+	Red Stock	2
2	Royal Prisoner		+	D$^{o.}$	1
3	Pompeii		+	D$^{o.}$	1
4	M$^{rs.}$ L. Stanhope		+	D$^{o.}$	2
5	In my teens		+	Papaver Hybridana N$^{o.}$ 1216	2
6	Helena		+	N$^{o.}$ 1182	2
7	D$^{o.}$		+	N$^{o.}$ 1202. Violet	2
8	D$^{o.}$	Pos	+	Sparaxis Alk. 1153	3
9	Pompeii	Neg	-	Cyanotype (a) F$^{3}/_{2}$	2
10	M$^{rs.}$ Sheridan		-	D$^{o.}$ (a)	1
11	Rosolia		+	D$^{o.}$ Deep blue vary (b)	1
12	Ships		-	D$^{o.}$ (a) light blue	2
13	In my teens		-	D$^{o.}$ (a) dark blue	1
14	Rosolia		+	D$^{o.}$ (c) before fixing	2
15	In my teens		+	D$^{o.}$ (c) purple half fixed	2
16	Ships		+	Guiacum green	2
17	Helena		-	Chrysotype (thin)	1
18	Burghersh fam		-	D$^{o.}$ Bwpon	1
19	M$^{rs.}$ L. Stanhope			725. Mercury	2
20	My Teens			750. D$^{o.}$	1
21	Scene.....			721. fixed $^{1}/_{2}$ by Chrom	2
22	Specimens of Mr Collen's			Talbot's Calotype	
23	portraits				
24	Calotype.				

Table 5.2. Specimens sent by Herschel to Julia Margaret Cameron 1842

The following Table 5.3 is a transcript of a list of specimens, sent by Herschel to Robert Hunt in 1842, which also contains references to the cyanotype processes designated as (a), (b), and (c). All three of Herschel's cyanotype processes are exemplified here in specimens numbered 7, 8, 9, and 10, and it is interesting to use this information to identify their nature and thus answer the question raised thirty years ago by Schultze.[395] The fact that one specimen of type (a), no. 7, is listed as a negative image, is strong evidence that (a) can therefore be identified as Herschel's negative-working cyanotype process. If (a) had been a positive-working process, this image would have to have been made from a negative of the original engraving – a singularly pointless exercise.

Photography

Specimens Distributed.

List of Photographs sent to Mr. Hunt Oct 2/42

1	Orpheus	+	Senecio Splendens.
2	Royal Prisoner	+	Papaver hybridium
3	Opening the Chest	+	Red Stock.
4	Rosolia	–	)
5	Italian Landsc	–	> Chrysotype
6	M$^{rs.}$ L. Stanhope	–	)
7	M$^{rs.}$ Sheridan	–	~~Chrysotype~~ Cyanotype (a)
8	Lady & Lute	+	D$^{o.}$ (a)
9	Rosolia	+	Cyanotype (b) deep blue
10	D$^{o.}$	+	Cyanotype (c) purple
11	D$^{o.}$	–	N$^{o.}$ 725. Aug 1
12	M$^{rs.}$ L. Stanhope	–	N$^{o.}$ 750 Aug 2
13	In my teens	+	Thermocyanotype
14	Rosolia	–	758. Oct 2 on blue wove Post NB
15	Specimen of + Cyanotype paper		

Table 5.3 Specimens sent by Herschel to Hunt 1842

The fact that no. 8, which is also of type (a), is listed as a positive, presents no problem, however, because the latter could well have been printed from a negative of the original image – what Herschel referred to as a 're-transfer'. In support of this hypothesis, in the Oxford archive there is a high-quality brown reversed negative print of '*Lady and Lute*' (presumably made by a silver process) which has been rendered highly translucent for just this purpose by waxing.[396] In his exhibition, Simcock displayed one of these negatives.

Most of Herschel's specimens are inscribed on the *verso*, in his own hand, with his prepared paper number, so the original light-sensitive coating may be identified with reference to the list of prepared papers in the *Memoranda* at HRHRC. It is more difficult, however, to discover how they were processed after exposure, because one sheet of prepared paper might suffice to provide ten or twenty smaller 'squares' which could be used for different tests.

For one of the listed specimens sent to Hunt, no. 10, it is possible to go further and make a unique identification with an existing positive cyanotype of '*Rosolia*' held in the collection of the NMPFT.[397] This print is reproduced in Schaaf's book;[398] it bears the number 10 at the top left hand corner of the *recto*, which is further annotated at the bottom in ink in Herschel's hand: 'Positive Cyanotype. Aug 17 1842. JFWH.' On the *verso*, is pencilled the prepared paper number '724', which we find from the Memoranda corresponds to a coating of ammonium ferric citrate. The chirality of '*Rosolia*' in specimen number 10 is reversed, i.e. it is the mirror image of the original engraving,[399] so we may infer that it was derived directly by one printing from the original, and that type (c) was therefore one of Herschel's positive-working cyanotype processes. Even the paper is identified by Herschel's annotation 'yell. w. post' as yellow wove post. The image colour, however, is not purple, as stated in the list, but blue. This does not present a serious objection because Herschel states subsequently that he observed the colour of type (c) to change from purple to greenish-blue. This does not resolve the difference between positive-working methods (b) and (c) however. A clue to this comes from another list, of specimens sent to the Royal Society in 1842,[400] of which the following Table 5.4 is a partial transcript. Although no (a), (b), (c) notation is used here, Herschel does distinguish between three cyanotype processes: negative working; positive-working 'half-fixed, without corrosive sublimate', and positive-working fixed with corrosive sublimate.

These specimens still exist intact: among the items in the Herschel archive at HRHRC are seven sheets of Herschel test prints, six containing six mounted specimens each, and one seven. Of these 43 varied experimental tests, some are now completely blank (especially those derived from mercury), but others are obviously surviving cyanotype and chrysotype images. The specimens are numbered and can be correlated exactly with Herschel's lists of specimens sent to the Royal Society in 1842, of which the contents of the fourth, fifth, and sixth sheets are transcribed in Table 5.4. Examples may be identified among them of negative-working cyanotypes (Nos 22, 24, 26) and positive working cyanotypes (Nos 20, 25, 27, 28, 30) as listed in the HRHRC photography collections database.[401]

Photography Lists of Specimens distributed
List of 4 additional sheets exhibited to RS. Nov/42

Nos.			
19	Mrs Stanhope.	–	
21	Rosolia	–	Chrysotype
23	Italian Landscape	–	
29	Lute Playing Lady	+	
20	Royal Captive	+	Cyanotype + process
28	Helena	+	Let go on and half fixed – without Corr. Subl.
22	Still in my teens	–	Negative Cyano–
24	Mrs Stanhope	–	(type. ACI + $F^{3}/_{2}CP$.)
25	Rosolia	+	Cyanotype + process
27	Mrs Stanhope	+	with corrosive subl. Nov. 1842.
26	Lady & Lute	+	Retransfer. Negative Cyanotype.
30	Rosolia.	+	Cyanotype, no corr. subl. arrested by water (b.w.p.)
31	Thermocyanotype	–	(Countess) 3rd revival
32	Ital.^{n} Landscape	–	758 one of the finest but 3/4 faded.
33	ACI + Pict...[??]	+	NS. ACI on both sides of paper.– Mrs Stanhope. very intense.
34	Rosolia.		(ACI + N[Hg]) + Pict...[??] + water made fine [?] cut out.+ O
35	No 758. In my teens		best specimen Iridescent – greatly faded
36	Italian Landscape.	+	Cyanotype very intense, Water + Perchlor Iron to fix yellow border.

Table 5.4. Specimens sent by Herschel to the Royal Society in 1842

I have attempted to estimate from the data in the *Memoranda* how many cyanotypes, in all, may have been made by Herschel. In the case of the standard negative-working cyanotype there are only three prepared papers to consider, and this is how Herschel described them in his list:

> “780 Aug 10 10 Amm^{o} Citr I + $10F^{3}/_{2}CP$ no precip greenish paper 20 grs [?] covers 3 squares
>
> 784 Aug 11 $F^{3}CP^{20}$ + $AmoCitrI^{30}$ + Tinct. Turmeric 10 on yell wove post. the turmeric proved of no value.
>
> 793 Aug 16 ($30F^{3}/_{2}CP$ + 50ACI) exceedingly sensitive when wet browns very rapidly in O this quantity did 18 squares 90 grs did 20 squares = 4½ per square”

The most likely interpretation of a 'square' is that it was of a size suited to printing Herschel's smaller diaphanes, and is therefore well represented by the specimens that are most commonly found in the archives. These are of fairly consistent dimensions, on average about 120 x 95 mm, bearing images about 100 x 80 mm.

The numerals in Herschel's notes, transcribed above, must define the relative quantities of the ingredients – but they raise the question: what units was he using for his measurements? The only plausible interpretation is that these numbers denote drops of liquid (or minims in apothecaries' measure – see Appendix IV) taken from his stock solutions, whose concentrations are specified elsewhere. This assumption is confirmed by the *Memoranda* entry dated 29 October 1842, where Herschel refers explicitly to his "method of drops". With this interpretation and the knowledge that one minim of water weighs approximately one grain, or 0.059 grams, we can calculate the 'coating weight' of Herschel's sensitizers and see if the result is consistent with experience.[402] 4½ grains, or minims, per 'square' of 120 x 95 mm corresponds to a specific coating volume of 23 cc/m^2, which is comparable with the specific coating volume used by the author, and others, for contemporary coatings of plain papers.[403] If the three coated papers cited above are the only ones that Herschel prepared with this formulation – and there is no indication in his memoranda of any others – it follows that the total number of negative cyanotype specimens that he could have made was about 34. His positive-working cyanotype tests may well have been more numerous than this, but the variability of the process and its frequent failure to yield a satisfactory image leave much uncertainty concerning the number of such specimens that we can expect to find. The Herschel archive at the National Media Museum has 16 from one sheet, which all bear the annotation of 'prepared paper number' 724, which consisted of a coating of ammonium ferric citrate alone. After exposure, these must have been treated with potassium ferrocyanide solution, and many of them bear Herschel's rather cryptic annotation 'yop' or possibly 'yoss', which could refer to this substance – 'yellow prussiate of potash'.

5.4 Cyanotypes of British algae by Anna Atkins

The first application of Herschel's cyanotype process for an illustrative purpose was begun in 1843 by a lady botanist called Anna Atkins (1799 – 1871). The full significance of her contribution to early photography and the history of book illustration was not brought to light until 1988, as a result of the research of the American photohistorian Dr Larry Schaaf, while he was Carnegie Trust Fellow in the Department of Art History at St. Andrews University, Scotland. Dr. Schaaf was able to curate an Exhibition in Glasgow, St Andrews, and Edinburgh, when he unfolded the history of Anna Atkins in his beautiful book *Sun Gardens: Victorian Photograms by Anna Atkins*.[404] Little has since emerged to add to this comprehensive and beguiling account of a most important, but previously uncelebrated, woman in the history of early photographic endeavour. For the benefit of readers who may not be acquainted with this work, the facts will be briefly summarised here, but with the proviso that this terse, unillustrated account is no substitute for Schaaf's deeply-researched and beautifully illustrated book.

Anna Children was born in 1799 in Tonbridge, Kent, the only child of Hester Anne and John George Children (1777-1852), a distinguished scientist who was elected to Fellowship of the Royal Society in 1807 and later became its Secretary. Anna's mother died within a year of the childbirth, and perhaps partly to compensate for her loss, the bond between father and daughter was always close. Their relationship also encompassed a publishing collaboration when Anna's considerable talent for draughtsmanship enabled her to undertake the illustration of her father's translation of a seminal work on the taxonomy of seashells.[405] Thus Anna was, as Schaaf describes:

> "...brought into touch with most of the tight-knit British scientific community of the early part of the nineteenth century." [406]

In 1825, Anna married John Pelly Atkins, a man of property, who fostered her interests in botanical collecting and illustration. In 1830 the couple, who remained childless, moved to Halstead, near Sevenoaks in Kent, where they were joined in 1840 by Anna's father, following his retirement from a lifetime's career as Keeper of Zoology at the British Museum. His proximity undoubtedly continued to provide an important channel of communication between Anna and the scientific world, which at that time seldom welcomed women wholeheartedly into its ranks. Children, as a member of the Royal Society's Committee on Publications, had been at the centre of things during the announcement of photography, and he had been in the chair at the meeting of the Society in February 1839 to which Talbot disclosed his method for making photogenic drawings. From the outset, Anna showed great interest in this innovation – to the extent that in 1841 she was presented by her father with an early Ross camera, although no camera photographs by her are presently known. Anna's husband was also a friend of Talbot, sharing a common interest in transport engineering, so she could not have failed to be aware of the early use of Talbot's photogenic drawing process for making botanical photograms, such as that illustrated in facsimile in the popular periodical *The Mirror* of 1839.[407]

In 1840 the Herschel family also moved residence to Kent, taking a house in Hawkhurst, only about 30 miles away from the Atkins; the Herschel daughters were friendly towards Anna, whom they regarded as an aunt. When Sir John's 1842 paper was published, containing details of his cyanotype processes, a copy was sent directly to John Children, but it is likely that Anna, as a frequent visitor to the Herschel household, also acquired experience of the process by more direct and less formal means. Anna must have quickly realised that cyanotype offered a method for botanical illustration by photography which was altogether more expeditious and inexpensive than Talbot's silver halide processes; she was not then to know that it would also prove more permanent.

No evidence has yet come to light to tell us precisely the method or formula that Anna adopted to make her cyanotypes, but from their appearance (the colour is usually in the range 21E7–22D7) and the productivity of her work (as we shall see, her edition of *British Algae* alone demanded the hand-printing of over 5000 cyanotypes), it seems likely that she used Herschel's rapid, standard negative-working Method (a). The means to carry out this process would not, for her, have been hard to come by: her father had constructed several powerful galvanic batteries for the purposes of electrochemical research, with which he could have prepared the necessary potassium ferricyanide from readily available potassium ferrocyanide, using Smee's electrolytic method. Ammonium ferric citrate was growing in popularity as a pharmaceutical preparation by then, and was available at most druggist's. A suitable fine paper, Whatman's Turkey Mill, which had already been used extensively by Talbot for silver images, was widely marketed as a superior writing paper; and, of course, the processing of the cyanotypes needed nothing more than pure water, which the well at Halstead could supply in abundance.

By 1843, Anna had set to work on the production of her monumental hand-printed publication, *British Algae: Cyanotype Impressions*, which she intended as a supplement to the treatise on seaweeds by Hervey, which was not illustrated.[408] Anna's work consists of negative cyanotypes made directly from diaphanes of the seaweeds themselves, dried and pressed, but usually unsupported. Each is labelled with its Latin name written in Anna's hand on a translucent slip, and the illustrations are preceded by a title page, a dedication of the work to her father, a list of contents, and a handwritten prefatory note, which with modest anonymity, is signed 'A. A.' Herein she explained her intention:

> "The difficulty of making accurate drawings of objects as minute as many of the Algae and Confervae, has induced me to avail myself of Sir John Herschel's beautiful process of Cyanotype, to obtain impressions of the plants themselves, which I have much pleasure in offering to my botanical friends." [409]

Anna issued the work as a privately-distributed part-book over the decade 1843-53. Each of the soft-bound sewn fascicles contained about 12 plates at first, but this number increased considerably with the later parts, and there were twelve parts issued in all, making an approximate total of more than 400 plates for the final work, although this number varies in the known copies, partly due to Anna's retrospective issues of 'improved' prints of certain specimens. It was her intention that the entire work should be bound in three volumes. The size of the edition is uncertain, but seems to have been at least 13 in number. Schaaf has identified a probable 12 known copies, in varying states of completion, and he has also listed their original provenance, and their whereabouts in 1985.

Notable among the recipients of Anna's part-work was Robert Hunt, who reported favourably upon this use of the cyanotype process in his early (1848) review of progress in the new photography:

> "They are so exceedingly simple, the results are so certain, the delineations so perfect, and the general character so interesting, that they recommend themselves particularly to ladies, and to those travellers who, although not able to bestow much attention or time on the subject, desire to obtain accurate representations of the botany of a district. We have seen specimens of the British Algae executed by a lady, by the Cyanotype process, that are remarkable for the extreme fidelity with which even the most attenuated tendrils of the marine plants are copied." [410]

Hunt's compliment is double-edged in being tainted with a patronising implication that this was a process for women and therefore, dilettantes. Henry Fox Talbot was also on Anna Atkins' distribution list, and much later in 1864, he commented approvingly on the permanence of the process, having by then suffered grievously from the impermanence of many of his own silver images:

> "Moreover, we know that some photographic processes are permanent; for instance, the cyanotype of Sir J. Herschel, by which process a lady, some years ago, photographed the entire series of British sea-weeds, and most kindly and liberally distributed the copies to persons interested in botany and photography. The whole of these prints remain unaltered after the lapse of several years."[411]

These words, published in *The British Journal of Photography*, were read two decades later by the Scottish photohistorian and book collector, William Lang, who was then President of Glasgow Photographic Association. Lang was a compulsive book collector – he described it as an "incurable disease" – and was spurred on to seek a copy of this remarkable botanical work, although he was not even aware of the identity of its author. After a search lasting several years, he eventually acquired, in 1888, the complete set bound in two volumes that Anna Atkins had originally given to Robert Hunt.[412] Lang proudly displayed and lectured upon his acquisition on several occasions,[413] although he only knew the work was by "A.A.", but a curator at the British Museum identified the "lady" for him as Anna Atkins. Lang even made his own cyanotypes as frontispieces to the *Journal of the Philosophical Society of Glasgow* where he published his account.[414] It is indeed fortunate that we have his clear description of it, because this copy disappeared in 1910, following the auction of Lang's library, and only re-emerged for re-sale at Sotheby's on 10 May 1990, realising £229,250.

There remain seven substantially complete copies of *British Algae* in British institutions, including the Royal Society, Lacock Abbey, the British Library, the Linnean Society, the British Museum, the Royal Botanic Gardens, Edinburgh, and the Art Gallery and Museum, Kelvingrove, Glasgow. Three other holdings are seriously depleted. Two copies are in the USA, including Sir John Herschel's personal copy, which was sold at auction by Sotheby's of London in 1985 for £48,400, and is now in the collection of the New York Public Library. The entire set of images in this item may now be browsed and viewed online, courtesy of the Digital Collections of the NYPL.[415]

The exciting discovery of a thirteenth intact copy was made in 1995 by David Park of Bonham's auction house, London, who recognised the work among the uncatalogued contents of the small library of the Natural History Museum of Eton College.[416] This fine copy, having 411 plates, bound in three volumes, was sold at auction by Bonhams for £130,000 in 1996 and was granted a licence to be exported to the collection of Tel Aviv Museum, where it now represents one of the great achievements of early British photography. The attention of the popular media was briefly attracted by this significant sale of a hitherto unrecorded treasure, so Anna Atkins' achievement was finally celebrated in the popular press, 144 years after its completion.[417]

Anna Atkins distributed more than a dozen copies of the first fascicle of her *British Algae* in October of 1843, whereas the first part of Talbot's *Pencil of Nature*, illustrated with silver salted-paper prints, was not published until June 1844. *British Algae* therefore takes precedence in the claim to be the first photographically illustrated book,[418] albeit a privately-published one, and earns Anna Atkins a permanent place of honour among the pioneers of publishing. Anna's 'herbarium', the collection of dried, pressed botanical specimens, or *exsiccati*, that she had been amassing and using since 1830, containing many of her diaphanes, was finally presented to the British Museum in 1865.

5.5 Cyanotype albums by Anna Atkins and Anne Dixon

Upon the death of Anna Atkins' father in 1852, the bereaved daughter was much comforted by the companionship of her lifelong friend and 'almost sister' Anne Dixon.[419] At John Atkins' request, she came to stay at Halstead for the summer, in order to offer solace to Anna and help her sort out her father's papers for the substantial biography that Anna was preparing for private publication in early 1853.[420] It is likely that, finding action a remedy for despair, Anne Dixon also assisted Anna in progressing her printing for British Algae, which was completed later in 1853, just ten years after its inception.

The two women may well have continued cyanotyping together, and their collaboration seems to have broadened their horizons regarding subject matter, which first encompassed ferns, then flowers, leaves, feathers, and lace as diaphanes. One of the fruits of their joint endeavour was an album, nominally authored by Anna, entitled *Cyanotypes of British and Foreign Flowering Plants and Ferns* which she presented to Anne Dixon in 1854 as a token of gratitude for her dear friend's support during her mourning the loss of her father. The binding was simply stamped 'A.A. to A.D. 1854'. This unique and beautiful work survived until 1981 when, immediately following its sale at auction, it was broken by dealers in an act of collaborative philistinism.

In 1853, probably with Anna's help, Anne Dixon herself completed two very similar presentation albums entitled *Cyanotypes of British and Foreign Ferns.* One was dedicated 'A.D. to H.D.'; the recipient is known to have been Henry Dixon, her young nephew, who became a noted photographer of India. This album is preserved in the collection of the J Paul Getty Museum, Los Angeles. The other album by Anne Dixon was previously unrecorded until its existence, in private hands, was first brought to light in 1988 by John Wilson.[421] It carries the dedication 'A.D. to C.S.A.' and it is now in the collection of the National Media Museum (previously the National Museum of Photography, Film & Television) at Bradford, England. The researches of Wilson into the history of cyanotype have included a careful comparison of these two albums.[422] He found that both were printed from the same set of 98 botanical diaphanes, some of which were also used by Anna Atkins, but in a substantial number of the images the specimens are reversed or have other differences in positioning between the two albums.

The identity of the recipient bearing the initials 'C.S.A.' remains something of a mystery. Wilson has reviewed the rather slender evidence, in particular the suggestion put forward by Fred Woodward of the name of Miss Catherine Allardyce (1802-1886) of Cromarty, a known collector of algae. Although Wilson has found no reference to her in the contemporary botanical literature, I have come across an obscure acknowledgement to her in Johnstone and Croall's *Nature-Printed British Seaweeds*, as one of the contributors of specimens.[423] The first volume of this elegant four volume set of nature prints was reviewed in The Athenaeum in 1859. The very name of Miss C. Allardyce evidently fired the imagination, if not the heart, of the reviewer, whose fantasy waxed quite rhapsodical:

> "The only relief we experience in poring over these densely technical pages is not a sea breeze, but an occasional name of a fair spinster who has contributed some weed to the author. We cannot restrain our imagination from picturing "Miss C. Alardyce," who has found *Bonnemaisonia asparagoides* at Moray Frith [sic] (p. 77), ... O, for a weed-walk and a weed-talk this very day with Caroline Alardyce, or any and all of the spinster phycologists! ... But why not immortalize the spinsters, even though they should change their names, by affixing them to the weeds? ... how much more euphonious would be *Melobesia Alardycii,* or, sweeter still, *Alardycia Virginea!*" [424]

This whimsical eulogy by the anonymous reviewer (discovered to be John R. Leifchild)[425] drew forth a reply from Johnstone and Croall in the preface to their fourth volume. It pays tribute, if rather patronisingly, to the important role that many gentlewomen played at the time in collecting and cataloguing botanical specimens – it was one of the few scientific pursuits available to them that was not deemed unladylike. A 'C. Allardice' [sic] is acknowledged again in the second volume of Johnstone and Croall's work.

In 1861 Anne Dixon created a third album of cyanotypes which she again dedicated to her nephew, now Captain, Henry Dixon.[426] This beautiful compilation is anonymous and simply titled *Cyanotypes* in gold on the spine. A flyleaf bears the handwritten inscription in ink: 'Capt Henry Dixon with his Aunt Henry's Kind love – Ferring Vicarage June 21 1861'. The album contains 74 cyanotypes of a most varied kind: ferns, grasses, algae, mosses, leaves, feathers, fabrics and needlework, chosen rather for their aesthetic qualities, than for any systematic purpose. The handwriting of both Anne Dixon and Anna Atkins is apparent on the labels, and some of the specimens have been used in other albums by the two ladies; the paper used, where watermarks can be discerned, is J. Whatman 1845.

Anne Dixon died on 20 March 1864, and Anna Atkins died at Halstead Place on 9 June 1871. After the death of John Pelly Atkins in 1872, the house later became a school, but this was demolished in 1954 to make way for a new building. In 1997 Anna Atkins was finally honoured for her pioneering contribution to photography and book illustration by the unveiling at Halstead Place of an appropriately blue commemorative plaque, one of ten in the Photographic Heritage Programme promoted by the Royal Photographic Society and Olympus Cameras.[427] Concerning this fruitful episode in early photography, it is fitting that the last word should come from Schaaf:

> "Anna Atkins and her circle had been the primary users of Herschel's cyanotype process. With her own hands she crafted thousands of lovely and significant photograms of natural objects, and in an imaginative and brilliant undertaking, she had exploited the most practical technology of her day to produce the first photographic book. Anna Atkins' legacy embodies all that was promising about the invention of photography. Her cyanotypes not only provide documentation of scientific interest, but in an intriguing duality, they also remain some of the most creative and beautiful artefacts from the earliest days of photography." [428]

5.6 An anonymous cyanotype album of 1843

In 1993 the National Museum of Photography, Film & Television, Bradford, acquired a very early and unusual album entitled *Dried Ferns*, containing both cyanotypes and the botanical diaphanes (*exsiccati*) that they had been printed from. The author of this work is unknown. It was bought at auction, and no information was available as to its provenance. This is a red morocco-bound, quarto album of mounted specimens of *exsiccati* (pressed and dried ferns) which, as is evident from their labels, have been gathered from extremely diverse locations: Borneo, East Indies, Guernsey, Philippine Islands, Britain, Java, Tropical America, Chile, New Zealand, etc. On the pages following, the volume also contains 16 cyanotypes of some of these dried ferns, of dimensions 9 x 7.5 inches (one is 9 x 15 inches, and folded) made on chain-laid paper, watermarked T. Edmonds 1821. The versos of all the cyanotypes carry rather faint pencil annotations, most of them legibly inscribed as ‘Herschel formula cyanotype impression’ and variously dated during March and April 1843. Many of the annotations also specify the exposure, which was generally between one and two hours, and two notes refer to ‘very hot sun’ and ‘bright sun’. Such references to the weather in the months of March and April are hardly consistent with the meteorological record for typical locations in the British Isles (although, on occasion the record described conditions as ‘fine’),[429] which suggests that these cyanotypes may not have been printed in Europe – or even in the Northern Hemisphere. It may be significant that an analytical investigation of the album by X-ray fluorescence spectrometry has recently revealed that its pages are heavily contaminated with arsenic – possibly applied as an insecticide, arsenious oxide, especially for protection in tropical environments.

The handwriting on the versos of these cyanotypes is not that of Anna Atkins or Anne Dixon; it even appears to differ from the handwriting on the labels of the botanical specimens in the same album.

The colour of the images is a consistent, slightly greenish-blue (around 23D8 – ‘sapphire blue’), unlike the cyanotypes of Anna Atkins (which are typically 21D7), and which correspond with that of cyanotypes made by Herschel’s standard method (a). The greenish-blue colour 23D8 is obtained when potassium ferricyanide alone is used as the sensitizer (see §4.1.1), moreover the relatively long exposures of one or two hours to ‘bright sun’ are consistent with the use of this much less light-sensitive substance alone. Exposures of Herschel's standard sensitizer (using ammonium ferric citrate and potassium ferricyanide) for hours would have resulted in massive over-exposure, to the detriment of the image quality. The highlights of the cyanotypes in this album are clear white, again characteristic of the simple ferricyanide method, and unlike the somewhat blue-stained highlights of Atkins' and Dixon's cyanotypes. The versos of the prints are also clean white, unlike the more or less blued versos of many of Atkins' and Dixon's prints, again suggesting a different coating technique, of brushing rather than immersion.

Without further historical and graphological research, the author of this album will remain unidentified, but it can be suggested with some confidence that it did not issue from the hands of Anna Atkins or Anne Dixon. It is interesting that there should have been another botanical cyanotypist active within a few months of the publication of Herschel's invention; particularly in view of the circumstantial indications that the prints may not have been made in Northern Europe: the fine weather conditions prevailing at the season of exposure, and the printer's apparent lack of (or possibly, ignorance of) ammonium ferric citrate as a means of greatly accelerating the exposure.[430] The exotic origins of some of the specimens might also suggest a widely-travelled author, although exchange of specimens between collectors was a common activity. However, the identity of this 'anonymous autobotanographer' must, until further evidence comes to light, remain a rather tantalising mystery.

5.7 Later botanical cyanotypes

Following Anna Atkins' pioneering endeavours, the cyanotype process continued to be used sporadically for botanical photograms; but over the years the purpose in this can be seen to shift away from the recording of plant taxonomy towards the making of works of art. Connoisseurs have always maintained that the vision and sensibility displayed in Anna Atkins' and Anne Dixon's botanical cyanotypes transcend mere scientific illustration, and elevate their images to the status of art-works, although there is very little to suggest that they originally intended them as such. It is interesting to observe how the recognition of creative botanical cyanotype as art has slowly gained ground over the 160 intervening years, to the point where such works are now to be found on the gallery walls, rather than the herbarium shelves. A recent celebration of botanical drawings and photograms as "exhilarating artistic experimentation…in drawing with light" may be found in the sumptuously-illustrated book *Ocean Flowers*.[431]

A later echo of Anna's work may be found in the albums prepared by Eric Craig (1829?–1923), who was a fern mounter and curio dealer in Auckland, New Zealand. He had a shop near Auckland Museum in 1892–3, from which he sold books of pressed ferns. He published two editions, in 1888 and 1892, of 100 cyanotype illustrations of 172 varieties of fern, following the layout and some of the typography originally employed by Herbert Boucher Dobbie in his *New Zealand Ferns* published in 1880; it is also apparent that he used some of Dobbie's labelling but his specimens are different.[432] Examples of Craig's work exist in the National Library of New Zealand and in the National Museum and Gallery of Wales, in Cardiff.

The traditions of the botanical cyanotype were also carried on in the USA by Bertha Evelyn Jaques (née Clausen, 1863–1941) of Iowa, who used the process around 1905 to record images of numerous plant species, some of them endangered. Attractive examples of her work have recently commanded substantial prices at auction. The modelling of the light permeating her diaphanes confers a delicacy of gradation on the photogram which gives it the illusory appearance of a photographic image of a three-dimensional original (see §6.2). Some of her work from the collection of Hans P. Kraus, Jr., is illustrated in DiNoto and Winter's *The Pressed Plant: The Art of Botanical Specimens, Nature Prints and Sun Pictures.*[433]

More recently, in 1996 a touring exhibition of 'Floral Blueprints' by Alexander Hamilton, created as part of the Scottish 'Fotofeis' photography festival and sponsored by the Scottish Arts Council, brought botanical cyanotypes to a wide contemporary public in several exhibition venues. Hamilton's technique differs from the customary use of *exsiccati* for botanical photograms: his flower specimens, which he grows himself, are fresh, and the act of pressing the flower into the surface of the sensitized paper leaves an impression of its fleshy centre, and traces of the natural pigments and pollen stain the image, adding sepia and other tones to contrast with the blue.[434] Although cyanotype is still the principal medium, there is also a distant echo here of Herschel's early anthotype or phytotype process of 1840, which used the natural pigments from flowers to make photographic images. Hamilton's preoccupation with light is manifest in the delicate translucency of his flower heads and petal arangements, which are formally and symmetrically set against a large ground of very dark blue, shading almost into black; their mandala-like quality invites deep contemplation. One reviewer has also likened them to astronomical photographs of distant galaxies.

5.8 Early pictorial studies in cyanotype

While platinotype was still being developed in the 1870s and 80s, a few photographic artists, concerned for the endurance of their work, had begun to reconsider the humble cyanotype, whose simple processing in water avoided any use of the fixing agents that tended to later degrade the silver image. The French artist, Henri Le Secq (1818–1882), became one of the most significant users of the process for this reason. His entire oeuvre is reviewed in the *Catalogue Raisonné*, compiled by Janis and Sartre,[435] and a brief biography can also be found in *The Art of the French Calotype* by Jammes and Janis.[436] Although Le Secq virtually gave up making new photographs after 1856, he continued to be concerned about the longevity of his work. Of his architectural studies, those mounted with gum into albums and presented to the Bibliothèque Nationale in 1853–4 now contain faded silver prints of a pale yellow-brown, which contrast starkly with the rich, unmounted specimens that were deposited at the Bibliothèque des Arts Décoratifs. Having observed that his silver prints were prone to fade, Le Secq, quite late in his life, used the cyanotype process to reprint many of his negatives.[437]

It is not known exactly when, around the 1870s, Le Secq made his important cyanotypes; his *Fantasies Photographiques* in still-life are engaging and mysterious works, but studies of sculpture and architecture predominate, and there are also some portraits, including Le Secq's father and mother, which suggest that he did not have any particular aesthetic difficulty with using the process for this genre. These cyanotypes constitute his enduring legacy: not a single still-life print by him is known to have survived on silver salted paper.[438] Among the cyanotypes by Le Secq in the collection of the George Eastman House, Rochester NY, is his famous image *Farmyard Scene*, and several of his architectural studies, most of which are in excellent condition, except one which shows some evidence of fading in comparison with its edges, which were presumably matted at some time when the picture was mounted and 'exposed'. Jammes and Janis attribute the cyanotype process that Le Secq used, and possibly the source of his sensitized paper, to Marion and Company, or to Testud de Beauregard, but offer no information as to whether this method differed from that originally invented by Herschel.

A more recent example of the ‘artistic rehabilitation’ of the cyanotype can be seen in the treatment of the photographs of Paul Burty Haviland (1880–1950), who was one of the lesser-known members of Stieglitz’s Photo-secessionist circle in the first decade of this century. An exhibition of Haviland’s work was recently mounted in Paris, including a substantial number of beautiful cyanotype studies in portraiture and the female nude.[439] As a curatorial footnote in the catalogue, Heilbrun and Bajac observe that these were most likely intended by Haviland himself only as trial proofs of his negatives, which he subsequently preferred to print in platinum or gum bichromate for exhibition or sale:

> “Quelques tirages au platine, destiné probablement à l’exposition voire à la vente, portent un monogramme et, plus rarement, une date, à la diference des cyanotypes, tirés sur des papiers plus fins, sur lesquels ne figure aucune mention et qui furent peut-être utilisés par Haviland pour ‘vérifier’ ses négatifs, comme on utilise aujourd’hui une planche contact” [440]

Nonetheless these cyanotype proofs now stand as finished artworks in their own right, and the authors of the catalogue also suggest that Haviland may have had the issue of permanence in mind when he originally made them:

> “Ces images se caractérisent, en effet, par un manque d’afféterie, un charactère direct mais gracieux, une poésie simple et raffinée auquel le bleu du cyanotype – dont l’utilisation au départ n’était peut-être pas une recherche esthétique mais un simple désir de conservation, le cyanotype étant un procédé permanent – ajoute encore, du moins pour notre regard contemporain, charme, mystère et bien sûr couleur.” [441]

The renowned American artist and teacher, Arthur Wesley Dow (1857-1922), used cyanotype around 1899 to make a poetic study of his hometown of Ipswich in New England; he compiled 41 prints into a personal album dedicated to his friend, the poet Everett Stanley Hubbard. This privately owned and previously undocumented album of his vernacular cyanotypes was published in 2007 by the Addison Gallery of American Art as *Ipswich Days*.[442] Being a celebrated painter and man of means, Dow had no need of cheap expedients for his materials, so we may presume that the cyanotype – including its colour – was his medium of choice for this affectionate and wistful portrayal of his beloved environs. As its curator, Trevor Fairbrother, says of this choice:

> "He loved the blue monochrome of cyanotype prints, delighting in their capacity to give reality a strange or otherworldly cast." [443]

5.9 Documentary and topographical cyanotypes

Compared with the rather limited extent of its pictorial use, cyanotype has found considerable application for documentary purposes, including scientific, archaeological, ethnographic, topographical and engineering studies. A noted British user of cyanotype during the 1880s was the civil engineer, Washington Teasdale (1831–1903), from Leeds, who may have been the subject of Frank Meadow Sutcliff's complimentary observation already recorded in §1.2. Teasdale was a prominent member of several Victorian Scientific Societies – Astronomical, Microscopical, Geological, Photographic – and he used cyanotype effectively to illustrate his multifarious interests, as can be seen from an archive of his prints preserved in the Museum of the History of Science, Oxford,[444] which also provides a commentary.[445] It was said of him in a biographical note:

> "…the doyen of local scientists, Mr. Teasdale was well known and welcomed wherever men of science most do congregate." [446]

In the field of archaeology, an unusual illustration of the capability of the process to render atmospheric studies of sculptural artefacts is provided by a set of 30 cyanotypes produced around 1895 by Henri Ranoux. These are described in Ken Jacobson's beautiful catalogue, *Études d'après Nature*,[447] and they illustrate quite dramatically the Roman finds from an archaeological excavation in North Africa, which includes a self-portrait of the photographer himself working on the site. This album also contains three collodion or silver-gelatin prints, which look rather sadly washed-out and dull in comparison with the vibrant cyanotypes.

The Rijksmuseum in Amsterdam has substantial holdings of cyanotypes within its photography collection, including albums of documentary cyanotypes dating from the early 1900s by Hendrik Dooyer, showing the previous Dutch colonies such as Suriname, documenting life on the large colonial plantations of the time. [448]

The Canadian National Archive has substantial holdings of cyanotypes, including many full-plate architectural records of dwelling houses. The simplicity of the process in not calling for elaborate darkroom facilities may also be the reason for its employment to illustrate several personal diaries – accounts both of everyday life and adventure – which date from the 1890s. These include an album of about 100 cyanotype prints from half-plate photographs of North American domestic life by W. Braybrook

Bayley taken in the period 1889-91. In view of the apparent well-to-do character of his family, the economy of his chosen process is a little surprising and the prints are actually mounted in a ruled cashbook! A similar set of 17 cyanotypes of local Canadian landscape and family by Able Silver Bowers date from ca. 1895. An anonymous diary of 'An Account of a Trip to Hunters' Island' dating from 1899 is illustrated with 24 cyanotypes, and on another adventurous theme, there are 18 cyanotypes by Walter Strand of gold-rush scenes in the Klondyke, northern British Columbia, in 1899.

It is apparent from a substantial collection of photographic postcards in the archive of the George Eastman House, in Rochester, NY, that postcards were commercially available in the USA in the period 1900-1914 precoated with cyanotype sensitizer; amateur photographers could easily sun-print their personal pictures onto the cards, with minimal resources and processing, before adding their greetings, and posting them to friends and relatives.

In the area of ethnographic studies, the Canadian National Gallery, in Ottawa, has a set of fine cyanotype prints of photographs of Native North American Indians made by Edward S. Curtis around 1910. Several tribes are represented, Nootka, Piegan and Arapaho; the hunting scenes are particularly striking and the medium seems sympathetically well-suited to the subject-matter, moreover, cyanotype enabled him to proof some of his negatives in the field - which numbered 40,000 in total!

The Photographic History Collection of the Smithsonian Institution has an extensive archive of the chronophotographic work by Eadward Muybridge, proofed in cyanotype as strips from his *Animal Locomotion Series*.[449] There are 850 of these strips, which are believed to be contact proofs of the original glass-plate camera negatives, whose whereabouts are now unknown. Many of these images are particularly important because they reveal background details of his photographic *modus operandi* which were cropped out of the collotype prints in the published versions of his work. The unedited pictures reveal the setup at his outdoor studio, with its corrugated rubber track, the backdrop, props and cameras. In the animal series, a trainer can often be seen to lead the animal or urge it along the track.[450]

In the collection of the George Eastman House there is a topographical record, made as a survey for a railway company, which consists of approximately 50 full-plate cyanotypes, possibly printed on commercial blueprint paper, and entitled *Elimination of Grade Crossing Photographs,* *February 1907, Schenectady*. Also on the topic of railways, there are about 4000 cyanotypes, 6.5 x 8.5", held by the National Railway Museum at York, England, which are proofs of a large archive of 'engineering-works photographs' dating from the period 1910-1953; these are glass-plate negatives from the Great Eastern (later LNER) works at Stratford, illustrating the stages of locomotive manufacture, testing and maintenance, and many of the peripheral matters of a large engineering industry, which include even portraits of the employees.[451] The whole archive is well-documented and the images are of excellent quality and colour, generally 20/21E8.

All engineering projects depended on blueprinted plans, and some were also nicely complemented by cyanotypes documenting the actual progress of the construction.[452] The ready availability of blueprint paper 'on site' must have provided an easy and inexpensive way of immediately proofing the large format camera negatives made to record some of the largest projects in history. The Irn-Bru Company has a slogan: "Made in Scotland from Girders" which also serves as a most apt description of that engineering wonder, the Forth Rail Bridge in Scotland. Begun in 1883, this first steel structure in Great Britain took seven years in the building.[453] Besides the blueprints proper, in the Institute of Civil Engineers in London, the gigantic construction of the Bridge during 1883-1890 was also documented photographically by one of the project's engineers, Evelyn George Carey, whose negatives were proofed in cyanotype, as well as albumen, and specimens now exist in the archive of the Canadian Centre for Architecture, in Montreal.[454] The recent book by Michael Gray and Angelo Maggi describes the achievement of the photographer:

> "The building of the Forth Bridge was marked and controlled through photography; the official photographer: Evelyn George Carey, a young engineer and personal assistant to the designer, Benjamin Baker worked on the project over a period of eight years between 1882 to 1890. His pictures capture, clearly and lyrically, the scale, tensions and inherent dangers of such a project." [455]

An engineering enterprise of comparable magnitude was the cutting of the Panama Canal. The National Library of Australia, Canberra, has an album containing 37 full-plate cyanotypes, entitled *Percement du Canal de Panama,*[456] which makes an interesting comparison with an album of 57 albumen prints having the same title.[457] These were probably assembled from the work of French photographers during the period

1888–1893. Ferdinand de Lesseps attempt during 1881–90 ended with his bankruptcy, and the project was taken over by the US Army Corps of Engineers and completed *ca*. 1904–14.

The same Corps was also responsible for the survey of the Mississippi river which gave rise to topographical studies printed over 1883–93 by Henry Peter Bosse, who was a draftsman with the Corps of Engineers. In the 1990s, seven albums of cyanotypes by Bosse came to prominence, showing the survey, mapping and maintenance of that great river.[458]

The New York Subway was constructed during 1901–09, and extensively documented in cyanotype by Pierre Pullis.[459] Likewise, above ground, the construction was recorded of the Boston Elevated Railway Line. An eclectic online exhibition and anthology of historical cyanotypes, featuring many engineering and commercial objects, may be found on the Luminous Lint website.[460]

5.10 Cyanotype currency notes and postage stamps

A curiously resourceful use of the cyanotype process arose in Southern Africa during the Anglo-Boer War (1899–1902); the following account of the episode is substantially condensed from the detailed study published by the philatelic historian, Robert Goldblatt.[461]

In October 1899, shortly after the commencement of hostilities, a Boer force laid siege to the town of Mafeking, in which were stationed about 1200 British and Cape troops. The beleaguered town was well-provisioned and defended; it survived the bombardment and consequent privations until, after 217 days, the siege was eventually lifted in May 1900 by British columns arriving from Kimberley. But by the end of January 1900, a shortage of currency had arisen in the town, so to provide for payments during the siege, the military commander, Colonel Robert Baden-Powell, ordered the minting and issue of garrison siege notes – popularly known as “good-fors” – in several denominations, which would be redeemed on the resumption of civil law. Of these, the £1 note was designed by Baden-Powell personally and unlike the other notes, which were printed, it was duplicated photographically onto glass plates by Mr E J Ross, the local auctioneer who was a skilled amateur photographer. Since there was insufficient photographic paper on hand to print the issue, Ross decided to employ the recipe for cyanotype to make the printing paper locally.

It is said that one of the two ingredients, potassium ferricyanide, was in short supply in Mafeking, so native runners were appointed to the unenviable task of smuggling the chemical through the Boer lines by night. On the first attempt, the runners returned safely – but bearing potassium ferrocyanide: the message had been badly written. At a second attempt, the correct chemical was secured, but the unfortunate runners were caught and shot, and their potassium ferricyanide confiscated.[462] The third attempt was successful, and Ross was then able to prepare the blueprint paper for sun-printing, followed by processing in the 'Mafeking Mint', which was a bomb-proof subterreanean dark room. The £1 siege note was issued in March 1900, as an edition of 683 individually numbered specimens, each having taken fifteen to twenty minutes to make, signed by the bank manager and countersigned by the paymaster. Of these, only 44 were ever redeemed after the relief of the town and the return to civil law.

The success of the cyanotype printing of the £1 siege notes must have suggested to Baden-Powell that the same process could also be employed to solve a growing crisis in the shortage of postage stamps for internal use. Mafeking was defended on a perimeter of six outlying fortifications, up to one mile distant, but traffic and communication between the garrisons manning these posts and the town centre was necessarily restricted. To provide an internal postal facility, Baden-Powell set up a corps of messenger-cadets using bicycles, under the command of Cadet Sergeant-Major Goodyear, who at the time had just achieved the tender age of 12 years – the very model of an ideal future Boy Scout. Postage rates per half ounce were 1d. within the town and 3d. to the outposts, a small price considering the risks the messengers ran. Not surprisingly, the demand for these denominations of postage stamp was heavy and when the supply of official Cape stamps, overprinted 'Mafeking Besieged', ran out, a special issue was printed locally by cyanotype. Dr. D Taylor, another local amateur photographer, took a portrait of young Goodyear mounted on his bicycle for the 1d denomination, and Ross photographed Baden-Powell himself for the 3d. To these were added appropriately designed ornamentation and the wording 'Mafeking Beseiged' to form two 'master dies' which were then each duplicated photographically twelvefold, and re-photographed in reduction onto glass plates, from which the stamps could then be contact-printed by cyanotype in sheets of 12 at a time, which were then gummed and perforated. The 'Mafeking 1d and 3d Blues' were issued on 9 April 1900, nearly 800 sheets of each denomination were minted by the local printer, Townshend.

The idiosyncratic postage stamps and £1 banknotes that resulted from this historic episode are now highly-prized – and highly-priced – collectors' items that have naturally intrigued philatelists and numismatists over the years. The rarest varieties of the postage stamps are deemed by collectors to be those of a pale grey colour, rather than the deep blue, but in view of the ease with which cyanotypes can be chemically bleached it might be imprudent to invest too heavily in such 'rarities'. The interest in these items is especially high in South Africa, where there is also an historical awareness of Herschel's presence at the Cape over the years 1834 to 1838, just prior to the invention of photography, and the subsequent visits there of other British photographers.[463] The debate rumbles on regarding the suggestion that Queen Victoria personally considered it an act of lese-majesty on the part of Baden-Powell to have allowed his portrait to appear on a postage stamp, which was a privilege normally reserved for the British Sovereign alone. Certainly, the Queen gave no outward sign of displeasure, and the defender of Mafeking became General Sir Robert Baden-Powell, now also remembered as the founder of the Boy Scout Movement in 1907.

5.11 Linley Sambourne's cyanotypes

Edward Linley Sambourne (1844–1910),[464] an artist in black and white, became the cartoonist-in-chief for the humorous British weekly *Punch* in 1900, having contributed to the magazine since 1867. To assist his drawing he kept an archive of reference images for his illustrations that has been preserved at Leighton House Museum, in the Royal Borough of Kensington and Chelsea, and is in the process of being conserved and catalogued at the item level.[465] His working environment may be seen nearby at his dwelling, Linley Sambourne House, which has also been preserved by the Borough as a museum. Sambourne used photography extensively to provide 'model' images for his illustrations; it is estimated that he has left about 30,000 photographs – mostly 5x4 inches – perhaps the largest collection known,[466] and he proof-printed many of his negatives of posed figures by the cyanotype process. The blue colour of his prints was of little consequence for his line-drawings provided the material could resolve adequate detail. When necessary for his illustrative purposes, he had enlargements made by others in silver-gelatin. From the consistent size and accurate regular rectangular shape of his cyanotype prints, it seems very likely that he used small pre-cut sheets of a commercial blueprint paper of the kind then currently marketed by

Marion, Rouch, or Bemrose for pictorial purposes rather than for plan copying.

It is likely that he found cyanotype a most convenient process because he did not possess a proper photographic darkroom, with safelighting, but just used a curtained-off area of his bathroom at home, in which he probably printed privately while his wife was away, because many of his images were also *blue* in the more pejorative sense. In 2002 an exhibition entitled *Public Artist, Private Passions*, conveyed something of the voyeuristic nature of his image archive.[467]

5.12 Contemporary cyanotypists

There are now, in 2014, so many artists working with the cyanotype process that this unillustrated text cannot possibly do them justice. A few references to exhibited and published work and websites follow, that will lead the reader to a number of present-day practitioners, but with the frank admission that the choice is the author's personal one rather than being representative or exhaustive. Many more *afficionados* of the cyanotype medium can be found, for example, participating in the Facebook open group for Cyanotype with over 765 members,[468] on Flickr,[469] and on the Alternative Photography website,[470] whose editor, Malin Fabbri has published a thesis on the subject of the contemporary professional use of cyanotype in graphic design.[471]

To begin our survey in the UK: photogram artist Angela Easterling was inspired by the work of Anna Atkins, and has demonstrated the cyanotype process for botanography in workshops at the Eden Project in Cornwall, and in collaboration with the Royal Botanic Gardens at Kew, as well as using it on a human scale for making live figure photograms in socially involving workshops.[472] In Kent, Nick Veasey has made very striking cyanotype prints from some of his extraordinary X-ray photographs.[473] Master printmaker David Chow, now known chiefly as an exponent of the palladium-platinum medium, began his exploration of alternative process printing with studies of cyanotype flower photograms, bound into handmade books.[474] In Scotland there has been a significant resurgence of interest in cyanotype, as exemplified by the plant photograms of Alexander Hamilton, described in §5.7. The link between cyanotype and the blueprinting practice of engineering drawings has been explored by Roger Farnham and Harry Magee of Glasgow Print Studio, and brought to the public in a program of lectures and exhibitions throughout the city of Glasgow during early 2013.[475] In

Stockholm, Malin Fabbri has set up, and edits the popular alternative photographic process site *AlternativePhotography.com*, which is a valued resource for information and research, representing more than 200 artists, over half of whom have contributed to her published anthology of alternative work in many processes, including cyanotype.[476]

In the USA, Robert A. Schaefer Jr., has been a distinguished practitioner and noted exhibitor of the cyanotype process since the 1970s, and explains it thus:

> "My favorite 19th century process is cyanotype because it enhances the light surreal quality of my photography." [477]

The artist John Dugdale of New York has been celebrated for his body of sensitive personal work in cyanotype, carried out in spite of his serious visual impairment.[478] Collaborative artists, Barbara Ciurej and Lindsay Lochman, have assembled a fascinating series of composite images comprising plant cyanotypes montaged over pigment prints of statuary-like high-key portraits of women.[479] Jesseca Ferguson's cyanotype still-lives made from pin-hole photographs collaged into book objects convey a museum-like ethos that bears thoughtful examination.[480] Brian Pawlowski has written extensively on his blog of his journey of discovery in making expressive cyanotypes by the 'new' method (§7.4), and illustrates his work with beautiful examples.[481] The innovative work of John Metoyer in cyanotype has been very favourably reviewed by John Wood, whose essay has been mentioned in §1.8.[482] Brenton Hamilton [483] and Peter Nappi [484] are also noted practitioners with interesting websites showing cyanotypes.

6 Methodology of Cyanotype Practice

"Tui lucent oculi	*("Your eyes shine*
Sicut solis radii,	*Like the rays of the sun,*
Sicut splendor fulguris	*As the splendour of lightning*
Lucem donat tenebris."	*Illuminates the shadows.")*

Carmina Burana
(Codex from the Monastery at Benediktbeuern, ca 1230)

Instructions for making cyanotypes may be found in numerous publications on photographic practice, but most of these accounts are perfunctory, treating the process only as a curiosity. Recently, a few publications have acknowledged the cyanotype more seriously as a fine-print medium, to be ranked alongside other alternative processes.[485] This chapter and the following one are intended to provide all the information needed to make fine cyanotypes, assuming no previous experience on the part of the reader. As a preliminary, some consideration is given – possibly for the first time – to the geometrical-optical effects of sun-printing photograms from objects that are *not* flat like engravings and photographic negatives, but rather three-dimensional. Then follows a description of the material requirements and *modus operandi* that are common to all the processes and formulae for making cyanotypes – and indeed any other iron-based, plain-paper prints. But first, our language stands in need of a word to encompass all the possible objects that can be used.

6.1 The Diaphane: a neologism

Throughout the first fifty years of photography, prints, as distinct from camera negatives, were generally made without the aid of any optical device employing lenses.[486] A negative, or some other object, was simply interposed between the sensitised surface and the light source, which at that time was, *faute de mieux*, the sun or a bright sky. The print sensitizer could be chosen from a variety of formulations, including cyanotype. Close contact between object and surface ensures a sharp outline, and any translucency in the object will transmit a gradation of tone to the image, which can be both delicate and faithful. When the object is a negative originated in a camera, the resulting photograph is, of course, called a contact print, but the images derived from other objects we now refer to as 'photograms'.[487] A photogram is a camera-less image, usually negative-working, of the shadow cast by an object onto sensitized paper. If the object is at all translucent, it may modulate the transmitted light, and the photogram then ceases to be a mere silhouette, but acquires some internal structure. Some of the philosophical implications of this mode of photographic image-making have been discussed recently by Geoffrey Batchen in terms of Derridean concepts.[488]

The items used to generate photograms can be quite various, but a usual requisite is that they should be quite flat: leaves, ferns, sea-weeds, and other botanical specimens; feathers and insect wings; lace, silks, and other thin fabrics; *cliché-verre* plates, painted glass, printed text, handwritten notes, drawings on tracing paper, and printed images on paper, such as engravings, mezzotints, and woodcuts.[489] The most extraordinary object ever used to register itself as a photogram must be a thin frontal section, cut longitudinally with a microtome from the frozen torso of a human male cadaver; this display of the internal organs of the body was printed in cyanotype in the 1960s, and has been shown recently in exhibition.[490]

In writing about the practices of early photography, I have become increasingly aware that the English language lacks any word to encompass the whole class of objects, such as those listed above, which have been used to imprint their likenesses by interposing them in the path of the light falling upon a photographically sensitised surface.[491] To serve this semantic purpose, I propose a revival and re-definition of the obsolete noun *diaphane*, in the hope that it may find acceptance among photohistorians and possibly even lexicographers. The word has completely fallen out of use in its original meaning.[492] The Greek roots (δια- φανης, 'through-showing') seem appropriate,[493] and there are precedents for employing them in a photographic context, as evidenced by Thomas Sutton's obsolete *diaphanotype* process of 1856, and the *diaphanoscope*, one of the many names contrived for an optical device that could display transparent positive photographs, which are themselves known today as *diapositives*.[494] A *diaphanometer* was a nineteenth-century instrument for measuring transparency, especially of the atmosphere. The words *photophane* and *lithophane* are similarly derived. The practice of *photodiaphanie* entailed the use of an albumen stripping emulsion for making transparencies.[495] Among the genteel Victorian pastimes described in volumes such as *Elegant Arts for Ladies* is the art of *diaphanie*: 'the decoration of glass to the resemblance of stained windows and painted transparencies'.[496] In French, *diaphane* is an adjective meaning ‘transparent’. Even if it can plead no other recommendation, the adoption of this word would at least enable us to avoid the enforced solecism of having to refer to an engraving or a plant, for example, as a ‘negative’.

6.2 Skiology of contact printing

The casting of shadows on a photochemically sensitized surface can be treated by the application of the same geometrical-optical principles used to determine the appearance of light, shade, and shadow forms in pictures. This is the sub-science of ‘skiology’, which has existed since the early Renaissance, finding its origins in the discovery by Filippo Brunelleschi, about 1413, of the principles of geometrical perspective,[497] which are taken up in manuals of ‘sciography’,[498] and applied to the drawing of shadows in projection, mainly for the purposes of architectural illustration. In these treatments, however, the assumptions are made that the sun is a static, ‘point source’ of light. Skiology has a broader relevance, because it can also bring in the dimension of time, as well as space, to explain the appearances of those historic photographs which were ‘printed-out’ with the lengthy exposures required by early proto-photographic processes.[499]

The parameter most relevant to skiology is the spatial resolution of which the healthy human eye is capable. Under optimum conditions,[500] our vision can resolve objects separated by an angle subtended at the eye of 1/3000 radian,[501] and average vision can usually resolve 1/2000 radian;[502] but the criterion normally accepted for photographic purposes is less stringent than this: an outline is deemed to be acceptably sharp when subtending an angle at the eye of 1/1000 radian (0.05° or 3 minutes of arc).[503] This figure is taken as the limiting diameter of the ‘circle of confusion’, when a disc is just perceived as a point, and it is the figure customarily employed in the calculation of the effective depth-of-field of lenses.[504] A viewing distance of 250 mm is the usual nearpoint for normal vision, and is also the natural, comfortable distance for viewing a print of about ‘whole plate’ size; at this distance, an angular resolution of 1/1000 radian obviously corresponds to a linear resolution of two points in the image separated by a distance of 0.25 mm.[505]

The angular diameter of the sun viewed from the the earth’s surface is nearly 1/100 radian, or ca. 0.5°.[506] The sun’s disc is therefore not exactly a ‘point source’ of light, as usually assumed by sciography, and any shadow that it casts displays two distinct regions: the umbra and the penumbra (figure 6.1).[507]

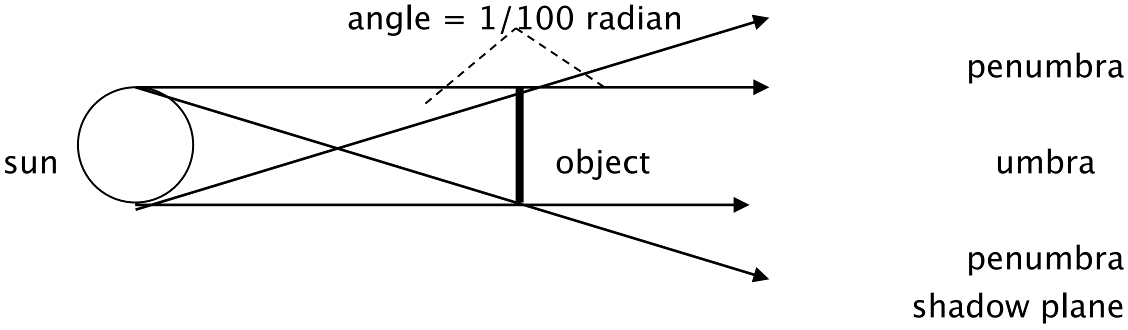


Fig 6.1 The structure of a solar shadow (not to scale).

The umbra is defined as the region of 'totality' where the sun's disc (or other light source) is completely obscured by the shadowing object,[508] and it is the dominant feature of most shadows. The penumbra is the region at the edges of the umbra where the illumination is partial, the tones graduating from full shade to full light as a greater portion of the sun's disc appears uncovered; so the penumbra confers a blurred or 'fuzzy' edge to any shadow cast by a light source of finite size. Any solar penumbra subtends an angle of 1/100 radian at the edge of the object casting it; *i.e.* the width of a penumbra is approximately 1/100th the distance of the object from its shadow. The apparent diurnal motion of the sun is, thanks to the earth's rotation about its axis, a full orbit of 360° over 24 hours; that is, an angular displacement of 15°/hour, as any sundial will attest. Therefore in a time interval of about 2 minutes, the sun travels through an arc in the sky equal to its own apparent diameter.

From these foregoing observations and data, four 'Laws of Skiology' may be posited:

I. Solar shadows look blurred (with a perceptible penumbra due to the apparent size of the sun's disc) when viewed from less than ten times the distance of the object casting them.

II. Exposure of a photogram of two minutes duration causes shadow edges to blur additionally by an amount approximately equal to the limiting value in Law I, due to the sun's apparent motion of 15° of arc per hour.

III. The umbra of a narrow object of width, w, at distance, d, will vanish entirely within a photographic exposure of duration *ca.* $4w/d$ hours.

IV. The light scattered from a clear hemispherical sky can 'fill-in' an umbra to the extent of *ca.* 3 stops less exposure than the direct illuminance of the sun. The extent of 'fill-in' is proportional to the solid angle of irradiating sky 'seen' by the sensitized surface.

When making photograms it is usually advised that, to obtain a sharp image, the object and paper must be in close contact – but this is not necessarily so. The criterion for sharpness in a projected photogram is easily determined based on the resolution: if we assume that the finished image will be viewed at a minimum comfortable distance of 10 inches (254 mm), then by the First Law of Skiology, a sun-printed image will appear sharp to the eye if the object that makes it is distant from the sensitized paper by no more than 1/10th of this – *i.e.* 1 inch (25 mm).

Moreover, the exposure for such a projected image must be relatively short (less than 2 minutes by the Second Law of Skiology) if the sun's apparent motion is not to blur the edges significantly.[509] Many cyanotype and photogenic drawing photograms (using the old, insensitive processes) were probably made with exposures substantially longer than two minutes, which would have extended the depth of the penumbra and caused considerable blurring if the objects were not in contact. This explains the early photographers' preference, in their choice of subject matter, for objects that were already substantially two-dimensional, flattened into close contact with the paper under a sheet of glass or mica: *eg.* leaves, algae, feathers, silks, and lace.

However, the criterion does suggest that, provided sun exposures can be kept short, as with the new cyanotype process, there is no need for an object to be in overall contact, and it explains why objects with some three-dimensional quality can also produce interesting photograms with apparently fairly sharp outlines.[510] That an object can project a sharp photogram without being in overall contact with the sensitized surface leads to a further interesting effect on the 'modelling' of such images. While totally opaque objects in close contact always yield simple silhouettes, even incomplete contact can still maintain a sharp outline with little or no penumbra, provided the object remains no more than an inch or so away from the sensitized surface. Now, if there is a convexity of shape, the skylight can penetrate exposed regions of the umbra, causing a gradation of 'fill-in' light within the umbra, that appears in the image as a 'false shading' for the shapes of curved objects (Fourth Law of Skiology). This phenomenon imbues the photogram with a 3-dimensional quality,[511] which is well-exemplified in the botanical studies of Bertha Evelyn Jaques (§5.7),[512] where the 'modelling' caused by the thickness and curvature of the plant stems and florets, should be compared with the ‘flat’ photograms by Anna Atkins. To achieve this ‘modelling’ effect in a photogram, three conditions must be met: a bright sun, a clear hemisphere of sky with a low unobstructed horizon which is ‘seen’ by the paper, and a short exposure, if the outline is to remain sharp.[513] Obviously the specimen should not be flattened onto the paper, but simply allowed to rest upon it – no printing frame is required. This method of making photograms in three dimensions is exemplified in new cyanotypes of apples and sea urchins – *Hellenic Impressions* made by the author in the Aegean island of Samos.[514]

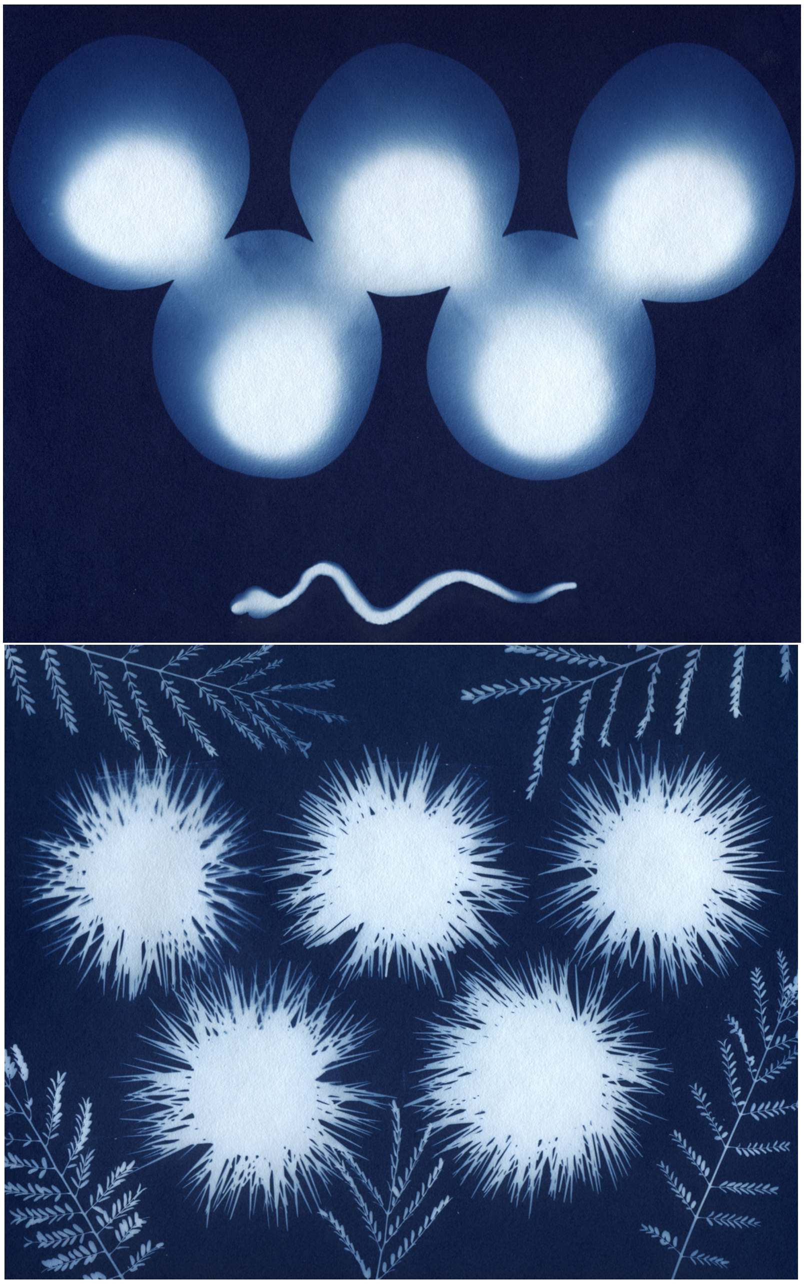


Fig 6.2 Cyanotype photograms of apples and sea urchins

6.3 The processing environment

A benefit of the low sensitivity of alternative printing processes like cyanotype is that you do not need a photographic darkroom or special safe-lighting to work under. Ordinary curtains or blinds should subdue daylight sufficiently for a ‘dim-room’, but for preference the working area should be illuminated by incandescent (tungsten) light: a 40 watt bulb, distant two meters or more, is safe for the time periods normally needed. Avoid fluorescent light if you can; some types of tube have a significant output of ultra-violet light which may cause fogging of the sensitized paper.

You will need a clean, flat, dry surface for preparing the sensitized paper and enough wet-processing space, preferably a sink, for one or two photographic dishes of an appropriate size, together with a means for washing your prints in running water, and an indoor drying facility that need be no more sophisticated than a ‘clothes-line’ and pegs (you should, however, select the design of your clothes-pegs very critically!) The sensitizers and processing chemistry used are odourless and no fumes are normally evolved, so there is no need for special ventilation in the workplace. However, it is essential to observe clean working methods, and any spilt substances must be removed immediately; remember that the sensitizer will stain most surfaces and materials rather strongly. Before commencing any practical work, it would be prudent to acquaint youself with the hazards associated with the chemicals, which are summarised at the end of this chapter.

6.4 Materials and equipment

The following items of equipment will be needed:
Pencil
Ruler
Adhesive masking tape
Blower brush for dusting-off negatives
White blotting paper
Sheet of plate glass (4-6 mm thick and larger than the paper)
Jug to measure 1 litre (1000 cc)
Dropping pipettes 2 to 3 cc (or small syringes - the plastic disposable type without needles - can also be used)
Small mixing glass (a liqueur or 'shot' glass is ideal)
Scales accurate to at least 1 g, or a chemical balance

Small spatula or plastic measuring spoon
Brown bottles for sensitizer solutions (ca. 100 cc is suitable)
A photographic dish (larger than the paper)
Means of print washing
Timer (a wristwatch will do)
Sheets of artists' paper suitable for coating*
Glass spreader rods or brushes for coating the paper*
Contact-printing frame*
Ultra-violet light source*
Suitable negatives*
*The specifications for these last five items are described in detail below.

6.4.1 Paper characteristics

Since the changes in industrial papermaking practice in the 1980s, it has become increasingly difficult to source paper suitable for coating with siderotype sensitizers. Paper chemist Dr. John C. Roberts of the University of Manchester Institute of Science and Technology summarises this historical shift in commercial practice as follows:

> "For the period from around 1840 to the early 1970s paper was usually made in an acidic environment at pHs of around 4-5. This was because many grades required the use of rosin and aluminium sulfate for the control of water penetration (sizing), and solutions of aluminium sulfate exhibit a pH of around 4.5. Aluminium sulfate has also been popular with paper makers because it assists the flocculation of colloidal particles and therefore behaves as a mildly effective retention aid. However, since the early 1970s there has been a move away from acidic systems towards neutral and even slightly alkaline pH. The advantages of operating at higher pH are that there is reduced corrosion, greater strength arising from better swelling of fibres at higher pH, the possibility of using high filler additions and the energy savings associated with the easier drying of filled paper. This change has had a profound effect upon the whole of the chemistry of the aqueous fibre suspension." [515]

The traditional cyanotype process can be applied, with some degree of success, to almost any absorbent surface, including tee-shirts, trainers, cushion covers, plywood and old grocery bags, (§4.6, 4.7). But if your objective is high-quality cyanotype printing, it is best to work on paper having the following characteristics:

1 High (>98%) alpha-cellulose content (i.e. a paper made solely from cotton linters or linen fibres). Papers with a mixed furnish can absorb sensitizer unevenly, causing granularity or blotchiness. The presence of lignins will ultimately cause deterioration.

2 Internal sizing with Aquapel -or other equivalent alkylketene dimer- the modern neutral sizing agent for fine papers. Alum-rosin sized papers seem to work well, but their archival quality has been questioned. Gelatin-sized papers are now less commonly available, but can work well.

3 The paper should be free of alkaline buffering agents such as calcium carbonate (chalk) which is often added to protect archival quality papers from the effects of acid. Calcium carbonate reacts with the sensitizer chemicals in a disadvantageous way, precipitating insoluble calcium oxalate (also responsible for some kidney stones). Alkali also tends to destroy the Prussian blue image (§9.2). The quoted pH of the paper should be 7 or preferably less.

4 A fairly smooth, hot-pressed (HP) surface is desirable – unless you wish to make a highly textured print. 'Not' and 'Rough' surfaces may prove difficult to coat and cause loss of resolution. However, some very smooth, heavily calendered commercial papers do swell and roughen on wet processing.

5 A weight of paper around 160 to 200 grams per square meter (gsm or g/m^2) is generally sufficient to ensure adequate wet strength for smaller prints up to A4; larger prints benefit on heavier, 240-300 gsm paper, but very heavy papers will be slow to wash completely. Thin tissue can yield exquisite prints – if you have the skill to coat and manipulate it.

6 The paper should not contain any other additives, such as clay fillers, retention aids, wet-strengthening agents, optical brightening agents, bleaches, alkaline buffers or dyes.

7 A 'wove' mould paper texture is preferable to 'laid' for pictorial purposes.

Several mould-made fine art papers intended for watercolorists or printmakers have been found to work well, including:

Arches Aquarelle
Arches Platine
BFK Rives
Cranes AS 8111
Cranes Crest Parchment
Cranes Parchmont Wove
Fabriano 5

Hollingsworth Kent
RKB Arches
Saunder's Waterford
Strathmore 500
Van Gelder Simili Japon Nacre
Whatman Watercolour

A handmade paper with characteristics that have been specified by the author for alternative printing is made by Ruscombe Mill in Margaux and called 'Buxton' paper.[516] The greatest imponderable in 'plain paper' printing is the effect of paper-manufacturers' additives on the reactive chemicals of the sensitizer. Each commercial paper has its own idiosyncrasies, which may vary from batch to batch or be changed by the manufacturer without notice. There is no substitute for personal trial and experiment.

The two sides of a sheet of fine paper are often discernably different in a way that reflects the method of manufacture: the so-called 'wire' side ('screen' side in the USA) shows, on close examination under bright light, a very fine geometrical mesh pattern; the 'felt' side ('nap' side in the USA) has a random texture. Paper may be coated on either side, according to your taste. The watermark should be excluded from the coated area. Always handle paper only by the edges, using both hands to avoid creasing; never touch the picture area, either before or after coating, and do not touch the reverse either, because moisture from the fingers can rapidly diffuse through the sheet.

6.4.2 Coating paper with glass rods

In place of the traditional brush, the more economic coating implement is a glass rod or, preferably, thick walled capillary tube, which is usually manufactured to higher standards of straightness than solid rod. The external diameter should be between 6 and 12 mm, with a straight central section equal in length to the width of the coating area. The end portions of the rod should be bent at an angle, using a powerful gas burner; a 'bicycle handlebar' shape: _____/ is simple and ergonomically effective in use. The centre portion acts as the spreader, and determines the width of the coated area; the limbs serve as handles. This implement must be kept scrupulously clean and free of grease film.

Rod-coating paper with sensitizer solution

Follow this procedure:

1 Cut or tear your sheet of paper to an appropriate size that allows generous borders around the picture area – this not only looks well, but the margins also facilitate handling and protect the image. Mark the sheet of paper very lightly in pencil to locate the corners of the area to be coated. Time and trouble may be saved by devising a card template to guide this marking-up for standard formats. The dimensions of the coated area should be 1 to 2 cm larger than the negative to allow for irregularities and to make positioning easy. Avoid including any watermark within the picture area.

2 Tape or clip the sheet lightly to a very flat level surface: a heavy glass plate is ideal. Check with a spirit level that the paper is horizontal; this is critical, so adjust it if necessary. Dust off the surface with a blower brush.

3 First choose a syringe of appropriate size and ensure its plunger is fully depressed, then, keeping the nozzle below the liquid surface, draw up the mixed sensitizer into the syringe, some way above the volume required. By carefully expelling sensitizer back into the bottle, adjust it to the required volume: ignore the small air bubble in the syringe and take the volume reading from the *bottom* of the plunger. A 10”x8” print will require about 1.5 cc, or slightly less, and other sizes in proportion to their area. Try to ‘fine tune’ this volume with experience of a particular paper, so as to avoid excess sensitizer which may puddle and crystallise.

4 Expel the liquid slowly and gently from the syringe (use two hands) as you move it steadily from one side to the other across the width of the coating area between the pencil marks at the top of the paper; reverse and go back again if all the liquid is not expelled. For steadiness, touch the paper lightly with the syringe nozzle and try to form an unbroken strip of sensitizer, but do not be too slow or fussy – irregularities will even out in the coating.

5 Take up the spreading rod with one end in each hand, place the straight central portion onto the paper parallel to, and a little above, the strip of sensitizer. Then, with slight pressure draw the spreading rod down into the strip of solution. Pause briefly (a couple of seconds) while the liquid distributes itself uniformly along the length of the rod, then steadily draw the strip of solution down the paper, like a tiny tidal wave running in front of the rod. The rod is not rotated, and very little pressure need be applied. When you reach the pencil marks at the bottom of the coated area, hop the rod over the strip of solution and push it back to the top of the coating; then hop over the sensitizer strip once more and draw it down to repeat the spreading. Just five passes over the paper will suffice for its surface layer to become saturated with a uniform coating of sensitizer. The first two passes should be made quite rapidly (3 or 4 seconds each) to ensure complete wetting of the surface, and the last three as slowly as possible (10 to 15 seconds each) to allow maximum absorption. At the end of the fifth pass, drag the spreader well below the picture area, with its excess sensitizer (when you have fine-tuned the exact volume to use with your chosen paper, there should be very little waste).

6 Gently lift off the spreader, and soak up any residual liquid left at the bottom of the coating with the edge of a clean strip of blotting paper, otherwise crystals may be formed which can damage the negative. Rinse the spreading rod immediately under the tap.

Occasionally a paper may be encountered that is difficult to coat by this method, because the strip of sensitizer contracts into ‘beads’ and blank areas are left in the coating. This may be corrected by applying two strips of the sensitizer solution, one at the top and one at the bottom of the coating area; if the continuity of the coat ‘drops out’ on the first pass, the fresh strip of sensitizer picked up from the bottom will put this right. It may also be helpful to place a thin sheet of sponge rubber or plastic foam between the paper and the glass plate, to take up any variation in thickness (e.g in a handmade paper) or unevenness in the glass rod. Additional wetting agent (Tween 20 – see below) may also assist evenness of coating.

Brush coating is the traditional method, for those who prefer a more ‘painterly’ style of coating, or who wish to apply the sensitizer more selectively. It tends to be rather wasteful – although this is of little consequence with an inexpensive sensitizer like cyanotype, it is a serious disadvantage when one comes to coat platinotype. Brushes with metal ferrules should be avoided. A broad Japanese 'Hake' brush, available from most art shops, is very suitable. The sensitizer is poured along the paper, just outside one edge of the picture area, and spread by means of a damp brush, making long even strokes in a consistent direction to cover the area, then repeating the brushing at right angles.

Sensitized paper is dried after coating, but the paper should be left horizontal for a few minutes until the liquid is sufficiently absorbed for the reflective sheen of the surface to disappear. The sheet may then be hung up to dry in the dark for about an hour before use or left on a screen. Alternatively some heat may be used – a uniform stream of warm air at 40 °C for 10 minutes is adequate, and makes little difference to the final result, provided that heat-dried paper is allowed to 'rest' for a half, to one hour before exposure, otherwise a slight loss of density may occur. Heating directly,e.g. with a hairdrier, tends to produce uneven results. The prevailing relative humidity has very little effect on the results of printing in cyanotype, but it can profoundly affect some of the other iron-based processes.

6.4.3 Contact-printing frames

Some form of contact-printing frame is essential for applying enough pressure to maintain the close contact between negative and paper. The simplest option is a sheet of plate glass (4 to 6 mm thick – not 2 mm picture glass, which may bend or crack under pressure) and a flat baseboard with a thin sheet of foam rubber or plastic to take up unevenness. This sandwich is held together by strong clips. Alternatively, one of the commercial contact-printing frames for proofing negatives may be used.

The cyanotype process gives a print-out which is to some extent solarized – that is, a fully detailed image is formed during the exposure; but subsequent processing will modify the appearance of this. It is therefore a great advantage to be able to inspect the progress of the printing (away from the UV source!) without destroying the registration between negative and print. This can be achieved with a hinged-back printing frame of the traditional design common in the nineteenth-century, when printing-out was the standard practice. These can still be bought and are often of high craftsmanship (and cost), but it is easy to construct one from a strong picture frame of extruded aluminium with a deep rebate. It is important to include an impervious sheet of rubber or plastic, larger than the sensitized area, sandwiched between the paper and the hinged pressure back; otherwise diffusion of air or moisture through the hinged joint may cause unevenness in printing. Very large contact prints demand more sophisticated technology such as a vacuum easel.

If you prefer clean edges and a white border around your image, rather than the overexposed worked edges which some find fashionable, then mask the glass front of the printing frame with a window of ruby-lith, or other adhesive film that is opaque to UV and blue light. Such masking brings two benefits: it avoids the generation, in the wet processing, of large quantities of redundant (non-image) pigment, which may bleed into and stain the picture area. Moreover, the unexposed but coated borders will provide a tell-tale check on the effectiveness of your clearing, as evidenced by the removal of all traces of yellow stain. If you do not mask your negative when printing but expose the entire coated area, then you will never know for certain if the print is properly cleared. These are the disadvantages of ‘showing the brushmarks’ to prove it’s a handmade print.

Precious negatives may be protected during contact printing by interposing a very thin sheet of archival polyester film – such as Mylar™ or Melinex™ – between paper and negative. The negative will be particularly vulnerable if the paper is fully humidified. Such a sandwich will, of course, diminish the edge sharpness (acutance) of the print, depending on the geometry of the light source: if a diffuse light bed is used at a close distance, the protective film must be no thicker than 20 microns; if a small source at greater distance is used, e.g. the sun, then more robust film of thickness 50 to 100 microns can be tolerated without perceptible diffusion of the image.

6.4.4 Ultra-violet light sources

Any light source with a substantial ultra-violet content will serve for printing the iron-based processes. However, sources like 'sun-guns' and quartz-halogen lamps also emit infra-red radiation, which has the undesirable effect of heating the paper as the exposure proceeds. The best sources are fluorescent-coated mercury-discharge tubes, emitting mostly the so-called ‘long-wave ultra-violet’ (or UVA, with a wavelength range of 320–400 nm) with a maximum output around a wavelength of 365 nm. Lamps with a peak output around 410 nm are not effective for cyanotype, because this wavelength corresponds to an absorption maximum in the spectrum of ferricyanide, which acts as an ‘internal filter’. There is no advantage, and much additional risk, in employing the more dangerous ‘short-wave’ ultraviolet mercury lamps which rapidly damage eyes and living tissue.[517] Long-wave UVA lamps are marketed for graphic arts purposes as well as for domestic sun-tanning.

The following UV sources are listed in ascending order of cost:

1 The sun. This is free, but an uncertain and variable source in many locations, the sun is nearly a point source giving high acutance. It subtends a 0.5 degree angle, and moves through an arc of 0.5 degrees in 2 minutes. In intensity the sun is about four times faster than a small UV source like no. 4. There is a considerable heating effect which may discolour the highlights. The north summer sky is a diffuse source with intensity about 3 stops (8x) less than direct sun with about half the speed of no. 4.

2 Small domestic sunlamps such as the Pifco 300 watt UV lamp No. 1012. These should be used at a distance of about 30 to 50 cm from the printing frame, providing about half the speed of no. 4.

3 Mercury discharge reprographic lamps, such as the Philips HPR 125W, used at a distance of about 30 cm from the frame.

4 A convenient unit such as that once marketed by Gordon Audio-Visual as a Diazo printer. This provides a ‘light bed’ of four Philips fluorescent tubes, type TLADK 30W/05 UV, distant about 8 cm from the print, and is adequate for an image size up to 25x30 cm.

5 A similar array can be made quite cheaply by purchasing from a lighting supply house a commercial luminaire fitting, which is equipped with all the sockets and control gear to take four 600 mm fluorescent tubes. UVA tubes marketed as ‘insect attractors’ are suitable, but not the ‘super actinic’ variety of plant or aquarium light. Filtered BLB ‘black-light blue’ lamps will work, but less efficiently.

6 A domestic suntan bed - for large prints. The ‘facial solarium’ is a smaller and more convenient version of this type of source such as the Philips ‘Cleo’, which uses six UVA fluorescent tubes (actinic/09) with a power of 20 watts each, and easily covers an area 30x35 cm.

7 If cost is no object, a commercial mercury exposure system such as those manufactured for the graphic arts and screen printing industry. The NuArc is a popular model for alternative printing.

Whatever source you use, be sure to protect your eyes with appropriate UV-absorbing goggles.

6.5 Making suitable silver-gelatin negatives

The light sensitivity of iron-based papers like the cyanotype is about a million times less than that of silver-gelatine enlarging papers, so with the technology commonly available they cannot be projection-printed, only contact-printed to achieve a sufficient throughput of UV light. The reproduction scale of 1:1 leaves the photographer with four options:

- to make very small prints from miniature camera negatives
- to photograph using a large format camera
- to make enlarged silver-gelatin internegatives in the darkroom
- to inkjet-print negatives on transparency film from digital files

Each of these strategies has something to recommend it, but whichever you adopt, it will be essential to make your negatives to a density range suited to the printing process. The UVA density ranges required in the negatives (ΔD) should be the same as the logarithmic exposure scales (ΔlogH) of the iron-based sensitizers, because in contact printing there is no Callier Effect, where light-scattering enhances contrast.

The traditional cyanotype process has ΔlogH ~ 0.9-1.2 (3 or 4 ‘stops’) which matches the density range of camera negatives developed to a contrast suited to a Grade 3 or 4 silver-gelatin enlarging paper. For the new cyanotype process the ΔlogH scale may vary typically from about 1.6, equivalent roughly to a Grade 0 silver-gelatine paper, to a ΔlogH around 2.4, which is a far longer scale than any silver-gelatine paper. To yield a full tonal range in a new cyanotype print, negatives must be made with a correspondingly long density range. This will be obtained by giving a good continuous-tone camera film normal exposure, but developing it for 75% to 100% more than the normal time period recommended for silver-gelatine enlargement printing. Trial and error can be lessened by consulting the film manufacturers' published data for the variation of Contrast Index (Kodak's C.I. or Ilford's G) with development time or with developer concentration. As a guide, negatives for cyanotype printing should be developed to a C.I. value in the range 0.7 to 1.3, depending on subject and interpretation. These C.I. values are more or less incompatible with normal silver printing in an enlarger, so you cannot expect to use the same negative for both. A convenient compromise is to make your original negatives in the usual way for silver printing, ensuring adequate exposure to give plenty of shadow detail, and then prepare internegatives of higher contrast from them.

Much of what was originally written here 15 years ago about making enlarged internegatives has become obsolete as a consequence of silver-gelatin materials ceasing to be manufactured. However, I will let it stand in the hope that equivalent materials may still be found. The user of 35mm and roll film formats is best advised to enlarge the original camera negative to give an internegative, which has the added advantage that the precious original is not put at risk by the rigors of contact printing. There are several ways to do this:

1. Direct reversal duplicating film makes a negative directly from a negative. A convenient (but expensive) method was to make internegatives by enlarging onto Kodak Professional Direct Duplicating Film Type SO-339, which was available in 5"x4" and 10"x8" formats only but is now discontinued. Dodging and burning may be carried out at this stage if desired. Very vigorous development is necessary to achieve an adequate maximum density in this material. As a starting point for experiment, develop it in the Kodak high contrast developer D19 (undiluted) for 6 to 8 minutes at 22-24 °C with continuous agitation. This film has orthochromatic sensitivity, so a red safelight is necessary. See the Kodak literature for further information. N.B. SO-339 is a very slow material and needs a heavy exposure under the enlarger. Even modest enlargements may require a minute's exposure at full lens aperture. Remember that it is a reversal material - more exposure gives less density. Remember always to make your internegatives as mirror images: i.e. place the original negative emulsion up in the enlarger so the duplicate will make a ‘right-reading’ image when exposed emulsion-to-emulsion on the print.
2. The longer route is via an interpositive, using normal negative-working continuous tone films such as Kodak Gravure Positive Film 4135 or Agfa Gevatone N31p or N33p, which are available in large sheet sizes. The choice of size for the interpositive will depend on your available enlarger formats and budget, but to minimise the degradation in quality introduced by the extra copying step, the larger you make the interpositive, the better. (Contact-printing an interpositive from a 35mm negative can introduce serious dust problems.) The interpositive should be printed quite heavily to ensure no loss of information; the highlights should appear somewhat grey and the tonal separation should still be visible in the shadows. Development to a Contrast Index value of one is recommended, and dodging and burning may be

carried out at this stage so that the results can be readily judged. The negative is then made from this interpositive by enlargement or, preferably, contact, onto the same film, using more vigorous development to raise the contrast. Kodak HC-110 is a convenient developer, offering control of contrast by varying concentration as well as time. Agfa market a continuous-tone orthochromatic sheet film, GO210p, which has the advantage of a variable contrast that can be adjusted by yellow or blue filters.

3. By starting with a positive transparency from the camera (such as Agfa Dia-Direct), an enlarged internegative can be obtained in one step on the films specified in 2. If the original small-format image is a colour transparency, projection onto these orthochromatic materials (which are insensitive to red light) will not faithfully reproduce the tonal balance. To maintain this, a panchromatic sheet film, e.g. Ilford's FP4 or HP5, will be necessary, possibly with a colour head or a filter to bring the enlarger light source to a daylight colour balance.
4. The sheet film on which a negative is projection-printed may be reversal-processed to give another negative directly. Directions for carrying out this rather lengthy procedure are to be found in the standard photographic manuals. Kodak market a reversal-processing kit for their T-MAX films.
5. Paper internegatives are a very economical but low-quality option. Obviously a thin-based paper stock will be needed to avoid long printing exposure times. The ‘Resin-coated’ (RC) variety is said to work well, and methods have been suggested for delaminating the emulsion layer from the base. If exposures become intolerably long, a paper negative may be waxed to improve its translucency: beeswax dissolved in turpentine at a concentration of 50% and used warm is a convenient waxing agent. Alternatively the wax may be ‘ironed in’ between sheets of blotting paper.

Variations in paper texture, including any lettering on the back, can be cancelled out by giving white light exposure to the back of the paper, in addition to the normal image exposure to the emulsion side. A test strip is necessary to determine this additional compensating fog exposure.

6.6 Workflow for inkjet-printed negatives

The modern technology of digital photography, with all its capacities for image manipulation, provides new possibilities in the realm of negative preparation for alternative process printing, since the scope for adjusting the image and its characteristic curve is almost unlimited.

6.6.1 Summary and purpose

Herein follows a stepwise sequence of explicit instructions for making monochrome digital photographic negatives, using a personal computer and ink-jet printer, starting from original medium format camera negatives or transparencies, or from digital picture files. The software used for this image manipulation is Photoshop CS™ (Version 8) and Epson Scan, using an iMac, running OS 10.4. No additional software or 'latest upgrades' are required. The files are printed out onto ceramic-coated transparency material (such as Pictorico OHP Transparency Film or PermaJet Digital Transfer Film)[518] using an Epson photo-quality ink-jet printer. This procedure provides internegatives, suitably matched in optical density at UVA wavelengths, for contact printing in any of the 'alternative' photographic processes. This digital negative workflow differs significantly from the customary practices in several respects:

- For calibration, 100-step-tablet negatives having intervals of 1% relative opacity, are inkjet-printed onto the film, identical in all their print parameters and materials with the actual negatives to be output. All the colours of the printer's ink-set are used, blended in a smooth greyscale.
- The Standard Printing Exposure (SPE) is found by printing these 100-step-tablet negatives in the process of choice with the standard printing setup, so that the clear filmbase (relative opacity of 0%) produces 'nearly' the maximum print density (Dmax) that the process is capable of, while some tonal separation is still visible in the deepest shadows (0-10%).
- The correct ink density range (at UVA wavelengths) for the negative to match the exposure scale of the chosen process is found by adjusting the printer driver settings: trial 100-step-tablet negatives are output and test-printed at the SPE, until the 99% relative opacity step in the negative prints as 'just white' background of the paper used for the process.
- Having established the 'black and white' end-points for the process, when making the negatives appropriate for analogue

printing, the image levels are redistributed in Photoshop to ensure that mid-grey tones also print correctly. This is achieved simply by using the gamma slider in the Levels window, which applies a suitable 'generic curve' automatically; making the laborious derivation of a 'personalised' curve generally unnecessary.

6.6.2 Calibration of equipment and materials

The optical density range of the ink laid down on the film depends on:

- the particular make and model of printer
- the particular ink set being used
- the choice of settings in the printer driver software
- the film substrate used to receive the negative image

If any of these are changed, it is necessary to re-calibrate, as follows

1 Output the digital file for the 100-step-tablet to your printer, loaded with the identical film that you will use for all your negatives.
As a starting point, the ink density range may be approximately provided by the printer’s ‘premium photo-quality’ media settings for glossy or semi-glossy paper, preferably an 'Advanced Black & White' setting if one is provided.
Use 'matt black' ink rather than 'photo black' if there is a choice.
The software for driving modern printers now usually includes a means of adjusting the maximum ink density; this control may be buried rather deeply in the options. Record its setting before outputting the 100-step-tablet files. Let the test negative dry and cure overnight before use, as inks have been observed to change density with time.

2 Assemble the standard printing setup for your chosen process. Take care that the light source, distance, and other conditions of printing and wet-processing are maintained constant throughout.

3 Use your 100-step-tablet negative to make trial exposures. Increase the exposure until the test print is perceptibly overexposed.
['Overexposure' is judged by the analogue photographer's negative-working criterion of shadow tones beginning to 'block up' and become indistinguishable – it is NOT judged by the digital photographer's positive-working criterion of high values being 'blown out'.]
Call the exposure for this test print, E. If you are making timed exposures to a constant light source, E is the duration in minutes or seconds. If you employ an exposure system with a light integrator, E will be measured in the instrument's arbitrary 'exposure units'.

4 Examine the test print carefully when it is dry. The lowest part will appear dense and ‘blocked up’ with no resolution of the sequential steps. Compare each step with the lighter one immediately *above* it – *i.e.* the one resulting from 10% less transmittance in the negative (=10% more opacity, corresponding to a density difference of ~0.05, or 1/6th of a 'stop'). Try to locate the first step, starting from the bottom, that is just perceptibly resolved in tone from the one above it; this lower step gives the transmittance in this negative needed to produce your *effective* maximum print density. Call this transmittance P %.

5 Calculate your Standard Printing Exposure (SPE) by taking P % of E, the exposure for the test print made in **3**:

$$SPE = E \times P/100$$

The SPE should apply approximately for all prints made in the chosen process, with your digital negatives, provided that the light-source and other printing and processing conditions are kept the same.
Note that the SPE is *not* sharply-defined, but can be varied slightly, because the *effective* maximum print density depends on how far up the shoulder of the characteristic curve of the printing process you choose to place it. However, the higher the effective maximum density is placed, the greater proportion of the 256 image levels will need to be allocated to increasing separation in the shadow tones, so there will be fewer left for the lighter tones of the image, which compresses the contrast. Furthermore, if you seek to produce a 'maximum black' by extending the SPE excessively, the printer inks may not have sufficient UVA blocking opacity to produce a 'paper base white' at all.

6 Make a test print of the 100-step-tablet negative at the SPE. Inspect the test print carefully, when fully dry, to find the step that appears ‘just white' – *i.e.* the first one that has no upper boundary and which precedes the step with the first perceptible print tone.

7 If *no* steps print white, adjust the printer driver settings to lay down *more* ink when making the negative.
If several steps print white, adjust for *less* ink in the negative.

8 Return to Step **1** and make a new 100-step-tablet negative using the new settings, and re-test it through Steps **2** to **7**. The ideal aim is to get 'just white' for the *first* step of the tablet – that having 1% transmittance or 99% opacity – but it should be satisfactory to get within 2% or 3% of this.

Experiment carefully with your printer driver settings: change the maximum optical density of the ink (a control usually found in the "colour management" window) and *note its value* when you make each new test negative. Print each one in your process with the same SPE until you come close to the ideal highlight tones.

6.6.3 Fine-tuning negative opacities

This is only necessary in case your printer driver controls do not allow you to get the first white step close to 1% transmittance or 99% opacity. If it is still significantly different from this ideal value, then it will be necessary to reset the maximum opacity of the negative file to a value equal to the opacity observed for the first white step, before you output it on transfer film, so that the negative will print the white level correctly. The Layer Opacity Slider in the layers palette provides a convenient means of making this fine adjustment. All the other opacity values will then be scaled proportionally. Setting the Layer Opacity to less than 100% makes the tonal separation a bit coarser in principle, because the tonal scale of the image will be resolved across fewer than the full 256 levels. If the printer driver settings result in a white value close to 100%, it's unlikely the eye will notice this, so this adjustment in the following Workflow should be no more than 'fine-tuning'.

6.6.4 The 'gamma slider' for tonal correction

There usually is a need to redistribute the levels of a digital image file before it can provide a useful negative. If this is not done, a print made with the SPE will usually appear too dark in overall tonality, even though the black and white end-points print correctly. In effect, what is needed is a transformation of the linear scale of Relative Opacity %, used for digital files, into the logarithmic scale of Optical Density needed for a negative to yield a visually acceptable print by any analogue photographic process having a typical (D/logH) characteristic response.

If we are prepared to accept an approximate transformation, it becomes unnecessary to use experimentally-derived curves, with all their burdensome and inaccurate measuring of many experimental points, because essentially the same result comes from re-setting one parameter in Photoshop: this parameter is the middle slider in the Levels Histogram window, which controls the gamma (or contrast) value shown in the central box, and which always has a default value of 1.0 when the window is opened. The gamma needs to be increased to a value in the region of 1.8 to 2.2 in the ***positive*** image, which – be warned! – will then appear horribly overexposed in the digital sense, or ‘blown out’ on-screen. This adjustment usually suffices to re-map the relative distribution of levels from most positive digital image files to provide, ***on inversion***, a negative with sufficient density to be printable by analogue processes. This one simple adjustment with the gamma slider effectively applies a built-in ‘generic curve’ for transforming *all* digital negatives to analogue status. In practice, it is found to agree with individually-derived personal correction curves for platinum-palladium, which have been scrupulously plotted by expert workers from point-by-point reflectance density measurements of their actual step-tablet test prints.

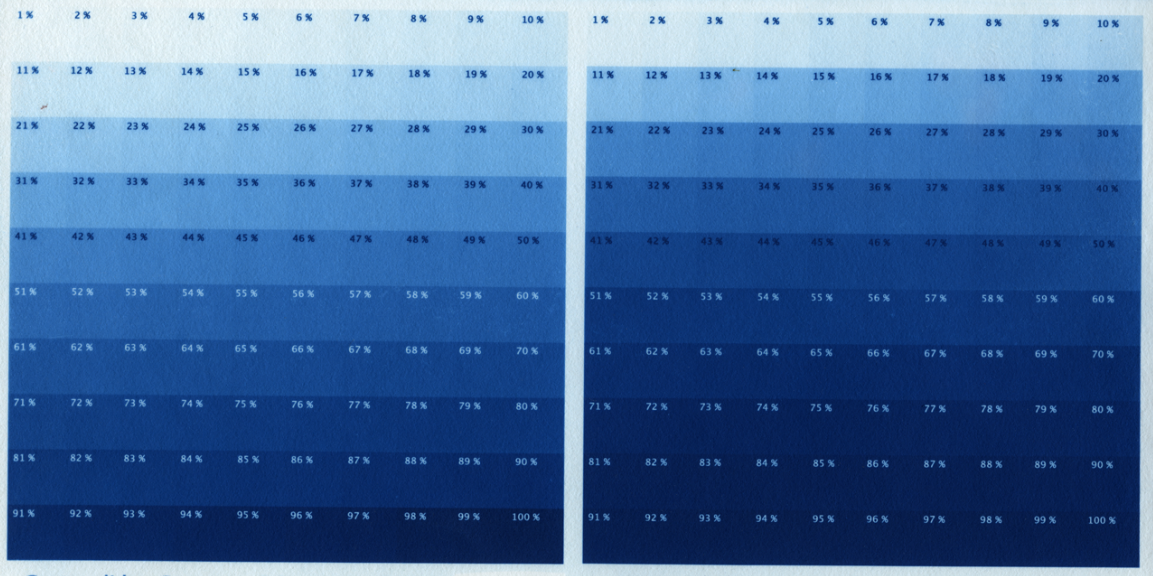


Fig 6.3 100-step: Gamma = 2.2 on left; default Gamma = 1.0 on right

6.6.5 Workflow for digital negatives in Photoshop

Summary of the sequence of '*Things that may need to be done*'

Phase I: Acquisition and digitization of image

1 Turn off Colour Management in Photoshop
2 Open Image File – if already available, or –
3 Scan Source – if necessary – and Save

Phase II: Preparation of positive image file

4 Preliminary Image Adjustments – if needed
5 Crop & Re-size Image
6 Monochromatize – if an RGB colour image
7 Burn & Dodge – if desired (a crude tool)
8 Set Black & White Levels
9 Adjust Local Contrast – in areas where needed
10 Retouch Flaws – where necessary
11 Save 'Perfected' Positive Image

Phase III: Preparation of negative image file

12 Apply Tone Correction Curve to Positive by resetting Gamma
13 Reverse Handedness – if image reads correctly on screen
14 Invert Tonality from Positive to Negative
15 Sharpen Image with Unsharp Mask
16 Mask Print Border – if desired (expensive in ink)
17 Flatten Layers & Save 'Adjusted' Negative Image File

Phase IV: Printing the negative image onto film

18 Fine-tune Negative Opacity to Match Exposure Scale – if needed
19 Connect Printer, Load Film & Check Inks
20 Select Printer & Page Setup
21 Reduce Image File to 8 bits per channel if necessary
22 Set Printer Driver & Maximum Ink Density & Output the Negative
23 Number the Negative & allow ink to cure

Workflow for Making Digital Negatives in Photoshop CS

Phase I: Acquisition and digitization of image

Key	**Menu or Tool**	**Procedure**

Keys are Shortcuts to Tools and Menus: F6, F7, F8 are re-defined: Edit>Keyboard Shortcuts

1) Turn Off Colour Management in Photoshop

Key	Menu or Tool	Procedure
⌘⇧K	**Photoshop**>Colour Settings>	In order to turn Colour Management OFF:–
	RGB:	‘Monitor RGB – iMac’
	CMYK:	‘Euroscale Coated v2’ or suitable choice
	Gray:	‘Gray Gamma 1.8’
	Spot:	‘0% Dot Gain’ or as low as possible
	Colour Management Policies:	All OFF

2) Open Image File – if already available

Key	Menu or Tool	Procedure
⌘O	File>Browse…>Open>	Acquire raw image, preferably 16 bit/channel Negative or positive, preferably RGB
	If colour profiles mismatch:	Discard any embedded colour profile

3) Scan Source – if necessary

Key	Menu or Tool	Procedure
	File>Import>Epson Scanner	Use Epson Scan App in Professional Mode
	Settings:	Save the following settings:
	Document Type:	‘Film (with Film Holder)’ if negative or slide
	Film Type:	‘Positive Film’
	Image Type:	‘48-bit Color’
	Scanning Quality:	Best
	Resolution for 360 ppi negs: (Use higher if heavy crop)	see below

Final Format:	**A5**	**A4**	**A3**	
Source Format:				
10x8 in.	300	425	600	ppi
5x4 in.	600	900	1250	
9x6 cm	900	1300	1850	
6x6 cm	1300	1850	2700	
35 mm	2100	3050	4350	

Check Document Size:

10x8 in.	9.69x7.68 in.	246x195mm
5x4 in.	4.72x3.70 in.	120x94 mm
9x6 cm	3.25x2.20 in.	82x56 mm
6x6 cm	2.20x2.20 in.	56x56 mm
35 mm	1.417x0.945in.	36x24 mm

Key	Menu or Tool	Procedure
	Target Size:	‘Original’; Trimming: Off
	Click Zoom button in Preview panel	for enlarged preview image of 6x9 etc
	Set marquee	cropping as little as possible
	Click Histogram button	to open histogram adjustment window
	Check Output Levels	full range 0 to 255
	Set Input Levels B&W sliders	on histogram; RGB channels; avoid clipping
	Click & Hold Show Output button	to see if there’s any clipping bars at ends
	Tone Adjustment	none: linear, centre slider gamma = 1.00
	Auto Adjustments	none: turn off any
	Densitometer	is useful to check B&W levels before scan
	Click Close button	in histogram window
	Click Scan button	to scan image and import into Photoshop
⌘⇧S	**File**>Save As>‘Raw Scans’	Save scan as .tif file in folder ‘Raw Scans’ no compression

Phase II: Preparation of positive image file

4) Preliminary Image Adjustments – if needed

	Double Click 'Background' layer	to select it in Layers palette
	Click OK button in New Layer window	Converts Background to Layer 0 for adjust
	IF not suitably oriented:–	
	Image>Rotate Canvas>…	to rotate image for normal viewing
	IF a negative:–	
⌘I	**Image**>Adjustments>Invert	to invert tonality to positive for easy viewing
⌘0	(zero) **View**>Fit on Screen	Gives optimum image window size
	OR:–	
Z	**Select** 'Zoom' tool	**Click** 'Fit on Screen' button

5) Crop & Re-size Image

	Image>Image Size…	Check re-sizing parameters correct selected
	Tick boxes for	Scale Styles; Constrain Props; Resample: Bicubic
C	**Select** 'Crop' Tool	to frame and re-size the image:–
	Click Tool preset picker bar top left	**Select** tool to re-size image at 360 ppi
	(allowing margin of ~0.15")	**A5**: 8.0x5.6 in 203x142mm 2880x2016px
		A4: 11.4x8.0 in 290x203mm 4104x2880px
		A3: 16.3x11.4in 414x290mm 5868x4104px
⌘**R**	**View**>Rulers	to show rulers, if desired
⇑	**Shift Lock**	to replace crop icon cursor with crosshairs
⌘⇑ ;	**View**>Snap	to switch 'snap to edge' on/off as desired
	Click & Drag within image	to generate a marquee defining image
⌘'	View>Show>Grid	to generate grid – if useful for placement
↔	**Keys**	move whole marquee finely: it rotates about Registration point – can be dragged
	IF desired to correct perspective:–	
	Tick perspective box in toolbar	to transform marquee:–
	Click & Drag corners of marquee	onto a would-be rectangle for the image
	Pull edge centres of marquee	to resize – keeping corners within frame (only possible if crop undimensioned)
√	**Click** √ button	to execute Crop
	OR:–	
Ø	**Click Ø** button	to cancel and re-set

6) Monochromatize – if an RGB colour image

F8*	**Image**>Adjustments>Channel Mixer	opens window to convert to monochrome
	Click Load… button	for preset channels file
	Select 'mono.cha' file	saved file from Documents:
	Click Load	L = 30%R + 59%G + 11%B (visual response)
	Tick Monochrome box	Output Channel: Gray
	Click OK button	to apply channel mix and close window
	OR if desired to set channels manually:–	
	Click each RGB channel	Study them for noise, or use as filter, then:–
↑↓	**Arrow Keys** to set channels	as preferred; total must sum to 100%
	Click OK button	to apply channel mix and close window
	Image>Mode>Grayscale	to revert image to grayscale (smaller files)

7) Burn & Dodge – if desired (a crude tool)

O	**Choose** 'Burn' or 'Dodge' Tool	as required – **alt click** switches between
	Tool Options Bar>Brush Preset:	**Brush Diam**: 100–1000 pixels; **Hardness**: 0
	Tool Options Bar>Range:	**Select** from: Shadows, Midtones, Highlights
	Tool Options Bar>Exposure:	**Exposure** slider: *ca.* 10–20% for intensity
	Click & paint with tool	to burn or dodge areas of image. Can repeat
	IF correction needed:–	
	Edit>undo	or step back in **History Palette** and delete

8) Set Black & White Levels

⌘L	**Image**>Adjustments>Levels	opens Histogram window: Set B&W levels:
	Alt Click B&W level sliders	view effect on image areas for Dmax Dmin
		points. Keep all image levels: don't clip
	Click OK button	to execute Levels adjustments – or Cancel

9) Adjust Local Contrast – in areas where needed

⌘alt0	**View**>Zoom In or Zoom Out	Magnify area, and select it:–
	EITHER use 'Magnetic Lasso' Tool:–	
L	**Choose** 'Magnetic Lasso' Tool	**Feather**: ~5 px; **Antialias**: off; **Width**: 10 px
		Edge Contrast: 10–20%; **Frequency**: 100
	Click cursor on edge to select start	**Move** mouse round area to be selected
		Can back-delete anchors; **Click** sets anchor
[ ]	**Keys** change **Width** in use	Use wider for smooth edges
	Click to get marquee	when returned to the starting point
	OR use 'Magic Wand' Tool:–	
W	**Choose** 'Magic Wand' Tool	**Contiguous**; ±**Tolerance** = range of levels
	Select>Grow	Increases range
⌘L	**Image**>Adjustments>Levels	Accesses Histogram window:
	Re-set Slider for Centre Level	**Re-set** gamma <1.00 to increase contrast
	Check Preview box to see effect	Match densities using eyedropper if need be
	Click OK button	in Levels window to apply contrast or Cancel
⌘D	*OR ESC*	to deselect Lasso, or **Click** within marquee

10) Retouch Flaws – where necessary

⌘alt0	(zero)	Zooms magnification to 100%. Seek defects:
	Click & Drag in scroll bars	Scan frames from top left, raster-like
J	**Choose** 'Healing Brush' Tool	**Blending mode**: Replace; **Source**: Sampled
	Click Brush menu	**Aligned; Brush Size**: Off; **Brush Space**: 25%
		Brush Diameter: ~12 pixels; **Hardness**: 0
	Alt Click cursor on nearby area	to locate sampling of replacement density
	Click & paint	Repair defects with Healing Brush. Continue.
⌘0	(zero)	to revert Zoom to normal when finished

11) Save 'Perfected' Positive Image

	Layer>Flatten Image	Flattens image to Background Layer (small)
⌘⇑S	**File**>Save As>'Positives360'	Save positive as .tif file in appropriate folder
		no compression; Mac byte order

Phase III: Preparation of negative image file

12) Apply Tone Correction Curve to Positive by Resetting Gamma

	Double Click Background Layer	to select it in Layers palette
	Click OK button in New Layer window	to convert 'Background Layer' to 'Layer 0'
	EITHER use Centre-point slider:-	
⌘L	**Image**>Adjustments>Levels	opens Levels window & Histogram
	Re-set Slider for Centre Level	Set Gamma to ca. 2.2 Record value used
	Check Preview box to see effect	Positive image looks ~2 stops overexposed
	Click OK button	to apply curve & close window – or Cancel
	OR use a Stored Curve:-	
⌘M	**Image**>Adjustments>Curves	opens adjustment curves control window:-
	Alt Click on grid	to improve coordinate grid to 10 divisions
	Load a selected .acv Curve	options stored for adjusting as desired by:
↓↑	**Keys** move any selected control point	open or close highlights, mids or shadows
	OR Generate a Custom Curve: -	by placing cursor on image area to modify:-
⌘M	**Image**>Adjustments>Curves	opens adjustment curves control window:-
	⌘Click the image area	to set a control point on the Curve
↓↑	**Keys**	darken or lighten this area, respectively
	⌘Click in another area	to set a point to be further adjusted likewise
	Click & Hold eyedropper in an area	to see where that area lies on the Curve
	ctrl-Tab moves selected point	through control points on Curve
	shift ctrl-Tab	moves through in reverse
	shift-Click	enables multiple points to be selected
	Click OK button	to apply Curve & close window – or Cancel

13) Reverse Handedness – if image reads correctly on screen

F7*	**Edit**>Transform>Flip horizontal	Laterally reverses picture to a mirror image

14) Invert Tonality from Positive to Negative

⌘I	**Image**>Adjustments>Invert	Inverts image tonality to negative scale

15) Sharpen Image with Unsharp Mask

F6*	**Filter**>Sharpen>Unsharp Mask	**Amount**: 100-250% usually 200%
		Radius: 0.5-1.5 pixels usually 0.8 pixel
		Threshold: 2-4 levels usually 3 (skin ~6)
	Tick Preview box	to see effect of USM when image clicked
	Click OK button	in USM window to apply USM – or Cancel

16) Mask Print Border – if desired (expensive in ink)

	Image>Canvas Size...	8.0x5.6 in **A5**: 8.28x5.85 in 210x149 mm
		11.4x8.0 in **A4**: 11.7x8.28 in 297x210 mm
		16.3x11.4in **A3**: 16.65x11.7 in 421x297 mm
W	**Choose** 'Magic Wand' Tool	**Antialiased; Contiguous; Tolerance 0**
	Click with Wand in border area	to select border area to be masked
⇑F5	**Edit**>Fill...	Colour: Black; Blending Mode: Normal
⌘D		to deselect border mask

17) Flatten Layers & Save 'Adjusted' Negative Image

	Layer>Flatten Image	Flattens image to Background Layer (small)
⌘⇑S	**File**>Save As>'Diginegs'	Save negative as Tiff file in folder 'Diginegs'
	Click OK button	Tiff Options: No compression; Mac byte order

Phase IV: Printing negative image onto film

18) Fine-tune Negative Opacity to Match Exposure Scale – if needed

If White ~99% Opacity skip this whole box:	ink density will be adjusted in printer settings 22)
Double Click Background Layer	to select it in Layers palette
Click OK button in New Layer window	to convert 'Background Layer' to 'Layer 0'
Click Image Layer Opacity button	to reveal Opacity Slider in Layers palette
Adjust Image Layer Opacity slider	to a value matching process to be used: step % prints just white when 0 % prints near Dmax
Record the step% value used	See: calibration of equipment & materials
Click Image Layer Opacity button	to close the Opacity Slider
Layer>Flatten Image	Flattens image to Background Layer

19) Connect Printer, Load Film & Check Inks

Connect Printer & Switch ON	Load Printer with 1 sheet of transfer film
Launch Printer Utility	Ensure correct Printer selected from List
Click Status Monitor	to check ink levels & recharge if needbe
Choose Nozzle check	if printer long-dormant: head clean
Close Printer Utility window	

20) Select Printer & Page Setup

⌘⇑P	**File**>Page Setup…	Format for printer & paper size & Aspect
	Click OK button	in Page Setup window
	Click in Doc: edge area	to see fit of image on page
	Alt Click in edge area	to see size of image, resolution, etc.

21) Reduce Image File to 8 Bits per Channel if necessary

Image>Mode>8 bits/channel	to prepare for sending to printer – if 8 bit

22) Set Printer Driver & Maximum Ink Density & Output the Negative

⌘altP	**File**>Print with Preview…Check page settings:–	Check centred image
	Colour Management:	Document; Profile: Same as Source
	Click Print… button	to access Print Settings window:–
	Printer:	Check printer choice correct
	Presets:	Use saved Printer Driver settings file:
	Print Settings>Media Type:	Appropriate paper choice (photo or matte)
	Colour:	Colour ON
	Advanced Mode:	Premium Photo Quality: highest resoln dpi High speed OFF; Mirror image OFF
	Colour Management:	Mode: Epson Standard sRGB
	Colour Controls:	All sliders centred; gamma = 2.2 Advanced B&W mode: Neutral & 'Normal' tone Adjust maximum ink density to give White~99%
	Extensions:	Normal paper (not thick)
	Paper Configuration:	Colour density & head drying time – defaults
	Click Print button	to print the negative on transparency film Don't 'Save Changes' on closing file

23) Number the Negative & Allow Ink to Cure

Number the negative indelibly	Allow negative to dry in dust-free environment for at least 12 hours before use. Do not stack.

6.6.6 Short version of the workflow

The previous detailed workflow was designed to cope with most eventualities, but it has necessarily become so lengthy that it is “hard to see the wood for the trees”. If we are working with preformatted and ‘perfected’ positive images, the following are the only essential steps needed to prepare a tonally-corrected and density-adjusted negative. Numbers refer to the original ‘Things that may need to be done’ boxes.

1 **⌘⇑K** Photoshop>Colour Settings> Colour management OFF
4 **Double Click ‘Background’** in Layers palette
Click OK New Layer 0
6 **F8*** Image>Adjustments>Channel Mixer
Load ‘mono.cha’ file: L = 30%R + 59%G + 11%B
Image>Mode>Greyscale
8 **⌘L** Image>Adjustments>Levels
Alt Click Sliders & Set B&W levels
12 **Set Middle Slider to Gamma ≈ 1.8 – 2.4** for desired contrast
13 **F7*** Edit>Transform>Flip horizontal
14 **⌘I** Image>Adjustments>Invert
15 **F6*** Filter>Sharpen>Unsharp Mask
18 **IF** maximum ink density cannot give White for 99% Opacity step (22):
Adjust Image Layer Opacity to % Opacity of first 'white step'
Layer>Flatten Image
19 **Launch Printer Utility**: Ensure Printer connected, loaded, & turned on
Click Status Monitor to check ink levels etc
20 **⌘⇑P** File>Page Setup… Format for Printer, Page, Size & aspect ratio
22 **⌘altP** File>Print with Preview…
Click Print… Print Settings: **Advanced B&W mode**, Neutral tone, Normal
Adjust Maximum Ink Density to the value that gives ~99% Opacity in the negative printing as the 'white step'.
Click Print

* reassigned function keys

7 Formulae for Cyanotype Sensitizers

Gold is for the Mistress,
Silver for the maid,
Copper for the craftsman
Cunning at his trade.
"Good," said the Baron, sitting in his hall,
"But Iron, cold Iron, is master of them all."
Rudyard Kipling
Cold Iron, from *Rewards and Fairies* (1910)

This Chapter offers a choice between three cyanotype recipes: first, the traditional cyanotype formulation, which is easy to prepare, inexpensive, and non-toxic, second, a widely-recommended elaboration of this recipe, and third, my new formulation that provides finer results but requires a little more care and expense in the preparation of the sensitizer, and involves less benign chemicals. The traditional recipes are fully described in the useful practical guide for beginners by Malin and Gary Fabbri,[519] and many other sources. They are well-suited in their short exposure scale to conventional negatives such as are made for printing in commercial gelatin-silver halide papers of contrast grade 3 or 4. The new cyanotype process, on the other hand, is a good match for the long density range of negatives specifically prepared for salted paper, argyrotype, platinum-palladium and similar siderotype processes.[520]

7.1 The traditional cyanotype process

This is the time-honoured formulation; it is made up as two separate solutions, which are combined just before coating. The only innovation suggested here is the addition of Tween 20 surfactant, which will be found greatly to improve the quality of the print with many papers. The chemicals are not dangerous and can be safely handled by children under supervision.

Sensitizer chemicals needed

Ammonium iron(III) citrate (green variety)		25 g
Potassium ferricyanide	$K_3[Fe(CN)_6]$	10 g
Tween 20 (non ionic surfactant) 20% v/v solution		1 cc
Distilled water		200 cc

Ammonium iron(III) citrate is also known as ammonium ferric citrate; and is a very variable substance: the 'green' form is preferable to the 'brown', with an iron content between 14% and 18%. However, any variety will work up to a point. For the potassium ferricyanide GPR Grade (General Purpose Reagent: 98–99% purity) is adequate.

7.1.1 Making up the sensitizer solutions

Two stock solutions **A** & **B** are required; their concentrations are not critical so they do not need to be made up with great precision:

Stock solution A:

Dissolve 25 g of the solid ammonium iron(III) citrate in ca. 70 cc of distilled water at room temperature and make up to 100 cc.

Within a week or two in many environments, the surface of this solution will be covered by a growth of mould. This may be inhibited at the outset by adding a few crystals of thymol to the bottle, which float on the surface without dissolving, and should simply be avoided in extracting a sample of the sensitizer. (N.B. Thymol is a harmful chemical.)

Stock solution B:

Dissolve 10 g of the solid potassium ferricyanide in ca. 80 cc of distilled water at room temperature and make up to 100 cc.

These solutions must be kept in brown bottles, in a cupboard or box.

7.1.2 Mixing and coating

Before use, mix equal volumes of **A** and **B** to give a total volume of sensitizer appropriate for the amount of coating to be done. The surfactant Tween 20 is added at this point – see below. The mixed sensitizer only has a relatively short life. It is best to dedicate a separate, labelled syringe or pipette to each solution, and to use a third one for applying the mixture, in order to avoid cross-contamination during the work. As a guide to the volume needed for coating, about 1.5 cc should suffice for a 10x8 inch print, coated by rod; but brush coating may consume possibly twice this.

Although it is not part of the traditional formula, I would strongly recommend adding a few drops (2 to 5) of the 20% solution of Tween 20 wetting agent to each 10 cc of sensitizer, to improve its absorption by the paper fibres; the appropriate amount depends on the porosity of the chosen make of paper and should be arrived at by trial.

7.1.3 Printing exposure

Expose to sunlight or a UV lamp: the image prints out, with the uncovered regions of sensitizer first darkening to blue and then reversing back to a pale blue-grey. The image shadows should be somewhat reversed too, giving it a solarized look, and the highlights should be distinctly green. The exposure is correct when the image appears rather ‘blocked up’. Lamp exposure time may be around 20 to 30 minutes. Proponents of this version of cyanotype suggest that it is almost impossible to overexpose, because so much image substance will be lost in the wet processing!

7.1.4 Wet processing

Immerse the exposed print in gently running water (or several changes of static water), face down, until the yellow sensitizer has entirely disappeared from highlight areas (20 minutes should suffice). There will be considerable leaching-out of blue pigment, so the extended washing necessary to fully clear the paper will significantly ‘reduce’ the image, and truncate the tonal scale in the high values. The ‘reversed’ shadow tones will darken with time and the image colour will slowly intensify during drying over several hours, due to aerial oxidation of Prussian white to Prussian blue. If you wish to see the full density immediately, then immerse the print for about half a minute in dilute (0.3%) hydrogen peroxide (see below) before the final wash. This does not make any difference to the final densities. Hang the print to dry at room temperature, or in a uniform stream of warm air.

7.2 An “improved” cyanotype recipe

A widely-circulated ‘improved’ formula follows. It is claimed that the highlight areas remain whiter. But if you are prepared to go to this degree of trouble to introduce an admixture of oxalate and dichromate, which are poisonous, it would probably be more worthwhile to employ my new method, which uses oxalate entirely. This sensitizer should not be placed in the hands of children.

Sensitizer chemicals needed

Ammonium iron(III) citrate (green variety)		27 g
Potassium ferricyanide	$K_3[Fe(CN)_6]$	9 g
Oxalic acid	$(COOH)_2.2H_2O$	1 g
Ammonium dichromate	$(NH_4)_2Cr_2O_7$	0.2 g
Distilled water		200 cc

GPR Grade (98-99%) is adequate

Preparation of sensitizer

Solution A:

Dissolve 25 g of the solid ammonium iron(III) citrate in ca. 70 cc of distilled water at room temperature; add 0.5 g oxalic acid, stir well to dissolve, and make up with distilled water to a final volume of 100 cc.

Solution B:

Dissolve 9 g of the solid potassium ferricyanide in ca. 80 cc of distilled water, add 0.5 g of oxalic acid and 0.2 g of ammonium dichromate, stir well to dissolve and make up to 100 cc with distilled water.

These solutions must be stored in brown bottles in a dark box.

Mix equal volumes of solutions **A** and **B** just before use.

7.3 Process shortcomings and their remedy

Herschel's standard negative-working cyanotype formula has such an elegant simplicity and economy that it may seem presumptuous to seek to improve on it. In 1906 John Tennant, the editor of *The Photo-Miniature*, could confidently write:

> "...the blue print process reached finality long ago as far as any important improvement is concerned, and there is little that is new to tell about it." [521]

But any contemporary practitioner today, accustomed to siderotype processes such as palladiotype, who tries the traditional cyanotype formulation for pictorial purposes is likely to notice some of the following comparative drawbacks:

1 Ammonium ferric citrate is a notoriously ill-characterised chemical and can vary widely in composition, depending on the supplier. Even after 170 years of chemical manufactury, it continues to cause problems of unpredictability, inconsistency and poor keeping qualities. No two practitioners can be sure that they are using the same chemical.[522]

2 The two ingredients have to be stored as separate stock solutions, because when mixed the resulting sensitizer has an inconveniently brief shelf-life. The solution of ammonium ferric citrate proves to be an excellent nutrient medium for the growth of moulds, which will usually cover the surface within a week or two; a preservative fungicide such as thymol can be added to prevent this.

3 The traditional sensitizer is poorly absorbed by cellulose paper fibres and some tends to remain on the surface; being deliquescent, it may cause a tackiness which can damage negatives if the humidity is high. Much of the image washes off on wet processing.

4 Printing is rather slow compared with other iron-based processes such as the palladiotype; exposures of thirty minutes or more to a typical ultraviolet light source are not unusual for traditional cyanotype, compared with about two minutes for palladiotype.

5 A significant proportion of the image substance, ‘soluble’ potassium Prussian blue, tends to be peptized and wash out during the wet processing, due to poor absorption and retention by the paper fibres. This results in a serious loss of gradation in the high values, truncating the tonal scale, and conferring an artificially high contrast. The only remedy that is offered to counter this drastic weakening of the image is to overexpose it grossly, which adversely affects the quality and the ease of judging exposure. Some workers even recommend double coating with sensitizer.

6 In heavily exposed print areas, the traditional sensitizer tends to produce excess ferrous iron which diffuses into, and stains adjacent highlight areas with Prussian blue. This is the defect already referred to as ‘bleeding’.

7 The traditional process has an exposure scale of only about 0.9 – three ‘stops’ – comparable with that of a Grade 3 or 4 silver-gelatin printing paper, or the gum dichromate process, so it requires only a very short density range in the negative. The process is a very poor match and unsuitable for rendering the long density range negatives needed for other siderotype processes.

All the drawbacks listed above can be overcome, in principle, by replacing ammonium ferric citrate with ammonium ferric oxalate as the photosensitive agent, so employing the ferric salt that was shunned, or overlooked, by Herschel – whichever may have been the case. Ammonium ferric oxalate offers the following remedies for the disadvantageous problems listed above:

1 It is a well-characterised substance, widely available all over the world in an inexpensive, pure crystalline form, which is chemically consistent and highly soluble in water.

2 It does not promote any mould growth on the solution. The mixed sensitizer has a shelf-life of several years.

3 Its solution penetrates the fibres of cellulose paper much more readily than the citrate, and it mordants better onto fabrics. It is non-deliquescent. Image substance is better retained.

4 It is much more light-sensitive than the citrate by a factor of 4 to 8, so exposures are correspondingly shorter, by two or three ‘stops’. This can be important when sun-printing 3-dimensional objects.

5 It yields an ‘ammonium blue’ of very good colour, which is more resistant to peptization and alkalies. There is little loss of image substance, so it renders delicate gradation in high values and a high D_{max} in the shadows. It is readily toned by a variety of reagents.

6 It can be mixed in chemically equivalent amounts with ferricyanide to avoid excess iron(II) and therefore suppress ‘bleeding’.

7 Because there is little or no image loss the exposure scale of the new process is around 2.2 – an excellent match for negatives of long density range, also intended for salt printing, platino-palladiotype, argyrotype or chrysotype. One negative can serve all processes.

However, as the early experimentalists discovered, see §4.4.4, the use of ammonium ferric oxalate introduces one difficulty: if it is mixed with potassium ferricyanide solution at concentrations high enough to provide a good ‘pictorial’ sensitizer,[523] the sparingly soluble salt potassium ferric oxalate tends to crystallize out, rendering the mixture useless as a sensitizer.[524] A ‘gritty’ sensitizer produces pale spots on the print, and crystallization may also occur within the coated paper, giving rise to quite pretty, but totally unwanted fern-like patterns.

It is true that ammonium ferric oxalate was used in all the formulae for the later commercial blueprint papers, as described above in §4.8, but this was only made possible by keeping them sufficiently dilute in potassium ferricyanide, 5% or less, to avoid this crystallization; in consequence they yielded a rather low maximum density, for pictorial purposes.

In theory, there is an obvious answer to this crystallization problem: to use ammonium ferricyanide instead of potassium ferricyanide; but the former is not commercially available, is described as a “rare chemical” and is rather troublesome to make.[525] In 1994, I developed a new, simple procedure for preparing a cyanotype sensitizer that overcomes all the drawbacks besetting the traditional method.

The desired ammonium ferricyanide is prepared *in situ* by the simple expedient of using the low solubility of potassium ferric oxalate to eliminate most of the potassium ions from the solution. This is achieved by mixing very concentrated, hot solutions of ammonium ferric oxalate and potassium ferricyanide. When the mixture cools, the sparingly soluble potassium ferric oxalate crystallises out, is filtered off and rejected, leaving a solution of ammonium ferric oxalate and ammonium ferricyanide, in the necessary proportions for making Prussian blue when the former is photoreduced. The appropriate molar quantities are calculated as follows: what little evidence we have (IR spectra – see Appendix II.7) suggests that the cyanotype product Prussian blue may be closer to the "insoluble" form $Fe_4[Fe(CN)_6]_3$ *i.e.* it contains a 4 : 3 molar ratio of Fe(III) : Fe(II), rather than the 1 : 1 molar ratio of Fe(III) : Fe(II) which assumes that the form of Prussian Blue precipitated is $(NH_4)[FeFe(CN_6)]$. What follows makes that assumption, but the relative proportions are not critical.

Precipitation of most of the potassium ions requires a molar ratio of 1 : 1 for the two components, so in the former case the overall molar ratio of ammonium ferric oxalate to potassium ferricyanide needed for both precipitation and for the photochemistry would be 7 : 3. Taking the relative molecular masses of the two components, this molar ratio corresponds to a weight ratio of:

$7 \times 428.07 : 3 \times 329.26 = 2996.49 : 987.78 = 3.034 : 1$

which comes to a rounded weight ratio of 3 : 1 for the two components, and accounts for the formula used in §7.4 below. The filtrate is then diluted appropriately to provide a stable, pre-mixed sensitizer solution, which contains 0.4 molar ammonium ferric oxalate and 0.3 molar ammonium ferricyanide, and which offers much greater printing speed and a long storage life without mould growth. The coatings are non-deliquescent, unlike those made from ferricitrate, which reduces the likelyhood of damage to negatives during contact printing. The image colour and gradation are finer than the traditional process, and the 'ammonium' Prussian blue has less tendency to peptize, so the print-out image is a good indication of the final print. The only disadvantages of this method are a more complicated method of preparation, (which would not be the case if ammonium ferricyanide could be bought – see above!) a slight toxicity of the sensitizer solution, and a somewhat greater expense for the chemicals.[526] The preparation and procedure are described in detail next.

7.4 The new cyanotype process

Chemicals needed for making and processing 100 cc of sensitizer (sufficient for ~65+ prints 10x8 in.)

Ammonium iron(III) oxalate	$(NH_4)_3[Fe(C_2O_4)_3].3H_2O$	30 g
Potassium ferricyanide	$K_3[Fe(CN)_6]$	10 g
Ammonium dichromate	$(NH_4)_2Cr_2O_7$	0.1 g
Tween 20		0.25 cc
Citric acid (optional)		2 g
Nitric acid, concentrated (~65%) or hydrochloric acid		100 cc
Purified water		100 cc

Apparatus for making 100 cc of sensitizer

Pyrex glass beakers 2 x 100 cc
Measuring cylinder 100 cc
Scales or chemical balance sensitive to 0.1 g
Glass stirring rod
Conical filter funnel *ca.* 8–10 cm diameter
Filter paper Whatman Grade 1 *ca.* 15–20 cm diameter
Brown glass bottle 100 cc
Hotplate (or bath of very hot water)
Thermometer 0–100 °C
Tungsten lighting to work under, not fluorescent or daylight.

Equipment and materials needed for cyanotype printing (see §6.4)

Paper (100% cotton or linen, sized but unbuffered)
Glass coating rod or brush; Glass plate
Spirit level; Drafting tape or clips
Blotting paper strips
Plastic syringes or pipettes, Calibrated 2 cc and 5 cc
Printing frame (hinged-back); UVA light source; Timer
Plastic measuring jug 1–2 litre; Stirrer
Processing Dishes (2); Print tongs or plastic gloves
Drying line and pegs or drying screen

7.4.1 Making up the sensitizer solution

N.B. This sequence of instructions should be carried out under dim lighting (40-60 watt tungsten), not fluorescent or daylight.

1 Weigh 10 g of potassium ferricyanide into a 100 cc pyrex glass beaker.
Add exactly 20 cc of purified water using a measuring cylinder.[527]
Heat to ca. 70 °C (158 °F) and stir until all the solid is dissolved.
Keep the solution hot.
(A thermostatted hotplate is best for heating the solutions, but a basin of very hot water will do.)

2 Weigh 30 g of ammonium iron(III) oxalate into a second (100 cc) pyrex glass beaker.
Add exactly 30 cc of purified water using a measuring cylinder.
Heat to *ca.* 50 °C (122 °F) and stir until the green solid is dissolved.
(Ignore any small residue of colourless crystals.)
Add 0.1 g of ammonium dichromate and let it dissolve.
(Potassium dichromate may be used alternatively. This small amount of dichromate may be omitted, but the contrast and shelf-life of the sensitizer will be diminished.)

3 Add the hot potassium ferricyanide solution (**1**) to the ammonium iron(III) oxalate solution (**2**), stir well, and leave the mixture in a dark place to cool to room temperature (*ca*. 20 °C, 68 °F) and crystallize.
(For this quantity of solution, the cooling and crystallization will take at least two hours, but it may be better left overnight, especially if a larger scale of preparation is used.)

4 Separate the green liquid from the green crystals by decanting and filtration: use a conical filter funnel with a Whatman grade 1 filter paper, running into a 100 cc measuring cylinder.
(The volume of filtrate should be ca. 62 cc. The yield of green crystals should be ca. 15 g. Dispose of these crystals safely by washing away with hot running water.)

5 Make up the filtered solution with purified water to a final volume of 100 cc in the measuring cylinder. Mix well and transfer the sensitizer solution to a well-stoppered, labelled and dated brown bottle.
(The sensitizer solution is toxic if ingested and it will stain skin, etc. Stored in a cool dark place, its shelf-life is six months to a year without dichromate, and several years with dichromate added.)

7.4.2 Use of dichromate

You should recognise that this option does introduce a toxic substance into the working environment (see Notes on Hazards §7.5) but in very small amount. The addition of ammonium dichromate can prevent any impurities in your chemicals from causing a strong blue coloration from developing in the sensitizer over time. However, the presence of this reagent will tend to increase the contrast of the sensitizer significantly. If you cannot weigh out 0.1 g of the solid then make a 20% *w/v* solution of ammonium dichromate by dissolving 4 g of the solid in distilled water at room temperature and making up to a final volume of 20 cc. Mix thoroughly. Add 0.5 cc of this solution to the sensitizer in **2**.

7.4.3 Use of surfactant

The new cyanotype sensitizer solution is much more readily absorbed by paper fibres than the traditional sensitizer using ammonium ferric citrate, so the addition of a wetting agent is usually quite unnecessary. With a few, hard-sized papers such as Buxton, however, the wetting agent can improve the ease of coating and the retention of Prussian blue by the paper fibres. In such cases, I prefer Tween 20 (a non-ionic surfactant) which may be added to the sensitizer solution to produce a final concentration of *ca.* 0.1% to 0.25%. A stock solution of concentration 20% v/v is useful for this: if you find it necessary, add one or two drops (0.05 to 0.1 cc) per 10 cc of sensitizer and mix well just before coating. The appropriate amount will depend upon the paper, so do not add it to the bulk of the stock sensitizer solution. Tween may interact unfavourably with some gelatin-sized papers. The Tween solution is not stable indefinitely and should be replaced if it shows a deposit.

7.4.4 Choice of papers

Use only papers that are ***not*** alkaline-buffered with chalk (calcium carbonate). Alkalies are hostile to cyanotype chemistry. The best results will be obtained on unbuffered papers such as:

- ‘Buxton’ or 'Herschel' Handmade by Ruscombe Mill
- Weston Diploma Parchment
- Crane’s Platinotype
- Atlantis Silversafe Photostore
- Wyndstone Vellum

If buffered papers are unavoidable, such as Arches Platine, Fabriano Artistico, or Whatman Watercolour, they should be pre-treated in a bath of dilute (5% v/v) hydrochloric acid, or 5% – 10% w/v sulphamic acid, to destroy the chalk, then washed.

For prints up to 10 x 8 in. or A4 in size, a paper weight of 160 gsm (grams per square meter, g/m^2) is adequate. For larger prints of A3 size, a heavier weight of 240 gsm, or more, will minimise cockling and bellying of the coated sheet due to the stresses set up by the hydroexpansion of the cellulose fibres in the wetted area. The sheet will contact the negative better, and be more robust in wet handling.

7.4.5 Drying

Let the sensitized paper dry at room temperature in the dark for about an hour. Shorter drying times are possible, but very humid paper may damage precious silver-gelatin negatives, and not lie flat due to fibre swelling.

Alternatively, allow a 5-10 minutes for the sensitizer to soak in, until the paper surface loses its reflective sheen, then heat-dry it with an air stream at about 40 °C for *ca.* 5 minutes. The dryness of a cyanotype paper does not appear to influence image colour or contrast – the only difference may be that rapid drying can reduce any chemical fogging due to impurity in the paper; but note that over-rapid drying may worsen the loss of image substance during the wet-processing procedure.

The storage life of coated paper depends on the purity of the paper base, as mentioned above, so use the sensitized paper within a few hours of coating, if possible. It will keep longer in a cool, dark desiccated enclosure. The coated side should remain light yellow: if it turns green or blue the highlights are chemically fogged, so either reject it and find a better paper, or try adding citric acid as described below, for your next coatings. The new cyanotype sensitizer provides a sensitive test of paper quality, especially if the coated paper is left for some hours in the dark at normal relative humidity: any change of the yellow coating towards a green or – worse – blue colour signals the presence of impurities or additives in the paper that are hostile to this process (and possibly to other processes as well).

7.4.6 Addition of citric acid to prevent fogging

Chemical fogging (“greening”) of the coating due to paper impurities may often be prevented by adding citric acid to the sensitizer, before coating, to a final concentration of *ca.* 2%. Add one drop (0.05 cc) of a 40% w/v solution of citric acid per cc of sensitizer. Do not add citric acid to the stock of sensitizer, because it will shorten the shelf-life.

7.4.7 Negatives and exposure

Expose the sensitized paper within a few hours of coating, if possible. Negatives should have a long density range (in the UV): at least 1.8 and as much as 2.4, to produce a full tonal range in the print - as for my other siderotype processes.

Whether your light source is the sun or a UVA lamp, exposure will be much shorter than that needed for the traditional cyanotype recipes - this new sensitizer requires about two to five minutes exposure under a typical light source. With an 800 W HID UV lamp and digital negatives my exposure time is *ca*. 60 seconds.

Since this is substantially a print-out process, a traditional hinged-back contact printing frame will enable inspection of the desired result: the exposure is continued until the high values appear green, the mid-tones are blue, and the shadow tones are substantially reversed to a pale grey-blue, giving the image a solarized appearance.

7.4.8 Wet processing and contrast control

A consistent outcome, with a deep maximum density and a well-shaped characteristic curve, having a very long printing exposure range of about 2-2.4 density units (eight ‘stops’) is obtained by using a dilute mineral acid for the first development bath, see Figs. 7.1 and 7.2.[528]

The print should be processed initially by immersion in a bath of dilute nitric acid (*ca.* 0.25% - 1% v/v) for 5-10 minutes. For safety in handling, it is suggested that a stock solution of 10% v/v nitric acid is made up, by diluting the concentrated (~65% w/v) acid 10-fold (*i.e.* 100 cc of acid added to water and made up to 1 litre). Take care to avoid the corrosive fumes! This intermediate solution is then diluted a further 10-40 times before use. The final 100-400x diluted bath is not dangerous.

By varying the acidity of this processing bath, considerable control of the contrast may be achieved at the development stage. Figure 3 shows the characteristic (D/logH) curves for a new cyanotype sensitizer (without added dichromate) developed in water and in 1% nitric acid; the result using 1% hydrochloric acid is identical. These development baths tend to accumulate Prussian blue, which will eventually begin to stain the paper, so they should be replaced after a few prints have passed through them; typically, 1 litre will process five to ten 10 x 8 inch prints. If there are safety objections to using nitric acid, then 0.25% - 1% v/v hydrochloric acid may be used. If there are safety objections to this, then 5% - 10% w/v sulphamic acid could be used, or as a last resort, 1% - 5% w/v citric acid. Acetic acid is not recommended because it tends to form insoluble coloured basic ferric acetate.

The softest gradation will be obtained, but a somewhat reduced maximum density, if the exposed paper is simply processed with gently running tap water for at least twenty minutes; alternatively, several static baths of water may be used. To avoid undue loss of image substance, the water should not be significantly alkaline, preferably having a pH below 7, and a spoonful of citric acid may be added to ensure this. However, this method of processing can still result in some loss of image, depending on the paper and sizing combination used, and the shape of the characteristic curve that it yields is rather unusual and may not suit all negatives – see Fig 7.1.

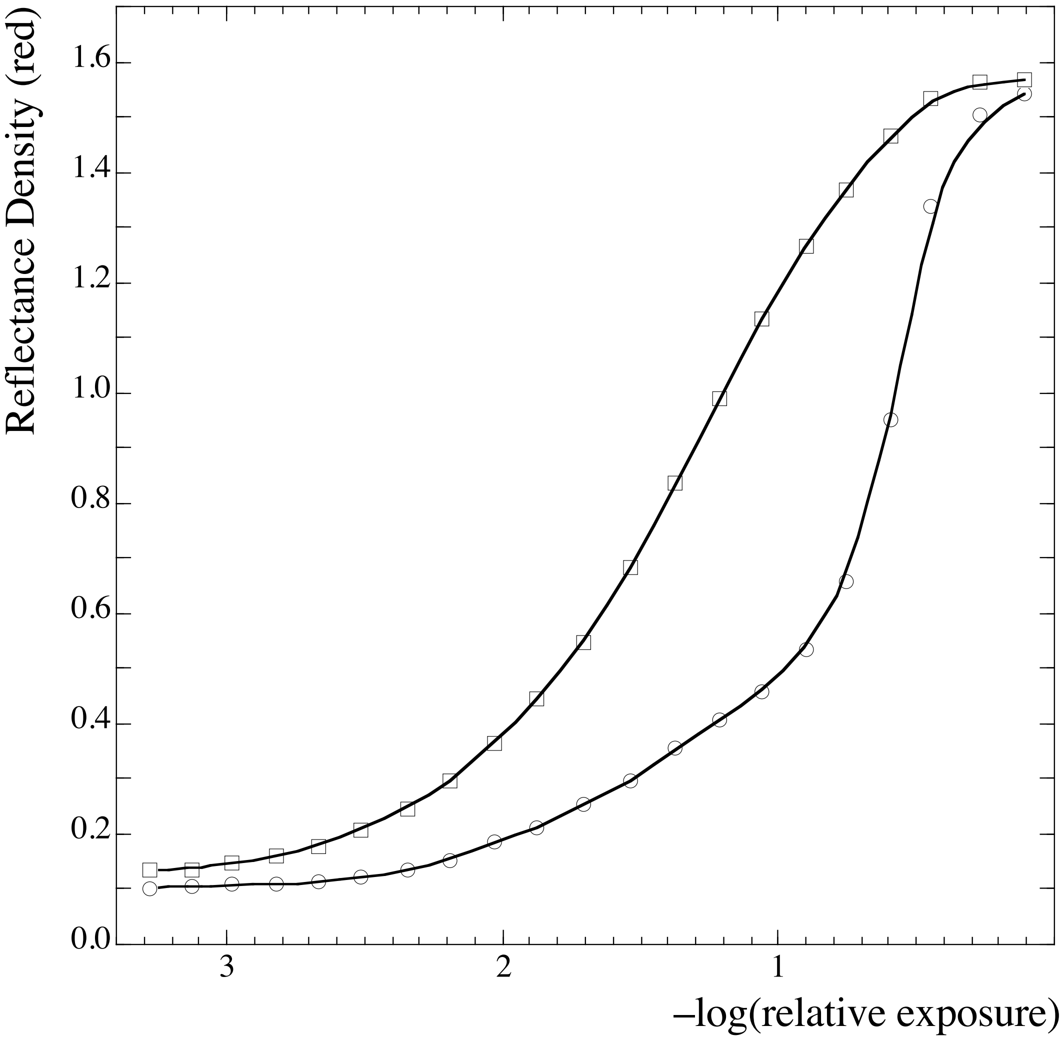


Fig. 7.1 Characteristic curve for New Cyanotype without dichromate. Acid developed (left) and water developed (right)

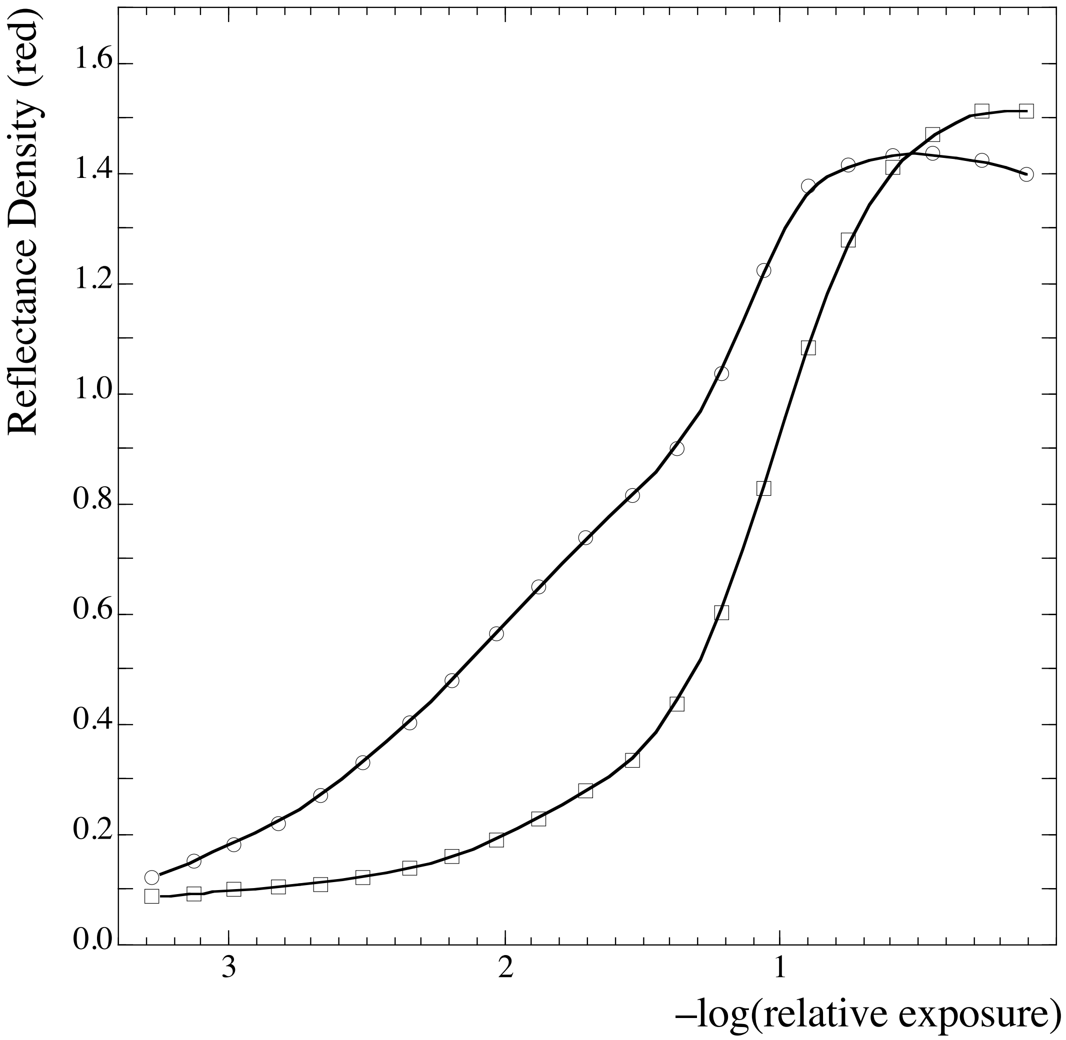


Fig. 7.2 Characteristic curve for New Cyanotype with 0.1% dichromate Acid developed (right) and water developed (left) 4x exposure

7.4.9 Print washing and finishing

Finally wash the print gently in running water for at least 20 minutes. Alkaline water (pH >7) must not be used, nor hard water, containing calcium salts, which will damage the Prussian blue image. The criterion for completed processing is the total removal of the yellow stain of sensitizer from unexposed areas – the print should be held up to a bluish light, or viewed through a blue optical filter, to check that no yellow stains remain in the interior of the paper; if any stain persists, further washing is required. Unlike prints made by the traditional recipe, there should be very little loss of image substance during this washing.

The reversed shadow tones usually begin to regain their values quite rapidly during the wet processing (nitric acid particularly assists this), and they will fully recover during drying for about 24 hours in the air. However, if you are anxious to see the final result immediately, then immerse the print in a bath of 0.3% hydrogen peroxide for no more than half a minute before transferring to the final wash. This solution of hydrogen peroxide is made up freshly by diluting 50 cc of the commonly available 6% solution of hydrogen peroxide (the so-called ‘20 volume’ solution) to 1 litre of water. This treatment, although apparently spectacular, makes no ultimate difference to the print densities in the final outcome.

7.4.10 Summary of the New Cyanotype Procedure

1. **Unbuffered paper:** choose side, mark up coating area
2. **Prepare sensitizer:** add citric acid (to 2%) and/or Tween (to 0.25%), if needed
3. **Coat:** *ca.* 1.5 cc per 10x8 in. area: 5 – 7 ‘passes’ of coating rod
4. **Dry:** 1 – 2 hours at room temperature, or hot air for 10 minutes
5. **Negative**: density range ~2 – 2.4 in the UVA
6. **Expose: UVA** source till highlights green and shadows ‘reversed’
7. **Develop:** 0.25–1% v/v nitric acid according to contrast desired; (concentrated nitric acid diluted 400x – 100x) for 5–10 minutes
8. **Wash:** in non-alkaline water for 20 – 30 minutes
9. **Drain** for 10 minutes and **Dry** flat

7.5 Material hazards and safety considerations

The following information has been condensed from the Materials Safety Data Sheets for the substances involved in making cyanotype sensitizers.[529] The quoted Hazard Ratings are on a scale running from 0 to 4, in which 0 = no hazard, and 4 = extreme hazard.

When handling any chemical, it should be standard practice always to wear the minimum laboratory protective equipment of safety glasses and a lab coat. Additional precautions will be indicated where necessary.

During the use of any chemical, avoid contact between it and your eyes, skin, and clothing. Wash your hands thoroughly after handling chemicals.

When a chemical is not in use, keep it in a tightly closed, properly labelled container, in a place inaccessible to children.

Ammonium dichromate.

	Hazard Rating	
Health	4	extreme (cancer causing)
Flammability	1	slight (involatile, but solid is combustible)
Reactivity	3	severe (oxidizer)
Contact	3	severe (corrosive)

Laboratory protective equipment: Goggles; lab coat; vent hood; proper gloves

Harmful if inhaled

May cause burns or external ulcers

Caution: contains chromium(VI), cancer hazard

Strong oxidizer – contact with other material may cause fire

Use in closed reaction vessels requires stringent precautions because of explosion hazard.

Keep from contact with clothing and other combustible materials. Do not get in eyes, on skin, on clothing. Wash thoroughly after handling. Flush spill area with water.

Unfortunately, this substance has a hazard rating of 4 on the health scale, because it is a known human carcinogen: external contact can cause ulcers and dermatitis. In spite of this hazard, ammonium dichromate (or the corresponding potassium salt) has long been used on a large commercial scale in the printing industry, occasionally giving rise to documented cases of occupational illness. It is also employed in large amounts for the Gum Bichromate and Carbon printing processes. The very small quantity used in the sensitizers described above does not represent a serious risk if the chemical is handled sensibly and proper precautions taken, but if the hazard is still considered unacceptable, its use may be avoided altogether as indicated above in the preparative section.

You are strongly advised against the use of a dichromate bath to 'fix' cyanotypes, which was once common practice, especially for prints on fabrics. The dire consequences of an uncontrolled use of dichromate in this way are described in some detail in the medical literature.[530]

Ammonium iron(III) citrate.

	Hazard Rating
Health	1 slight
Flammability	0 none
Reactivity	1 slight
Contact	0 none

This substance presents very low risk; it has even been prescribed as an iron tonic and is present in small amounts in a well-known soft drink![531] Unprescribed consumption is not recommended, however, because excess iron in the body can cause medical problems (siderosis).

Ammonium iron(III) oxalate.

	Hazard Rating
Health	3
Flammability	1
Reactivity	2
Contact	3

Like all soluble oxalates (see oxalic acid, below), it should be regarded as highly toxic, i.e. capable of causing death or permanent injury (especially kidney damage) if taken by mouth. However, several grams would have to be ingested to cause such extreme damage. The chemical takes the form of non-volatile crystals, so there is little risk of inhalation, but it is an irritant to skin, eyes and mucous membranes.

Nitric acid, concentrated (69% w/v HNO_3)

	Hazard Rating
Health	3
Flammability	0
Reactivity	2
Contact	3

Hydrochloric acid, concentrated (35% w/v HCl)

	Hazard Rating
Health	3
Flammability	0
Reactivity	2
Contact	3

Causes severe burns; may be fatal if swallowed or inhaled.

Do not get in eyes, on skin, on clothing.

Keep in tightly closed container. Loosen closure cautiously. Use with adequate ventilation. Wash thoroughly after handling. In case of spill, neutralize with soda ash or lime and place in dry container.

Causes damage to respiratory system (lungs): inhalation of vapours may cause pulmonary edema, circulatory system collapse, coughing and difficult breathing.

Emergency and first aid procedures: call a physician. If swallowed, do not induce vomiting; if conscious, give water, milk, or milk of magnesia. If inhaled, remove to fresh air. If not breathing, give artificial respiration. In case of contact, immediately flush eyes or skin with plenty of water for at least 15 minutes while removing contaminated clothing.

Oxalic acid.

	Hazard Rating
Health	2 moderate
Flammability	1 slight
Reactivity	1 slight
Contact	3 severe (corrosive)

Laboratory protective equipment: goggles; lab coat; vent hood; proper gloves.

Harmful if swallowed or inhaled. Avoid breathing dust.

Ingestion may cause severe burns to mouth, throat, and stomach and may cause headache, nausea, vomiting, gastrointestinal irritation, unconsciousness, convulsions. May have adverse effect on kidney function and may be fatal.

Do not get in eyes, on skin, on clothing: contact may cause severe irritation or burns.

Emergency and first aid procedures: call a physician. If swallowed, do not induce vomiting; if conscious, give water, milk, or milk of magnesia. If inhaled, remove to fresh air. Rinse mouth or gargle repeatedly with cold water. In case of contact, immediately flush eyes or skin with plenty of water for at least 15 minutes.

Potassium ferricyanide.

	Hazard Rating
Health	1 slight
Flammability	0 none
Reactivity	1 slight
Contact	1 slight

This substance is classified as a low toxic hazard. It is, however, incompatible with concentrated acids, which may release deadly hydrogen cyanide gas. Used correctly there is no risk.

Tween 20 (polyoxyethylenesorbitan monolaurate).

	Hazard Rating
Health	1 slight
Flammability	1 slight
Reactivity	0 none
Contact	0 none

This is a viscous, odourless liquid, soapy and innocuous, which presents no serious risks, provided contact with the eyes is avoided.

7.6 Suppliers of chemicals and equipment

Ready-made sensitizers, chemicals and equipment for the cyanotype processes, and in some cases complete kits, can be obtained from the following suppliers:

Fotospeed
Jay House Ltd
Fiveways House
Westwells Road
Rudloe
Corsham
Wilts
SN13 9RG
UK
Tel: +44 (0)1225 810 596
Fax: +44 (0)1225 811 801

Silverprint Ltd
12 Valentine Place
London
SE1 8QH
UK
Tel: +44 (0)171 620 0844
Fax: +44 (0)171 620 0129
WWW: http://www.silverprint..co.uk/

Phototec
Peter Loffler GmbH
Gewerbehof 1
26209 Hatten
Germany
Tel: +49 04481 1534
Fax: +49 04481 1895

Artcraft Chemicals Inc
PO Box 583
Schenectady
NY 12301
USA
Tel: +1 800 682 1730
WWW: http://www.nfinity.com/~mdmuir/artcraftB.html

Bostick & Sullivan Inc
PO Box 16639
Santa Fe
NM 87506
USA
Tel: +1 505 474 0890
Fax: +1 505474 2857
WWW: http://www.bostick-sullivan.com/

Photographers Formulary Inc
PO Box 950
Condon
MT 59826
USA

Tel: +1 800 922 5255
Fax: +1 406 754 2896

Fine-art papers may be obtained in the UK from:

John Purcell Paper
15 Rumsey Road
London
SW9 0TR
UK
Tel: +44 (0)171 737 5199
Fax: +44 (0)171 737 6765

8 Methods for Toning Cyanotypes

"To gild refinéd gold, to paint the lily,
To throw a perfume on the violet,
To smooth the ice, or add another hue
Unto the rainbow, or with taper light
To seek the beauteous eye of heaven to garnish,
Is wasteful and ridiculous excess."
William Shakespeare
King John, Act 4, Scene 2

Many procedures can easily be devised to change the composition of a Prussian blue image in order to modify its colour, but most of these prove to be 'more curious than valuable' and have little reproducibility and even less permanence. Handbooks on cyanotype often quote recipes for a variety of toning methods,[532] but their descriptions are usually accompanied by the author's reservations as to the worth of such a procedure, and sometimes even by a plea not to 'torture' the humble cyanotype in this way! The process historian, W. Russell Young III says:

> "My best advice for toning cyanotypes is this: If you want a color other than the Prussian blue natural to the cyanotype process, use some other printing method!" [533]

However, it is becoming increasingly evident that many present-day practitioners, who are attracted by the ease and low cost of cyanotype, are still dissatisfied by its natural colour, and so prefer to adopt toning procedures to convert their images to brown or black.[534]

There is little evidence how long toned cyanotypes can be expected to last: the identification of historical toned cyanotypes in photograph collections presents considerable curatorial difficulty, if visual inspection is the only non-destructive method that is permissable. In a survey of several major collections conducted by photograph conservator Megan Gent in 1992, no curator could report having definitely identified a toned cyanotype. However, Gent has discovered some prints in informal family snapshot albums in the Royal Archives at Windsor dating from 1906 that are probably toned cyanotypes: these are single layer prints of a purplish-brown colour indicative of toning with tannic acid, and they share the same album pages with conventional blue cyanotypes.[535]

The toning processes which are acknowledged to be the most reliable, and least impermanent, appear to fall into five categories, of which most have a commonality in commencing with the hydrolysis of the Prussian blue before further treatment.

8.1 Hydrolysis of Prussian blue

The print is hydrolysed with dilute (1% to 5%) alkali, which may be aqueous ammonia, sodium carbonate, sodium or potassium hydroxide or borax. The Prussian blue lattice is broken up by hydroxide ion, and the ferric iron is converted into insoluble pale yellow-brown ferric hydroxide, while the soluble ferrocyanide ion is eventually washed away in the solution. Prompt treatment with acid can partially restore this breakdown, but it soon becomes irreversible.

Trisodium phosphate (sometimes called TSP) is also very alkaline and will bring about hydrolysis, but the product is insoluble ferric phosphate, a golden yellow pigment, fairly stable in its own right. This method of toning is quite popular for fabrics.[536]

Exposure to ammonia vapour does not fully hydrolyse the Prussian blue but imparts to it a striking violet colour; this toning is reversible within a few hours simply by re-exposing the print to air, when the occluded ammonia is presumably lost, and the pigment reverts to its original blue colour.[537]

8.2 Ferro-gallate and tannate

The image is converted to ferric hydroxide as above, and this is reacted with gallic or tannic acid to form ferric gallate or ferric tannate ‘ink’.[538] As was described in §4.4.2, John Mercer can be credited as the originator of this toning process. The print is hydrolysed as in §8.1 and then treated in a bath of gallic or tannic acid (3% to 5%), with some precautions to minimise staining:

1 If the print is dry, presoak it in water for 1 minute.

2 Immerse the print in 1% v/v ammonia (ammonium hydroxide) for *ca.* 5 minutes until the Prussian blue image is bleached to pale yellow (ferric hydroxide). Caustic soda or caustic potash (sodium or potassium hydroxide) 1% w/v, or domestic washing soda (sodium carbonate) *ca.* 5% w/v, can be used instead of ammonia.
Curtailing the time in this bath can yield interesting split-tone effects.

3 Rinse in water for half a minute.

4 Immerse in 1% v/v acetic acid for one minute to neutralise any residual alkali.

5 Rinse in water for half a minute.

6 Tone in 1% tannic acid solution for 5 to 10 minutes.

7 Wash in water for 20 minutes.

This treatment generally intensifies the image, and imparts a rich purplish-brown colour. Staining of the paper base is a problem, however, and the colour is very sensitive to alkali. The best purplish-brown colours are said to result when the print is immersed first in gallic or tannic acid for a few minutes, rinsed, then treated with alkali, and finally, as an option, it may be returned briefly to the gallic acid bath.[539]

8.3 Assorted beverages

In recent years it has become fashionable to tone cyanotypes with "natural products" containing tannins and similar substances which react chromogenically with iron salts. Teas, black and green, and black coffee of several varieties have been used both with, and without preliminary bleaching and hydrolysis, to yield brown and black images.[540] A common by-product of this kind of toning is a stained paper-base - which some apparently find attractive. The working texts should be consulted for further details and examples.[541] It has not yet been established what the life-expectancy of such images may be, but the author admits that some of the procedures are "unreliable and capricious".

8.4 Iron-mordanted dyes

The Prussian blue is converted to ferric hydroxide as in §8.1, which then acts as a mordant for organic dyestuffs. This procedure was also invented by Mercer in his quest for generating 'chromatic photographs', and is particularly well-suited to toning images on textiles. The Prussian blue image is usually hydrolysed with lime or other dilute alkali as above, then washed and treated in a suitable dye bath, and the resulting ferric hydroxide then served as a mordant for a vegetable dye such as gall-liquor, logwood, quercitron bark, murexide, cochineal, or madder. When using madder dye, he found that if the Prussian blue was left intact and unhydrolysed, a very rich purple colour was produced.[542]

Out of a whole range of chemically-inventive processes,[543] perhaps Mercer's most remarkably circumambulant achievement was to make a cyanotype as described above, then to convert the image into silver ferrocyanide by treatment with silver nitrate, after which it was reduced to silver metal by sodium stannite, and finally substantially converted by a chloroaurate bath into gold in the form of Purple of Cassius. Examples of portraits made by this process on cloth, may be seen in fine condition, in the Mercer Archive at Lancashire County Record Office.[544] The Museum of Science and Industry in Manchester also has a photographic portrait of Mercer, from a negative taken ca. 1856 by John Benjamin Dancer, the famous instrument maker and photomicrographer; it is printed on cotton, probably by Mercer himself, and has a deep violet colour, which suggests it may be a madder-toned cyanotype.[545]

Forty years later, in 1898, Mercer's toning process was re-invented – apparently unwittingly – by Stewart Carter, and reported to the New York Section of the Society of Chemical Industry.[546] Cyanotypes, made in the usual way were treated first with dilute caustic soda, then, after washing, with sodium phosphate (a less toxic alternative to Mercer's arsenate), at which point it was ready to receive the hot 70-80 °C aqueous 3-5% dye bath, which could be selected from resorcin green, gallocyanine, alizarin, or logwood.

8.5 Black toners

The conversion of a cyanotype into a black silver image would seem to be a singularly pointless exercise when the same end can be achieved directly; however, it has been done.[547] The soaring expense of silver photography during the 20th century motivated the quest for other, cheaper ways to obtain a black image by toning the blueprint. An early process, due to Planchon, converted the image into copper(II) sulphide,[548] but there are better methods, as will be described.

The reaction products of bleaching the Prussian blue in a sulphite bath, can be used to catalyse the oxidative reaction of hydrogen peroxide with certain polyphenols, such as catechol, resorcinol and quinol, to form dark-coloured, near-black dyestuffs. This method was developed in the 1970s by Reginald Heron,[549] with the well-intentioned aim of transforming the strident blue image of the inexpensive cyanotype into a more photographically-acceptable black, thus providing a very economic non-silver medium of practice, especially for students who did not have access to a photographic darkroom. Heron's developing bath is a complex mixture, with a composition finely-balanced according to the characteristics of the original blueprint material that was commercially available at the time. The process is said to produce a 'fair imitation of a platinum print'. Thanks to its chromogenic nature, the colour can be modified, but the resulting dyes, like all those of chromogenic photography, are not totally stable. According to Heron: 'samples have survived the 25 years to the present day, but the original (reasonably attractive) black has faded to a passable (and inevitable) brown.'[550]

8.6 Heavy metal incorporation

The Prussian blue image is treated with a solution of a heavy metal salt: this may cause incorporation of the metal cation in the Prussian blue lattice which can modify its colour. Not all metal cations give a perceptible effect: it is conjectured that the metal needs to have two accessible oxidation states to intervene in the electronic transition giving rise to the colour. Lead (+2,+4), thallium (+1,+3), nickel (+2,+3) and copper (+1,+2) all have a perceptible effect, whereas alkali metals (+1) and alkaline earth (+2) cations do not.

8.6.1 Lead

If a cyanotype is treated in a bath of 5% lead(II) acetate solution, the colour is shifted towards a more violet blue within 1-2 minutes, which is due to the incorporation of lead(II) ions into the voids of the microporous Prussian blue structure.[551] The colour is permanent and stabilises the Prussian blue against light fading. The effectiveness of this toning procedure seems to depend on the cyanotype formula; it works well with the new cyanotype recipes. It is particlarly important that the lead acetate solution should not be acidic; adjustment of its pH to ca. 7.5 to 8 by addition of ammonia is recommended. Use a pH paper to check. (A slight precipitate doesn't matter, it can always be filtered off.) The lead toning can apparently be reversed by treatment in a bath of dilute nitric acid. Lead(II) acetate is a heavy metal salt which is seriously toxic by ingestion and should be handled carefully and stored safely; it is said to taste sweet, but experimental confirmation of this is definitely not recommended. It is also said – disputedly – to be one of the causes of the downfall of the Roman Empire! [552]

8.6.2 Thallium

In the same way that thallium(I) ions are incorporated when Prussian blue is used as a poison antidote (see §3.3), it could be used as a toner of cyanotype. A bath in thallium(I) sulphate solution of ca. 5% does itself cause a slight but agreeable colour shift in a cyanotype to a 'cornflower blue', but it cannot be recommended as a toning practice for the general public owing to the severe toxic hazard presented by this heavy metal (see §3.3).

8.6.3 Nickel

This method follows from the experiments reported by Holtzmann in §9.2.[553] Immerse the cyanotype in a 5-10% solution of a nickel(II) salt (e.g. the sulphate, chloride or nitrate) for an hour or so. The colour shift with nickel(II) salts is rather slight - towards a more greenish-blue. This treatment has the beneficial effect of making the cyanotype much more resistant to alkaline hydrolysis, but it may cause a slight loss of highlight density. Nickel(II) salts are listed carcinogens. Consult the MSDS.

8.6.4 Copper

This method of converting the image to a purplish-brown derives from a U.S. patent of 1889.[554] The stock reagent is a deep blue solution of tetraamminocopper(II) nitrate, made by dissolving 1 part of copper nitrate in 4 parts of water and treating the solution with one part of 30% (S.G. 0.90) aqueous ammonia solution sufficient just to re-dissolve the precipitate of copper hydroxide. The toning bath is made by diluting this blue stock solution sixteen times with water and adding up to one further part of 30% ammonia, depending on the colour desired, which is believed to contain some red copper(II) ferrocyanide.

8.7 Blue toning of silver prints

Finally, this is an appropriate point to mention those toning procedures for silver-gelatin materials which transform the silver image, wholly or partially, into Prussian blue, thereby generating a print with the cyanotype colour, but differing in that the image is not in the paper fibres, but is embedded in a gelatin binder layer which confers a more lustrous and reflective appearance to the surface. The chemical transformation of the silver image into ferric ferrocyanide is accomplished by first oxidising the silver to silver ferrocyanide using a bath of alkaline potassium ferricyanide, then treating it in an acidic bath of ferrous sulphate.[555] It is also possible to use a single direct toning bath of acidified ferricyanide and ferricitrate combined, which results in some degree of intensification, but the image is said to be less permanent.[556] The same effect can, of course, be achieved simply by adding gelatin to a standard cyanotype sensitizer.[557]

9 Vulnerability & Conservation of Cyanotypes

> *"But of course these tints must be used with judgement, and no one but a vandal would print a landscape in red, or in cyanotype."*
> Peter Henry Emerson
> *Naturalistic Photography for Students of the Art* (1889)

The chemical properties of Prussian blue described in Chapter 3, and at more depth in Appendices II and III, identify three distinct directions in which cyanotypes are vulnerable to attack. The weaknesses that need to be addressed by conservation science are: photochemical reduction, alkaline hydrolysis, and aqueous peptization. These pathways of destruction may more conveniently be referred to as 'fading', 'bleaching', and 'dispersing', respectively. Each of these damaging reactions leads to a loss of Prussian blue from the image, but each is chemically distinct in its causes, products, and remedies. In the first, the cause is light, the product is Prussian white, and the reaction is substantially reversible. In the second, the cause is alkali, the product is yellow hydrated ferric oxide (colloidal, becoming insoluble) and ferrocyanide ions (which are soluble), and it is not usually reversible. In the third, the Prussian blue is not changed chemically but dispersed as nanoparticles which are washed away by water – a loss which is quite irreversible. These pathways of vulnerability are summarised in Table 9.1 and will now be considered individually in more detail.

	Fading	**Bleaching**	**Dispersing**
Description	Photochemical reduction	Alkaline hydrolysis	Aqueous peptization
Cause	Visible and UV light and a reductant	Any substance of alkaline pH (pH >7)	Water and high ionic strength solutions
Product	Prussian white (ferrous ferrocyanide)	Hydrated ferric oxide and ferrocyanide	Colloidal sol of Prussian blue in water
Reversibility	Fully reversible by air in the dark over a few days	As ferric oxide ages it becomes irreversible	Pigment is washed out from image irreversibly

Table 9.1 Pathways of destruction for cyanotypes

9.1 Fading of cyanotypes by light

Notwithstanding the extravagant claims made for its stability by the discoverer of Prussian blue, its discolouration to a greenish hue under the action of sunlight was noted in a handbook of painting as early as 1757, quite soon after its adoption as a paint pigment. The historical evidence in the mid-eighteenth century for the awareness of this deterioration has been compiled into an interesting review by Jo Kirby of the Scientific Department of the National Gallery.[558] It is likely that impurities in the early preparations of Prussian blue may have been responsible for the variability observed in its behaviour. Even the reversal, in the dark, of the decolourization was noted in 1834. The light-fading of pigments is naturally a central issue for conservation scientists concerned with paintings, and the fading of Prussian blue in oil paintings, especially when in admixture with large quantities of an extender such as lead white,[559] has received close attention at the National Gallery.[560]

From the mercantile viewpoint, when used as a textile dyestuff the pigment also revealed its susceptibility to light at an early stage. In 1801, Desmortiers described his researches into the fading of fabrics dyed with Prussian blue in his *Recherches sur la décoloration spontanée du bleu de Prusse*,[561] in which he emphasised the importance of allowing access to the air in order to reverse the fading and restore the blue colour. Subsequently, around 1840, Michel Chevreul found that Prussian blue in an air-tight chamber became paler and liberated cyanogen in the direct rays of the sun, but in the dark it absorbed oxygen and recovered its colour.[562] These phenomena must have been widely known at the time because they were also reported in the standard English chemistry texts,[563] one of which observed that ‘the recovery of the colour is owing to the formation of the so-called basic Prussian blue’.[564] The chemistry of this reaction is considered in Appendix III.

Cyanotypes and commercial blueprints also acquired a reputation early on for fading partially in the light; and, although some contrary opinions were expressed, it is now generally accepted that they are susceptible, but the degree of fading has not been fully quantified.[565,566] A number of photograph conservators have cited evidence for the fading of cyanotypes. In 1989, Ian and Angela Moor described densitometric measurements on cyanotypes exposed to daylight, employing ‘facsimile material produced using Herschel’s original formulation’. They found a ‘loss of density ranging from 4% after 15 minutes exposure to 10% after

45 minutes exposure', but they do not report data on the absolute density changes. They attributed the fading to 'the presence of residual soluble ferric salts, not removed during the washing procedure.'[567] They found that the regain of the density on dark storage was not fully reversible, only 7% of the original 10% loss being recovered.

An extensive programme of densitometric monitoring of a variety of original historic photographs has been carried out by John McElhone, photograph conservator at the National Gallery of Canada, Ottawa. Specimens were displayed under stringent museum conditions, and periodically densitometered in order to determine how 'safe' these conditions are for the exhibition of the various types of image; this work and its curatorial implications have been described elsewhere.[568] McElhone's recent unpublished studies have included original cyanotypes by Atkins (1854) and Curtis (1868). Highlight, mid-tone and shadow densities were measured with a reflectance densitometer for the three primary colours at intervals during time periods extending from two to four years of display in glazed mounts.[569] Illumination was by 50-60 lux incandescent tungsten, filtered to remove the UV. Within the instrumental precision and reproducibility of the measurements, no significant effects (i.e. with permanent density changes $\Delta D \geq \pm 0.02$) were observed during total accumulated exposures that amounted to about 100 kilolux hours. This important finding should offer some reassurance to curators and conservators that historic cyanotypes can be safely displayed under proper conditions. However, these tests, having caused no harm to the objects, do not establish the threshold at which damage does begin to appear, and that is the purpose of the present work with facsimile material.

9.1.1 Experimental: preparation of specimens

In the present work, five different cyanotype formulations were tested, to represent the main categories of sensitizer used for the negative-working process (see Chapter 4). For brevity and ease of reference these formulae will be allocated the names of ***Smee***, for Herschel's 'proto-cyanotype' using potassium ferricyanide alone (§4.1.1); ***Herschel***, for his own modified recipe (§4.1.2); ***Lietze***, for the usual 19th century recipe using brown ammonium ferric citrate (§2.12); ***Valenta***, for the usual 19th century recipe using green ammonium ferric citrate; and ***Ware***, for the new cyanotype using ammonium ferric oxalate (see Table 9.2).

Process Name	Description	Ammonium ferric citrate	Potassium ferricyanide
Smee	Herschel’s ‘proto-cyanotype’	none	16%
Herschel	Herschel’s ‘standard’ recipe	6% (brown)	12%
Lietze	Typical C19th recipe	14% (brown)	12%
Valenta	Typical C20th recipe	14% (green)	12%
Ware	New cyanotype as described in Chapter 7	16% ammonium ferrioxalate	10%

Table 9.2 Varieties of cyanotype – final concentrations in sensitizer

The paper generally used for coating in the comparative tests was Atlantis Silversafe Photostore, of weight 120 grams/square meter. This is a pure cotton conservation paper, of high purity, sized with Aquapel™ which is a neutral-curing alkyl ketene dimer. It contains no added buffer, filler, or other agent that might interfere with the photochemisty.[570] Such a pure paper differs rather from the papers of the 19th century, so comparative tests were also performed on gelatin-sized papers, both contemporary (Fabriano 5 HP) and of the type used 150 years ago (Whatman’s Turkey Mill 1840 and J. Whatman 1849, made by Hollingworth and Balston, respectively).[571] Coating was carried out by a glass rod, and the volumes of sensitizer used were closely controlled to give comparable coatings. The sensitized paper specimens were all dried at room temperature in the dark.

The samples to be tested were made by conventional cyanotype printing and direct sunlight, using a glazed printing-out frame with a hinged-back, mimicking as accurately as possible the manner of exposure that would have been employed in the 19th century. Only the ***Ware*** formulation was printed by means of an artificial ultraviolet light source, which is now universally used, employing four Phillips TLADK30/05 coated fluorescent tubes (having a maximum emission at 360 nm) at a distance of 8 cm. The test prints were made through a calibrated Kodak No.3 step tablet, which produced a maximum of 21 steps of density in half stop intervals of exposure, which were large enough to be accurately densitometered. Exposures were usually sufficient to make the first two steps indistinguishable, so ensuring that the maximum density of which the sensitizer was capable had been reached. A direct comparison was made for the ***Herschel*** formula to see if the sunprinting employed in the nineteenth century produced any qualitative differences from the artificial UV source. The heating effect of the sun exposures was notable, and it was found that prolonged exposures to the sun resulted in a purple veiling of the highlights which, however, usually disappeared in the wet processing. Processing was appropriate to the sensitizer in use, usually by means only of gently running tapwater, and the specimens were dried in the dark.

Smaller control specimens were printed through Stouffer Graphic Arts T2115 step tablets[572] at the same time as the main K3 test piece, and were retained in a light-proof box, that had access to the atmosphere of the same environment through a set of baffles. These could be checked for any long term changes not due to illumination and were also useful for sacrificial experiments.

9.1.2 Experimental: fading apparatus and measurements

The light source used to induce fading was a commercial luminaire fitting, equipped with four 20 watt standard artificial daylight fluorescent tubes, of length 60 cm, General Electric type F20W/AD. This formed the lid of an enclosed box fitted with two fans to ensure a gentle constant stream of air to cool the lamps and maintain the samples in a constant environment. The temperature during exposure was maintained at 19 ± 1°C and the relative humidity at 50 ± 5 %. The fluorescent tubes were run initially for a period of time before testing to ensure constant emissivity. The illuminance at the plane of the samples was measured with a Weston Master V exposure meter fitted with an 'Invercone' attachment in its incident light mode, and checked with a spotmeter V and standard grey card. Both readings corresponded to an illuminance of approximately 4 kilolux.

The optical densities of the specimens were measured to a precision of 0.002 by means of an X-Rite model 310 densitometer in diffuse reflectance mode, which was checked by reference to a standard density plaque, and recalibrated when necessary to absolute density readings with an accuracy of ± 0.01 over the range 0.06 to 1.74, before and after each set of experiments. All densities recorded refer to the 'red' channel of the reflectance colour head, which corresponds to the waveband where the absorption by Prussian blue has its maximum value.

9.1.3 Results: characteristic curves and the 'fade'

The characteristic (or D/logH) curves of the typical negative-working cyanotype sensitizers are shown in Figures 9.1a–9.1f, in which the diffuse reflectance density is plotted vertically against the logarithm of the relative exposure horizontally. In each case the characteristic curve was remeasured after an exposure to artificial daylight of *ca* 2 kilolux hours, and this is also plotted on the graph. It can be seen that all types of sensitizer have suffered a loss of density in consequence of the light exposure, amounting to about 0.1 to 0.2 density units.

If D_i represents the initial optical reflectance density of any step of the pigment layer in a step-tablet test, and D_f is the measured density of the same step immediately following a fading exposure, the extent of fading is denoted by the change $\Delta D = D_i - D_f$. The measured values of ΔD have probable confidence limits of ±0.01 units of density, and they are generally less than 1, so it will be convenient, both typographically and with regard to numerical precision, to discuss the fading henceforth in terms of a whole-number parameter, which I shall call the 'fade', which is defined as $100\Delta D$. We will find it convenient to have a single parameter to express the measured susceptibility of a particular Prussian blue layer to fading. The maximum value of the fade for a given exposure is the parameter we seek, since it represents the greatest loss of image density within the entire tonal scale, and therefore the greatest loss of picture information.

When $D_i = 1$, the value of the *fade* is also the value of the % *relative fade*, $100\Delta D/D_i$, but it is not appropriate to make general use of the *relative fade* as the parameter to discuss the results for two reasons: psychometric experiments show that the JND is approximately constant over a wide range of densities; and the consequence of division by the very small density values in the highlights is to put a numerical bias on the results because it gives undue prominence to small changes.

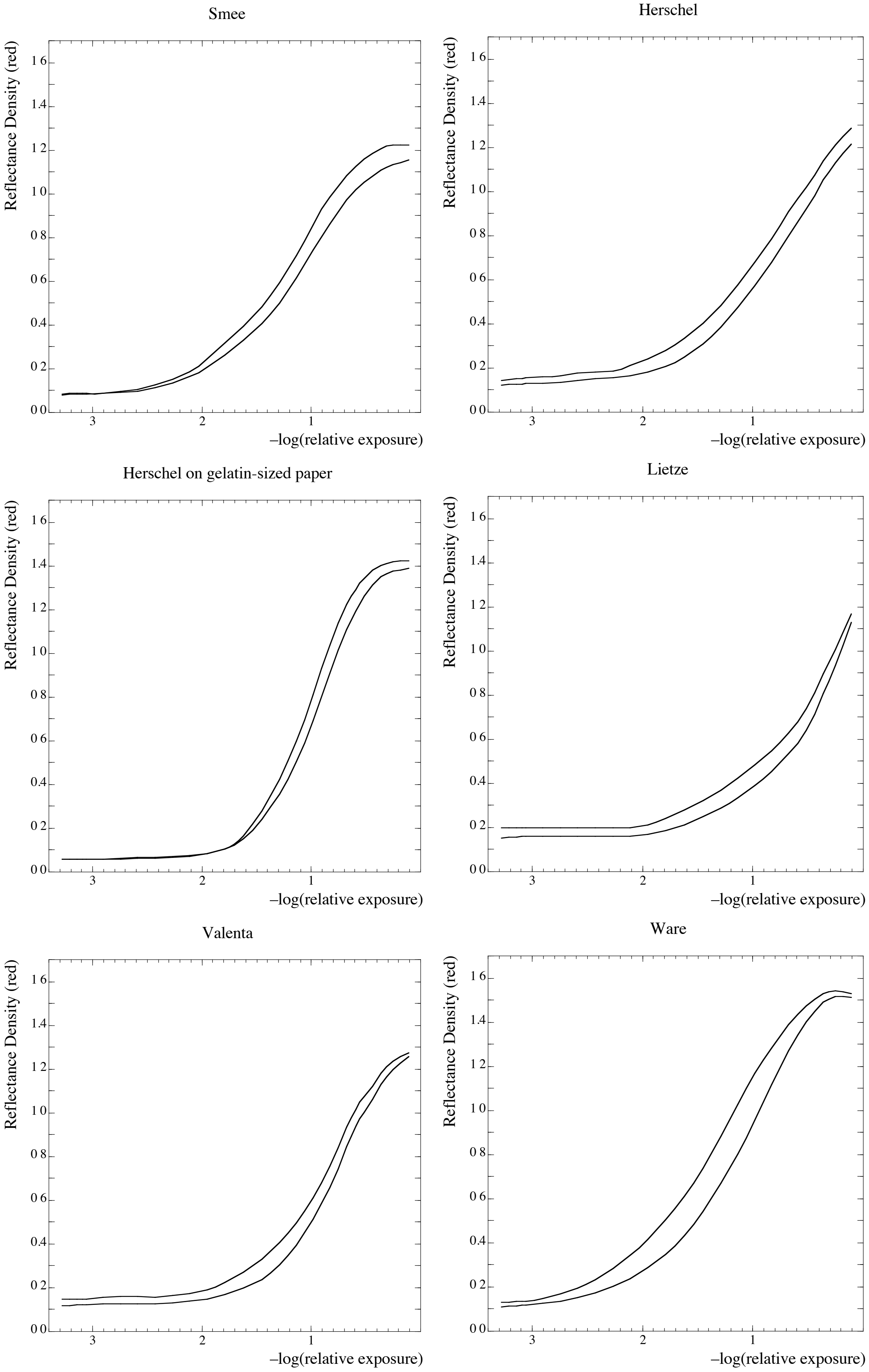


Fig. 9.1 Characteristic curves for cyanotype sensitizers, showing results of a daylight fading exposure of 2 kilolux hours

9.1.4 Results: variation of fade with initial density

To see how the fade varies across the tonal scale, typical results for the step-tablet tests printed by a variety of cyanotype sensitizers are plotted in Figs 9.2a–9.2f where the vertical axis is the fade, plotted against the initial reflectance density, D_i, of the steps which runs horizontally. The fade is seen to reach a broad maximum value (which varies between sensitizers) in the mid-tones of the density scale between D_i values of *ca* 0.5 to 1.0, and to fall off towards both ends of the scale. This trend is broadly true for all the cyanotype sensitizers examined. The fact that the maximum fade occurs over quite a wide plateau of mid-tones is a significant, and perhaps surprising, finding. It shows that the fade is not proportional to the concentration of Prussian blue – which might have been expected if the fading were an intrinsic property of the substance. Values of the maximum fade, and the densities at which they occur for some of the specimens investigated are summarised in Table 9.3.

Sensitizer type	Maximum fade 100ΔD	Over initial density range
Smee	13	0.90–0.95
Herschel on aquapel-sized paper	11	0.55–1.05
Herschel on gelatin-sized paper	12	0.80–1.20
Lietze	10	0.65–0.85
Valenta	10	0.35–0.85
Ware	22	0.85–1.15

Table 9.3 The maximum fade for cyanotype sensitizers

The near-constancy of the *maximum fade* for a given specimen over quite a wide density range makes further investigation of the other variables easier, because only the density of one or two typical mid-tones need be followed and not the whole scale of 21 steps. This finding also emphasises the importance of always carrying out cyanotype fading studies on mid-tones, where the loss of picture information will be greatest, and not just on a region of maximum density, where there may be a large ‘reserve’ of Prussian blue in which little change will be observed.

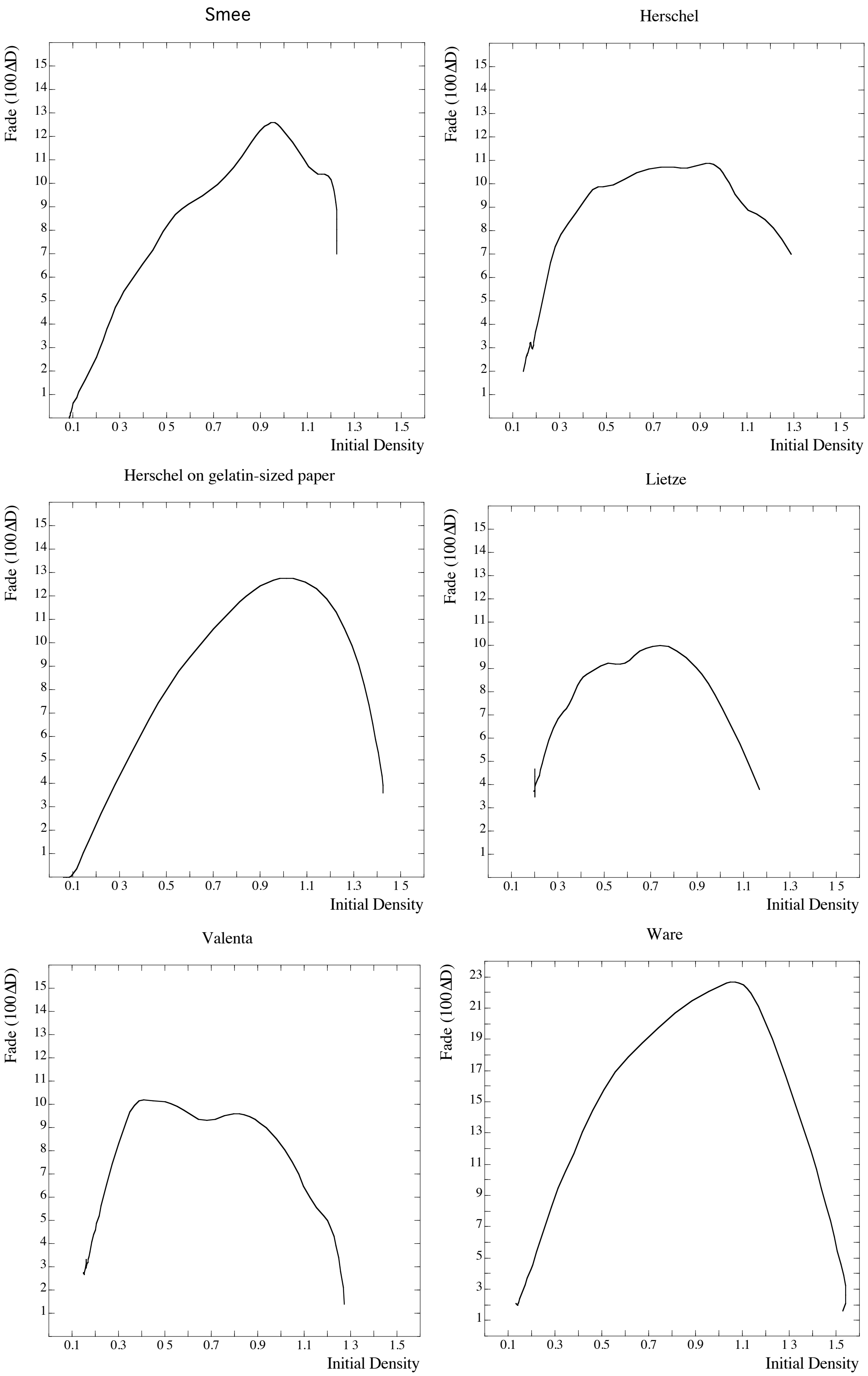


Fig. 9.2 Variation of fade with initial density

The fact that the *maximum fade* of a cyanotype tends to occur in the middle tones may also account for some of the disparities in the anecdotal evidence that has been reported concerning the fading of cyanotypes and blueprints. If the original image has a high contrast, with little or no intermediate tone, then the visible fading effect will be confined to the extremes of the tonal scale where it is minimal. This is particularly the case with ‘line’ images, such as contact prints from engravings, or photograms of opaque objects, where the image has only two densities in the limiting case: the density of the paper base plus fog, and the maximum density of which the sensitizer is capable. As can be seen from Table 9.3 the extent of fading varies little with sensitizer composition, except the sensitizer prepared from ammonium ferric oxalate, ***Ware*** type, which shows a deeper initial fade. As will become apparent, this is not in fact a disadvantage.

9.1.5 Variation of fade with exposure time

To ascertain how the fade varies with fading exposure time, test strips were exposed in the artificial daylight source and monitored at regular time intervals; only 4 of the 21 steps were selected for density measurement so that the time taken to perform this did not significantly detract from the exposure times. When the densities did not undergo any further decrease with exposure, the samples were removed to dark storage at ambient temperature and humidity (in the range 18 ± 2 °C and 50 ± 10 %RH), with full access to the atmosphere, and their densities remeasured periodically.

The results are shown in Figure 9.3a–9.3f for one step only (that giving rise to the maximum fade) of the five sensitizers, in which the maximum fade is plotted vertically against time along the horizontal axis. It may be seen that the fade quickly reaches a maximum value (i.e. a minimum in the measured density) after only about a half to one hour’s exposure to 4 kilolux. Following this it tends to decrease slightly but steadily with continuing exposure up to 24 hours, when the exposure was terminated. In one case the decrease in the fade (i.e. the regain of density *during* the fading exposure) was quite marked, as illustrated in Figure 9.3f. The knowledge that the maximum fade was reached within one hour’s exposure at this illuminance greatly simplified subsequent monitoring of repeated fading tests. The regain of density in the dark was also monitored in these samples and found to be effectively complete (final densities ≥99% of the initial densities) within five days.

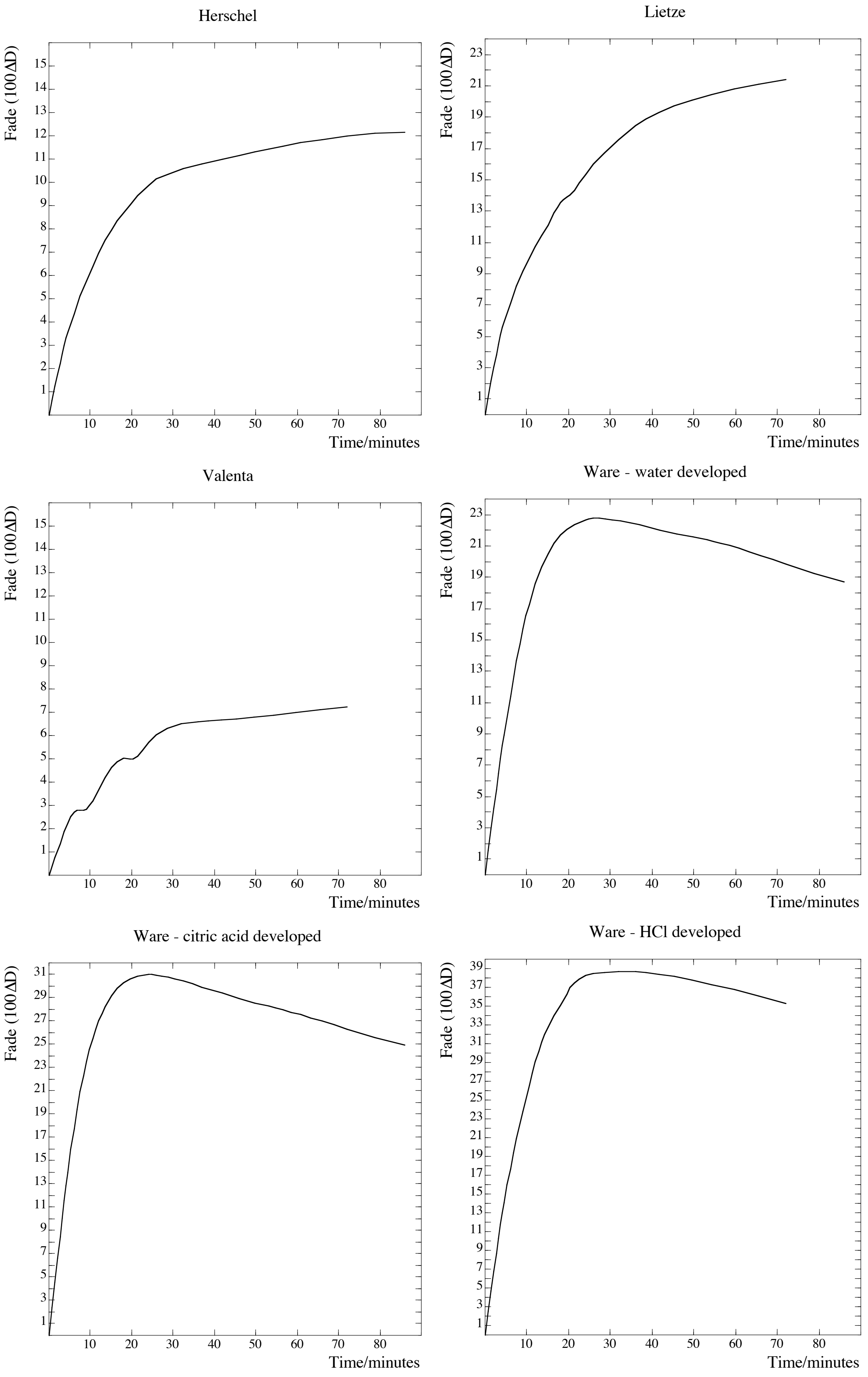


Fig. 9.3 Variation of fade with exposure time (4 kilolux illuminance)

9.1.6 Results: reversibility of repeated fade and regain

In view of the kind of exposure that cyanotypes receive when on exhibition, it was thought important to determine the reversibility of the fading, when subjected to repeated exposures. When the step densities had regained an almost steady value in the dark, the process of measurement and exposure was therefore repeated.

Figures 9.4a–9.4f show schematically the fluctuating density of one step (taken from those within the region of maximum fade), over several cycles of fade and regain. The fading exposure was 4 kilolux for half an hour, the regain period varied from one to several days in the dark. The most striking feature is the diminishing oscillation of the depth of fade, while the regain of density is usually greater than 95% within one day, and 99% within five days or more, i.e. it is complete within the limits of experimental error.

It is apparent from these results that the tendency of a cyanotype to fade may be dependent on its previous history. They are most susceptible when freshly-made, and, for some processes, each exposure to daylight levels of illumination, followed by regain, diminishes this susceptibility. The permanent loss of density incurred overall as a result of repeating the process is generally very small and not usually enough to give great concern, representing a fade at most in the order of 3 or 4 (i.e. ≥96% regain).

It is clear from the experimental results that the fading of cyanotypes does not obey the photochemical Law of Reciprocity,[573] but varies with the absolute exposure illuminance. At low light levels (*ca* 50 lux), we have the evidence of McElhone's monitoring program on cyanotypes to show that even illumination for 2000 hours, giving an exposure totalling 100 kilolux hours, causes no detectable fading. The probable reason for this behaviour is that the rate of density regain, due to air re-oxidation of the Prussian white, is superimposed on the effect of fading, and when the illuminance is so low that the rate of fading is less than or equal to the rate of regain, no fading at all will be observed, provided sufficient air can diffuse in to the vicinity of the print. This is the situation of cyanotypes exposed to stringent gallery illumination of 50 lux. When the illuminance is much higher, such as daylight at *ca* 4000 lux in the present tests, an identical exposure of 100 klux hours is reached in 25 hours. This incurs a measurable maximum fade of between 10 and 20, depending on the sensitizer. Conservators Jennifer Koerner and Karen Potje at the CCA have tested a variety of 22 blueprints to a 36 klux light

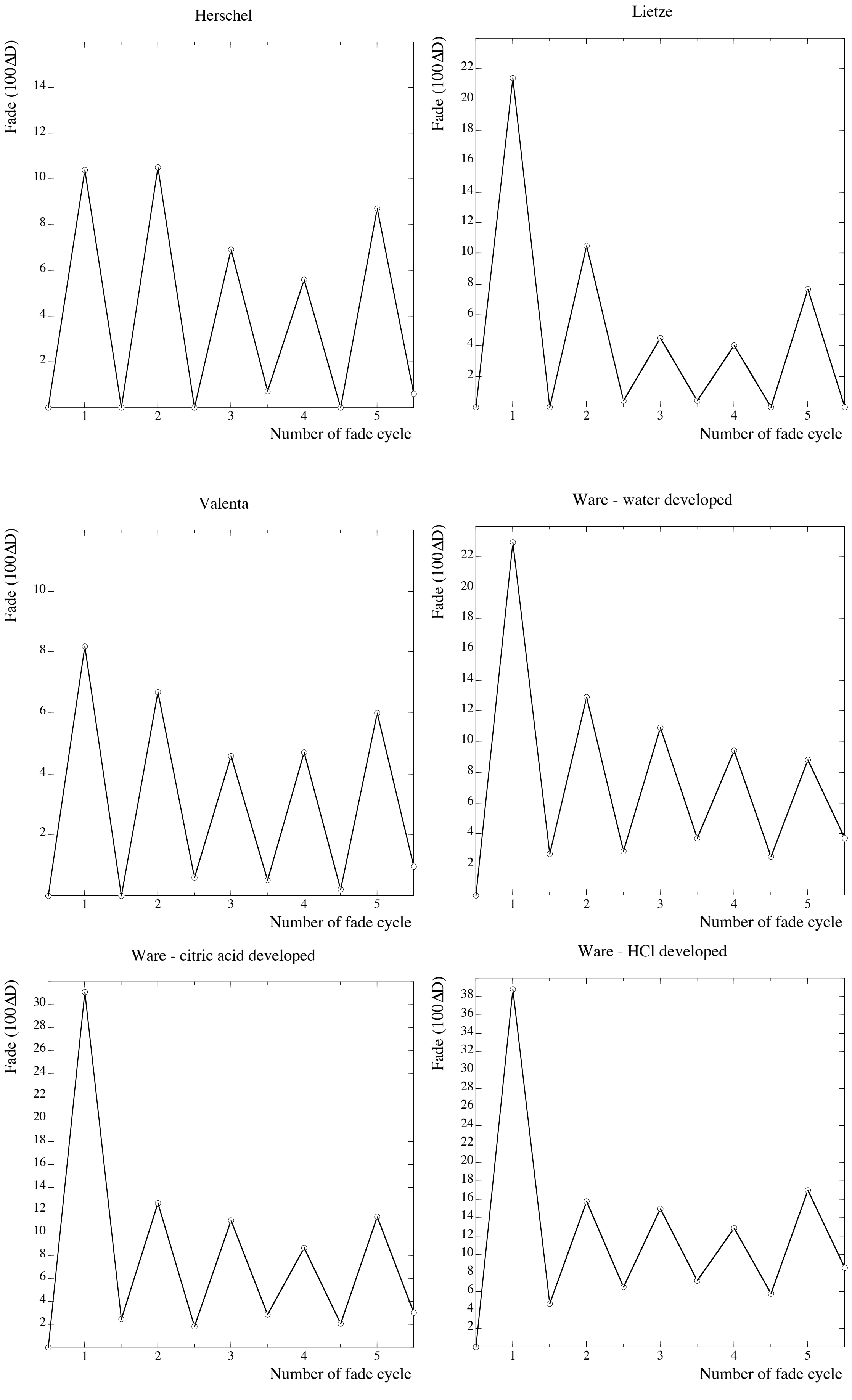


Fig. 9.4 Reversibility of fade (2 klux hr) and regain in cyanotypes

source, and found that all samples reacted similarly, showing a perceptible fading within 5 minutes exposure – a light dose of 3 kilolux hours.[574]

To demonstrate the important influence of the air on the outcome of fading, J. Dunbar performed an experiment in which cyanotype specimens were enclosed in an anoxic environment (a Marvelseal™ packet containing Ageless™ oxygen scavenger) and given a 24 hour fading exposure, which caused them to turn totally white. When opened and exposed to the air, they regained their full blue colour.

To determine the effect of very high illuminance on the fade, samples (of the Herschel and Smee sensitizer types) were given the same fading exposure as above, but to direct sunlight, *i.e. ca* 100 kilolux for one or two hours, which was found rapidly to cause a deep fade, as much as 40 or so, before a steady state was reached. Thus the same exposure of 100 kilolux hours, but delivered at three widely differing levels of illuminance, has three quite different outcomes in the degree of fading.

9.1.7 Results: effect of conditions on fading

To see if the fading of Prussian blue in cyanotypes was wavelength-sensitive, gel filters were placed around fresh specimens of ***Ware*** new cyanotype (which are the most sensitive) in the light exposure box, while still allowing access to the atmosphere; identical test strips were exposed side-by-side under red and blue filters, and compared with a strip exposed without filter.

Property	**Control**	**Red filter**	**Blue filter**
Transmittance of red light %	100	51	12
Transmittance of blue light %	100	10	84
Maximum fade = 100ΔD	16	12	12
Initial density = D_i	0.85	0.87	0.83
Time to maximum fade in mins	20	45	45

Table 9.4 Effect of wavelength of light in fading cyanotypes

The results are summarised in Table 13, where it may be seen that there is no significant difference between the fading experienced by the test strips exposed to red and blue light, indicating little or no wavelength dependence of the effect over the visible spectrum. Since Prussian blue has absorption bands in both the red and blue regions of the spectrum, presumably either is effective in promoting fading. The rates of fading are somewhat slower than the control which was exposed to unfiltered light, as might be expected from the attenuation of the illumination by the filters. It follows that there is no useful form of filtered ‘safelighting’ that can completely protect cyanotypes against fading.

To determine the effect of relative humidity on fading and regain, identical specimens of ***Ware*** new cyanotype were desiccated (both by pre-heating to 110 °C for 3 hours, and at room temperature) in an enclosure dried by silica gel to a relative humidity (RH) of ≤ 5%, and then given a fading exposure of 2 kilolux-hours within their desiccator vessel, which had a thin glass lid, versus a control which was also exposed under similar glass but with full access to the ambient atmosphere (RH ≈ 55%). It was found that the initial desiccation of the specimens had no perceptible effect on their densities. The values of the maximum fade for the desiccated specimens were 16 and 12, respectively for the heated and unheated specimens, compared with a value of the maximum fade of 15 for the control specimen. The specimens were allowed to regain density in the dark, respectively, in the desiccator vessel and the ambient air. After 4 weeks the fade had returned to values of 5, 3, and 2, respectively. On removal of the desiccated specimens to ambient atmosphere and allowing them to regain for a further 5 days, the fade values were 2, 1 and 2, i.e. the samples had returned to their original densities within experimental error, with a regain of ≥98%. It may be concluded that complete desiccation of cyanotypes has no significant effect on their tendency to fade, but it may somewhat inhibit their rate of regain. Since Prussian blue has a great avidity for water, attracting and retaining a proportion of water molecules within its structure, the effect of relative humidity on fading of cyanotypes under all normal circumstances is inconsequential.

The thoroughness of washing a newly-made cyanotype has a considerable effect on its susceptibility to fading. To demonstrate this, a Ware formulation new cyanotype, acid-developed, but which had only received a perfunctory wash of 4 minutes in running water before drying, was observed to suffer a maximum fade as high as 42 under a 2 kilolux-hour exposure. In contrast, a similar test-piece which had been washed in gently running tapwater for 20 minutes experienced a ‘standard’ maximum fade of only 16 under the same exposure. This provides further evidence that fading is promoted, at least partly, by impurities left in the print as a result of imperfect processing, as originally suspected by

I and A Moor. However such impurities cannot usually be fully washed out retrospectively, especially in old specimens, and prolonged washing in water can cause considerable loss of image by peptization of the Prussian blue, so a compromise in this regard must be reached.

To discover if there is any mitigation of fading if oxidants are incorporated in the print, specimens of ***Ware*** cyanotypes were treated, after development, with oxidants to restore fully the densities of the Prussian blue. Solutions of ferric chloride and ammonium dichromate (strength ca 3% w/v) were used, the latter being a common treatment for commercial blueprints at one time. Step tests were then densitometered and test-faded in the usual way. The results showed that these specimens were not immune from fading, indeed they showed a maximum fade of 17, comparable with the fade of 16 in an identical test that had not been treated with re-oxidants but simply allowed to regain density in the air. The only difference was that the maximum fade was reached more slowly - in about twice the time taken by the untreated specimen. This result suggests that there is no significant benefit in using the dichromate bath that has been recommended in the past. The experiment also shows that inorganic ferric salts, i.e. ferric ions *per se*, neither promote nor significantly inhibit the fading.

Of the many toning procedures suggested for cyanotypes, most de-stabilise the image, and cannot be recommended. In the lead toning method of Oscar Bolle (§8.6.1), the processed cyanotype is immersed in a 5% solution of lead(II) acetate, preferably at a pH between 7 and 8, which shifts the blue towards a beautiful deep violet. Specimens treated in this way were found to exhibit improved resistance to light fading, by a factor of about four. Analysis by X-ray spectrometry strongly indicated that the lead(II) ions are incorporated in the Prussian blue lattice. However, the strong colour shift and the toxicity of the lead acetate bath debar this as a conservation teatment, but artists originating cyanotypes might well consider incorporating this procedure into their practices.

9.1.8 Conclusions: mechanism of light-fading

The chemical reaction of the fading process (Appendix III.9) is essentially a light-induced reduction of Prussian blue to Prussian white, which necessarily entails the acquisition of an electron from some other substance, and an extra cation to balance this increased negative charge. For every reduction, there must be a corresponding oxidation.[575] The question naturally follows: what is there in a cyanotype print that can be oxidised? If this component can be identified, then it may be possible to prevent or inhibit fading. There are several candidates, which fall into three categories:

1. A component of Prussian blue itself.
2. Other constituents of the cyanotype print.
3. An impurity incorporated within the Prussian blue, arising from the circumstances of its preparation.

Let us examine each of these categories in turn:

1. The inherent stability of Prussian blue to light

The Colour Index describes the light-fastness of Prussian blue as 'excellent',[576] and the manufacturers of artists' pigments list Prussian blue as 'durable'. Kirby has reported a fading test on Winsor and Newton's powdered Prussian blue pigment, which was painted out as a moderately intense, simple wash with gum Arabic. The specimen was exposed continuously for 180 days to a standard artificial daylight source of 10 kilolux, which amounts to a total exposure of over 40 megalux-hours. Little or no loss of density or colour change was observed in the specimen.[577]

We also have the evidence of scientific investigations of the behaviour of pure Prussian blue in highly controlled environments, where it is also found to be very stable. The pure substance (as its 'insoluble' variety) in aqueous suspension shows no tendency to decompose under prolonged irradiation with visible light, establishing that Prussian blue does not significantly photo-oxidise water to oxygen, or its own bound cyanide ion (to form cyanate or cyanogen) under these conditions.[578] This is further discussed in Appendix III. Moreover, if Prussian blue were inherently light-sensitive we might have expected proportional behaviour for the fade, rather than the sub-proportional behaviour, which is more indicative of the presence of an impurity.

Set against these observations is the early nineteenth century report by Chevreul which suggests that very heavy exposures to UV-rich light, e.g. direct sunlight, will result in some decomposition of Prussian blue, but these are not conditions that will prevail in any gallery or archive, and they have not therefore been extensively investigated in the present work, which has adopted exposures to illumination that are likely to be encountered in exhibition and everyday handling.

2. Possible effects of the substrate and binder

In a cyanotype print, as opposed to a pure Prussian blue sol, the system is complicated by the presence of substances from the paper environment: primarily the cellulose substrate, any non-cellulosic constituents such as lignin, the sizing agent, and any other manufacturers' additives to the paper pulp. The surface contact between the Prussian blue particles and these substances may be rather restricted, but they cannot be excluded from consideration as potential reducing agents.

A number of experiments were carried out in the course of this research to determine if the substrate itself could promote photochemical fading. Cellulose is an oxidisable material,[579] so its possible contribution to fading was checked by preparing cyanotype test prints on a variety of other, non-oxidisable absorbent substrates, such as glass plates coated with silica or alumina (as used for thin-layer chromatography), fibreglass filter paper, and bisque-fired ceramic tile bodies. The general observation in all these tests was that cyanotypes formed on such non-reducing substrates faded in light as rapidly as those prepared similarly on pure cellulose paper. Thus, cellulose itself is not implicated as a major contributor to the fading process in cyanotype images.

The lignins that are present in inferior grades of wood-pulp paper are readily oxidisable substances and could promote the photoreduction of Prussian blue, but no tests have been made in this respect because there is every reason not to use such papers for making cyanotypes, and they are easily avoided. However, some commercial blueprint papers of the past may have contained appreciable amounts of lignin, which could contribute to their deterioration. The presence of gelatin size does not appear to increase the fading, as judged by the foregoing results.

3. Impurities destabilising Prussian blue

The most likely cause of light-sensitivity in cyanotypes is the incorporation within the image substance of impurities which derive from the sensitizer; the availability of readily oxidisable substances will facilitate the rapid photoreduction to Prussian white. This may not simply be a case of residual impurities left in the paper fibres by imperfect clearing of the chemicals during the wet-processing procedure; but there may also be a trapping of the impurity within the Prussian blue lattice, and once trapped no amount of washing may remove it. The susceptibility to fading is therefore likely to be highly dependent on the circumstances under which the Prussian blue is formed, i.e. the formulation and concentration of the sensitizer and the processing of the print.

The variability and history-dependent character reported for the light-fading of cyanotypes therefore becomes comprehensible, but there have been few proposals as to which substances or formulations are more likely to promote fading. It has been suggested that residual ferric salts, presumably the hydrated oxides, in the print can be a cause, but these are inherently oxidising rather than reducing agents and the experimental evidence cited above shows no such effect.

Fading of Prussian blue requires the simultaneous presence of several contributing factors: light; a reducing agent (electron donor) in intimate contact with the solid; and cations to migrate into the lattice and balance the increased negative charge brought about by reduction. Molecules that are small enough to be occluded within the voids of the Prussian blue lattice should be particularly effective in promoting the photoreduction. To test this possibility, pure Prussian blue coatings on paper were prepared by successive coats of potassium ferricyanide and ferrous sulphate, then part-coated with solutions of oxidisable anions such as citrate and oxalate, and allowed to dry. The density of the impregnated Prussian blue paper was compared with the control region after a period of dark storage to ensure that there was no reduction in the dark, then the whole sheet was given a standard fading exposure. The reductant-coated area was found to fade in the light much more rapidly than the control area, showing that these oxidisable organic anions do indeed promote photoreduction of the pigment. It may be significant that the anions effective in promoting fading in Prussian blue are also those that normally render iron(III) photoactive in its salts.

To improve the light fastness of cyanotypes, therefore, the presence of excesses of these free anions, such as citrate, should be avoided. Since an acid development bath is desirable in the processing of new cyanotypes (***Ware*** formula employing ferrioxalate sensitizer), it is better to use a very dilute mineral acid such as hydrochloric or nitric, rather than citric or oxalic acids, which have been previously recommended.

If, in the light-fading of the Prussian blue, the products of oxidation of the impurity are lost from the cyanotype (for example as carbon dioxide gas, in the case of oxalate), the impurity should be progressively and irreversibly destroyed as the dose of light accumulates, but the Prussian white will still be fully re-oxidised by air. The quantity of impurity should therefore diminish with successive cycles of fading and regain, and eventually the susceptibility to light fading should disappear when all the impurity is ‘burnt out’. This is the behaviour observed during the experiments on cyclic fade and regain described above, although the fading never dropped to zero, so there must be some irremovable cause also. Ferrocyanide ion is cited as a common impurity in Prussian blue; the oxidation-reduction equilibrium between these two substances is finely balanced; the oxidation product of ferrocyanide is ferricyanide, which will not be lost from the system, so although fading and regain may be reversible in this case, the susceptibility to fading cannot be 'burned out'.

It has long been appreciated that processing solarised or faded cyanotypes in a dilute dichromate bath re-oxidises them rapidly, but it has also been claimed that it improves their resistance to fading;[580] presumably because this powerful oxidant will destroy most reducing impurities. There is also the (as yet unproven) possibility that some dichromate or chromate may be incorporated into the Prussian blue lattice, where its oxidising presence might continue greatly to inhibit photoreduction. However the strong yellow colour of dichromate would tend to make the hue greenish if it were so incorporated. The effect of a dichromate re-oxidation bath on the fading susceptibility of new cyanotype (***Ware*** formula) was tested as described above and found to be ineffectual.

Regain of the Prussian blue in a faded layer requires an oxidant (electron acceptor), and probably some water to assist cation migration out of the lattice, and it will be further assisted by acid which enhances the action of most oxidising agents, such as oxygen, dichromate and hydrogen peroxide, and neutralizes the hydroxyl ions produced by them, so avoiding hydrolysis. The amount of gaseous oxygen needed to accomplish the re-oxidation of an average cyanotype is surprisingly small: a calculation for a typical coating of maximum optical density shows that, for an area of A4 size, the oxygen contained in about 0.7 cc of air should suffice to completely re-oxidise the Prussian white to Prussian blue.[581]

9.2 Bleaching of cyanotypes by alkali

Despite the false claim by the discoverer, Diesbach, that his blue was stable to lime, painters soon realised that this, and indeed any other alkali, rapidly destroyed Prussian blue and the pigment could not therefore be used for painting frescoes.[582] Alkaline sensitivity is the most serious drawback with this pigment, and there have been many endeavours to diminish it.

An extensive investigation of the effect of alkali on Prussian blues has been conducted by Holtzman,[583] who has also sought treatments to protect the pigment from this type of deterioration. He found that a buffer at pH 9.4 completely decolourises (*i.e.* destroys by irreversible hydrolysis) Prussian blue in 1 to 10 minutes, depending on the precise method of preparation.[584] This is not a highly alkaline pH, and is the same, for example, as that of a saturated solution of calcium carbonate, the buffer commonly incorporated in archival papers and boards. A stronger alkali is a solution of sodium carbonate of strength 0.25 molar, which has a pH of ca 10.7; this is high enough to destroy the Prussian blue of a cyanotype in less than half a minute.

Holtzman especially recommended the incorporation of nickel ions into the Prussian blue as a means of improving its resistance to alkaline environments.This is best done at the time the blue is prepared, by forming it in the presence of nickel salts, but it can also be incorporated retrospectively in high proportion by soaking the Prussian blue in a bath of a nickel(II) salt. Holtzman found that Prussian blue so treated was ‘stable indefinitely’ at pH 9.4 (or, at least, for 4 months – the duration of the work), and could even withstand the pH 10.7 solution of sodium carbonate for 4 to 5 hours.

I tested the nickel treatment on ***Herschel*** and ***Ware*** cyanotypes in case it could offer a possible conservation procedure for improving the stability of cyanotypes towards alkaline hydrolysis. The process of soaking a cyanotype test strip in a solution of 10 % w/v nickel(II) sulphate for one hour caused a perceptible shift in the hue towards a more greenish-blue: from 21D8 to 23D8 in the ***Herschel*** specimen, and from 20E8 to 21E7 in the ***Ware*** specimen (see also §8.6.3 on toning). Unfortunately the treatment is also accompanied by a distinct loss of density from the mid-tones, presumably due to peptisation of the pigment: using the same units (100ΔD) as for the *fade,* the loss was 10 from the ***Herschel*** specimen after one hour, and 15 after a 25 hour soak at room temperature; the corresponding losses from the *Ware* specimen were somewhat greater: 16 and 21, respectively. These specimens were densitometered then tested for their resistance to alkali by immersing them in a buffer solution at pH 9.4 for 10 minutes, in comparison with control specimens of the major processes that had not been treated.[585] The test strips were briefly (5 minutes) rinsed in tap water and then dried and re-measured. The losses (100ΔD) are shown in Table 14 for shadow-tone regions, from which it may be seen that the nickel(II) treatment is quite efficacious in protecting the Prussian blue from alkaline degradation at this pH.

Sensitizer type	**D_i**	**Loss (100ΔD)**	**Loss %**
Smee	0.953	58	61
Herschel	1.355	68	50
Herschel (Ni(II) treated 1 hr)	1.352	6	5
Herschel (Ni(II) treated 24 hr)	1.122	5	5
Lietze	0.952	65	68
Valenta	1.322	94	71
Ware	1.086	65	60
Ware (Ni(II) treated 1 hr)	0.929	12	13
Ware (Ni(II) treated 24 hr)	1.335	4	3

Table 9.5 Effects of alkaline hydrolysis at pH 9.4 for 10 minutes

There remains the question as to whether a cyanotype image that has been bleached by alkali can be restored (see Appendix II.8). It is likely that the ‘degree of irreversibility' of an alkaline bleached cyanotype will be dependent on the history of the object – for instance whether it has been washed after the bleaching action, which would remove the soluble ferrocyanide. When 'freshly bleached' there is some evidence that cyanotypes can be partially restored by dilute acid, such as hydrochloric or nitric, and added ferrocyanide, but over time the ferric oxide/hydroxide hydrolysis product becomes insoluble in dilute acid, and cannot regenerate Prussian blue. This is an area calling for further research.

9.3 Peptization of Prussian blue

The tendency of Prussian blue to peptize causes one of the major problems of the traditional cyanotype process, namely, a considerable loss of image substance, which washes out of the paper during wet processing, thus necessitating heavy over-exposure (as much as two or three stops, depending on the paper substrate and its sizing) to compensate for the loss.[586] Clearly it is desirable to inhibit the formation of ‘soluble’ Prussian Blue in favour of an ‘insoluble’ variety. Formulations for some commercial blueprint papers contain added iron(III) chloride, which may have this effect. However, if the potassium ions are eliminated from the sensitizer, then a less easily peptized form results in the first place. The use of ammonium hexacyanoferrate(III) in the sensitizer goes some way to solving this problem, with the result that the new cyanotype process described in Chapter 7 loses very little image substance on wet processing.

Similar considerations apply to conservation treatments of cyanotypes using aqueous washing. This procedure is unlikely to diminish much the susceptibility to light fading (which is substantially reversible, anyway) if the cyanotypes have been properly processed in the first place, but it is likely to cause some irreversible loss of image due to peptization.

Quantitative experimental results on this problem are scarce, but in 1989 Ian and Angela Moor reported some densitometered washing experiments on cyanotypes. The washing time was 15 minutes in all cases; in tapwater (pH 7.5–8.5) the ‘average loss in image density’ was 18%; in distilled water (pH 6–6.5) the loss was 4%; in deionised water (pH 6.3–6.6) the loss was said to be 0.00%.[587]

In 1991 Sarah Wagner reported some research at the Library of Congress on washing cyanotypes of both recent and historical origins: specimens were bathed in neutral pH tap-water or in de-ionized water at pH 6 for a period of 1.5 hours; some loss of pigment occurred, and was especially marked with the cyanotypes of recent manufacture for which: “dramatic lightening occurred by immersion in tap water... and slight lightening for samples which were immersed in deionised water”.[588]

The effects of aqueous washing on cyanotypes of different varieties was tested in the present work. Sets of four nearly identical test strips of a given process were immersed in a gentle flow of tap water at 20 ± 1 °C, the pH of which was monitored periodically and found to be 7.2 ± 0.1. The strips were removed successively from the washing process after time intervals of 5 minutes, 20 minutes, 1 hour, and 4 hours, dried, and their densities remeasured. A similar test was performed in a 2 litre static bath of ‘purified’ water at 20 °C, having a pH of 6.5 ± 0.1.[589] The results are summarised in Table 15, where the ‘Loss’ figures are 100ΔD.

Sensitizer Type	Water quality	Initial density	Loss in 5 mins	Loss in 20 mins	Loss in 1 hour	Loss in 4 hours
Smee	Tap	0.90	3.1	6.6	13.3	28.1
Smee	Pure	0.93	0.3	4.6	6.2	
Herschel	Tap	0.95	0.4	2.3	6.4	13.9
Herschel	Pure	0.96	0.1	0.4	2.2	3.2
Lietze	Tap	0.98	0.1	2.9	7.0	17.5
Lietze	Pure	0.98	0.2	0.5	1.7	1.9
Valenta	Tap	0.86	1.2	3.9	9.6	30.7
Valenta	Pure	0.85	0.7	1.0	2.2	
Ware	Tap	0.77	1.3	4.8	13.7	29.0
Ware	Pure	0.95	0.1	0.8	2.1	2.2

Table 9.6 Effects of aqueous washing. ‘Loss’ is 100ΔD

A phenomenon called the ‘edge etch effect’ was conspicuous on some peptisation step tests and requires explanation. This was the loss of image substance from the edges of a step, where it is adjacent to the surrounding regions of maximum density. That the effect is attributable to the adjacent area of high density was demonstrated by printing the step tablet up against the boundary of the sensitized area, in which case there was no loss. The ‘edge etch effect’ is invisible immediately after the print-out exposure; it only appears during the wet-processing. Nevertheless, it can be shown not to be due to migration of ions through the solution during the wet processing; because the effect still occurs even when the entire adjacent high-density region is cut off after exposure but before the wet processing. Evidently the loss is due to ions which have migrated through the paper from the adjacent area during the exposure. These promote peptization of the Prussian blue as soon as aqueous treatment begins. If such a test strip is allowed to rest in the dark at normal humidity for a few hours after exposure and before the wet processing, the effect disappears, presumably because the continuing diffusion of the causative ions has by then led to their uniform distribution throughout the specimen, and there is no longer a local effect. It is significant that some mobile by-product of the cyanotype photochemistry can promote peptization of the image substance; the effect is likely to cause an enhanced acutance in images. It was observed to be much worse in samples prepared from the brown variety of ammonium ferric citrate compared with the green variety. It was greatly reduced or absent in papers sized with gelatin – which may act by inhibiting the mobility of the ions causing the peptization. In general, solutions of high ionic strength tend to promote peptization of Prussian blue. Thus, treatment in a solution of sodium hexametaphosphate of strength 5–10% w/v can be used to remove the blue in the highlights of a fogged cyanotype.

9.4 Conservation issues

9.4.1 Recognition of cyanotype

It must first be established, by a magnification of 10 to 30 times if necessary, that the object under consideration is a true photograph having a continuous tone image, and not one of the several photomechanical printing processes, which all show a tell-tale micro-texture: a dot screen for letterpress halftone, a grain pattern for photogravure, or reticulation in collotype.[590] Cyanotypes may seem the easiest of all photographic processes to identify by virtue of their colour, but care should be taken to distinguish them from other types of image that can also be made in a similar blue: viz carbon prints, blue-toned silver-gelatine prints, and Woodburytypes. The essential difference is that all these processes include a binder layer of gelatin holding the pigment, which lies on the surface of the paper, and confers some lustre or reflectivity; whereas the cyanotype is a totally matte, single-layer print in which the pigment is contained within the surface fibres of the paper sheet, which should be clearly visible under magnification. However, prints made by the (relatively rare) positive-working Pellet process will also have a deposit of insolubilised gum retaining the pigment, so will show a binder layer in relief in the shadow regions; in consequence, Pellet prints will rather resemble blue Woodburytypes or carbon prints and may be more difficult to distinguish from them.

9.4.2 The threshold exposure and exhibition

The concept of the *threshold exposure* was introduced in my previous book on early silver photographs with the aim of providing a useful parameter for curators and conservators to describe and discuss, in a semi-quantitative way, the vulnerability of cultural objects to light.[591] The threshold exposure for a monochrome image is that exposure to light which results in a *just noticeable density change* in any significant area of it. The notion of ‘significant area’ is somewhat subjective, but could be taken to be in the region of 1 mm^2 upwards.

The psychometrics of human vision find that a density difference between adjacent areas in the order of 0.01 is ‘just noticeable’ under good viewing conditions. The *threshold exposure* therefore defines the exposure at which ‘perceptible damage’ begins to result, as assessed by the unaided human eye under good illumination. It is measured in the conventional units of exposure - lux seconds or, more conveniently, kilolux hours.

Regarding the criterion for human perception of loss in image density, one ‘Just Noticeable Difference’ (JND) is about 0.01 density units, which we will conveniently express as a *fade* (100ΔD) of 1 unit. The experimental results above have shown that a *fade* of *ca* 10 to 20 JNDs is brought about by an exposure of 2 kilolux hours. This implies that the *Threshold Exposure* is only 200 lux hours at this level of illuminance (4 kilolux). This may seem an alarmingly small exposure to cause perceptible change; it is comparable in magnitude with the *Threshold Exposure* values calculated, and observed, for Photogenic Drawings, which are deemed too light-sensitive for exhibition under any conditions. However, the behaviour of Photogenic Drawings is quite different from that of cyanotypes because the fogging of a Photogenic Drawing is irreversible, cumulative and permanent, but the fading of a cyanotype is reversible by air re-oxidation. As has already been explained, the failure of reciprocity in the case of cyanotypes means that the duration of exposure at 50 lux needed to fade them by even one JND may be very long indeed, if not infinite, and it is quite safe to exhibit them at, or near, this level of illumination. Even under moderate daylight exposure, the evidence is that recovery from fading will usually be effectively complete.

9.4.3 Avoidance of alkali

The extreme sensitivity of cyanotypes to alkali suggests that mildly acidic conditions are preferable for their storage, even if this is not deemed ideal for the paper substrate. From the evidence cited above, there can be no doubt that cyanotypes are destroyed by mild alkali (pH 8 to 10) much more rapidly than cellulose paper is destroyed by correspondingly mild acid (pH 6 to 4). Confronted with this dilemma, the conservator should be prepared to subordinate the best interests of preserving the paper substrate to the best interests of preserving the image upon it. Any sort of de-acidification treatment, aqueous or non-aqueous, is therefore out of the question for cyanotypes, because it will certainly damage, and probably totally destroy, the image. However, Prussian blue that has been treated with nickel(II) is much more resistant to alkaline hydrolysis, as was shown by Holtzman and confirmed for cyanotypes in the present work; it opens the possibility that such cyanotypes could be treated with a de-acidifying bath at about pH 9, such as magnesium bicarbonate, without serious loss, but this has not yet been tested as a conservation procedure. The preliminary treatment with nickel(II) would itself cause some loss from the image, as indicated above, so such a treatment would have to be carefully justified in the first place. Even simple aqueous washing should be avoided because of the risk of image loss through peptisation of the Prussian blue; if washing is considered essential for preservation, then float-washing of the verso only, or damp-pack treatment might be considered.

It is fortunate for cyanotypes that, among the likely volatile impurities in the atmosphere, alkaline gases are much less common in occurrence than acidic gases. Cyanotypes should never be stored with other types of process that might emit alkaline vapours, for instance diazo-copies, which are usually treated with ammonia as part of their processing (and are also, quite commonly, blue). Care should also be exercised with proprietory cleaning agents for picture-glass, which are sometimes used when framing a work for exhibition: some such cleaners can contain ammonia, so all should be pH tested before use. Having made this warning, it should be stated that the effect of ammonia gas – intensification to a violet colour – seems to be quite reversible on exposure to air. It is only aqueous ammonia that causes hydrolysis.

For the benefit of those making cyanotypes today, it may be useful to point out that precautions taken in their preparation could improve their resistance to light-fading and alkaline hydrolysis. Washing of the print should be thorough so that there is no trace of residual sensitizer. Moreover, the new cyanotype method described in Chapter 6 recommends development in dilute acid, which will destroy any unwanted alkaline buffer that may be present in the paper and ensure that the print is left in a condition favourable to the Prussian blue, possibly by the incorporation of acid cations into its lattice.[592] If a shift in colour towards greenish-blue is not unacceptable to the maker, then treatment with nickel solution might also be contemplated as a means of fortifying the resistance of the image.

9.4.4 Buffered storage enclosures

Buffered papers and mount boards contain chalk (calcium carbonate) which, with the best of intentions, is included as a reservoir to neutralise any excess acid from the environment, and to protect the cellulose molecules of paper objects against acid hydrolysis, which shortens the chain length with consequent embrittlement of the sheet. The use of buffered materials has become standard conservation practice in caring for all works of art on paper, and some types of photograph.[593]

Increased awareness of the need for conservation of paper documents and works of art has led to the formulation by the International Standards Organization of specifications ISO 9706:1994 for Permanent Paper, and ISO 11108:1996 for Archival paper, whose content is summarised as follows:[594]

> "**Permanent paper (ISO 9706 : 1994)**
>
> - shall have a pH value between 7.5 and 10.0
> - shall have an alkali reserve at least corresponding to 0.4 moles acid [H^+] per kilogram of paper (corresponding to at least 2% *w/w* calcium carbonate)
> - shall have tearing resistance of at least 350 mN
> - shall have a Kappa number less than 5, which means that the paper may contain only a small amount of easily oxidized material (*e.g.* lignin).
>
> **Archival paper (ISO 11108 : 1996)**
>
> - shall be made from cotton, cotton linters, hemp or flax, but may contain a minor fraction of fully bleached chemical wood pulp
> - shall have a folding endurance of at least 2.18 (MIT-, Köhler Molin- or Lhomargy-instruments) or 2.42 (Schopper instrument)
> - Archival paper shall meet the requirements for permanent paper.
>   The archival paper is stronger than the permanent paper and can withstand considerably more handling."

From these specifications, we may calculate the implications of the presence of this equivalence of 0.4 moles of alkali per kilogram of paper:

If the paper weight is, say, 250 g/m^2, then a 1 m^2 sheet contains:

$0.25 \times 0.4 = 0.1$ moles of OH^- equivalent.

A typical coating weight of siderotype sensitizer would be 25 cm^3/m^2 of a solution *ca.* 0.5 molar in Fe(III), *i.e.* a 1 m^2 sheet of paper would absorb 0.0125 moles of Fe(III) on coating.

It follows that, per unit area, the permanent and archival papers contain an 8-fold molar excess of alkaline reserve (equivalent to $[OH]^-$) available to react with and hydrolyse the Fe(III). There is clearly great potential for damage to the sensitizer chemistry if only a fraction of the alkali in the sheet can contact the iron(III) salt, area for area, in the wet state, although the chalk buffer is quite involatile and unlikely to migrate through dry paper.

This accounts quantitatively for the fact that, over the last few decades, it has become increasingly difficult to find papers which work well for iron-based printing, among the high quality cotton papers manufactured for the fine-art market of watercolorists, sketchers and printmakers and the archival document market, which all presumably conform to the above ISO standards. Such papers now always boast that they are "acid free" - implying that they probably contain an additive of chalk filler which, unfortunately, will rapidly cause the decomposition of any iron(III) sensitizer. Most contemporary practitioners have been driven to the last resort of soaking their chalk-buffered papers in dilute acid in order to destroy the calcium carbonate before coating them with iron(III) sensitizer. Unfortunately many practitioners think that oxalic acid is suitable for this purpose, but calcium oxalate is just as insoluble as calcium carbonate. Hydrochloric acid can be used, but recently it has been found very convenient and effective to employ 10% sulphamic acid for this purpose.[595] Nonetheless, it is a tedious and unnecessary procedure that tends to degrade the paper surface and strength.

However, it is now generally advised that cyanotypes should not be mounted on, or stored in such buffered materials, in case they suffer alkaline deterioration. A saturated solution of calcium carbonate is said to have a pH of 9.4,[596] and we have seen that solutions of this pH can rapidly destroy Prussian blue. To test the extent of the danger from chalk buffers, processed cyanotype tests of all five sensitizers were partially coated with a paste of calcium carbonate powder and distilled water, leaving a ‘control’ area for comparison, and housed in a high humidity environment (RH $\geq$ 95%) to keep the paste moist, in a simulation of the ‘worst case scenario’. Within 48 hours, there was a serious density loss ($100\Delta D \approx 40$ to 60) in the coated areas of all the sensitizers, compared with the adjacent ‘control’ areas. Calcium carbonate only poses a clear threat to cyanotypes when in direct contact with the image; it has little ability to migrate through cellulose, so the dangers of chalk-buffered enclosures may have been somewhat overstated. It would, however, be prudent to continue the use of unbuffered materials for the enclosure of cyanotypes.

With regard to wrapping materials, it is desirable that cyanotypes which receive any exposure to light should be allowed some access to the air, particularly when they are returned to dark storage, thus allowing density regain by air oxidation which reverses any fading incurred. The volume of air required to accomplish this is surprisingly small: for a typical 10x8 cyanotype, it is calculated that less than one cc would suffice. For this reason, archival polyester sleeves cannot be recommended as ideal enclosures for cyanotypes, because they allow the ingress of light but not of air. A preferable wrapping material is an archival wrapping paper of a non-buffered type, i.e. Atlantis Silversafe Photostore, in the traditional ‘four flap folder’ style. Being fairly opaque but relatively porous, it will have the desirable properties of attenuating the light but admitting the air. It has been demonstrated that cyanotypes contained in anoxic housings (with ‘ageless’ oxygen scavenger) are very susceptible to light-fading – the very converse of recommended conservation practice! When on exhibition, it is obviously preferable that the mount for a cyanotype should have a deep window mat, providing a reservoir of air, which is ‘in communication’ with the ambient atmosphere. Let your cyanotypes breathe!

Appendix I Chronology of Cyanotype

1706 Prussian blue first discovered by Johann Jacob Diesbach in Berlin

1724 John Woodward publishes method of preparing Prussian blue

1785 Turnbull's blue being manufactured in Glasgow

1811 Joseph Gay-Lussac isolates and analyses hydrocyanic acid

1818 First Law of photochemistry proposed by Christian von Grotthus

1822 Leopold Gmelin discovers potassium ferricyanide

1828 John Mercer detects action of light on ferric salts on cloth by test formation of Prussian blue

1831 Johann Döbereiner notes action of sunlight on ferric oxalate

1839 Announcement of the invention of silver photography

1840 Alfred Smee prepares potassium ferricyanide by electrolytic oxidation of potassium ferrocyanide

1842 John Herschel discovers effect of light on Smee's potassium ferricyanide and ammonium ferric citrate to form Prussian blue and describes cyanotype processes to the Royal Society

1843 Anna Atkins begins *British Algae: Cyanotype Impressions* using Herschel's negative-working formulation

1871 Death of Sir John Herschel

1872 Marion & Co launch 'Ferroprussiate paper' on the market for blueprint reprography

1876 First commercial blueprinting machine introduced into the USA

1877 Henri Pellet patents his positive-working cyanotype process

1889 Peter Henry Emerson denounces cyanotype as a pictorial medium

1897 Eduard Valenta prepares green ammonium ferric citrate

1900 Dorel brothers invent gel-lithographic photomechanical process

1950 Blueprint increasingly replaced by diazo copying process

1995 Mike Ware publishes the New Cyanotype process

Appendix II Chemistry of Prussian Blue

The chemical investigation of the 'iron blues' – for there are several – has a long and convoluted history. Although Prussian blue has been studied for over 250 years, it is only in the last two decades that the molecular structure of one of its forms has been confidently elucidated. The interpretations put forward in chemistry texts published earlier than the 1970s are all erroneous in varying degrees, and these misconceptions have been carried over into the technical photographic literature on the blueprint, none of which now represents the process correctly.597

This appendix attempts to summarise our present understanding of Prussian blue in its various forms, without detailing the physico-chemical evidence which underpins the conclusions; those who wish to read more deeply will find citations of the key references to the primary research literature.[598]

Prussian blue is now recognised as a model for a whole class of transition metal hexacyanometallates – insoluble mixed-valence compounds which share essentially the same cubic, cyanide-bridged, open polymeric lattice.[599] It should be appreciated, however, that knowledge of the structures of this family of substances is even now incomplete, owing to three difficulties:

- Most preparations of Prussian blue tend to result in colloidal precipitates which preclude the obtaining of single crystals for full 3-dimensional X-ray structure determination;
- The presence of disorder due to vacancies in the lattice; and
- The Prussian blue lattice is 'zeolitic', in that it offers interstitial voids to accommodate substantial proportions of impurity ions and molecules, the incorporation of which complicates its analytical characterization.

Rather than forming as a single substance, of well-defined stoicheiometry, the composition of Prussian blue is found to vary according to the method by which it is prepared. The inherent difficulties of characterization have been summed up by one principal group of investigators, thus:

> 'In fact, the chemical designation Prussian blue should be regarded as essentially a generic term for complex materials which may contain coprecipitated or occluded ions, indefinite amounts of water, possibly hydrolysed ferrocyanide, variable stoichiometry, and structural disorder.'[600]

This variability often precludes Prussian blue from lending itself to the rigorous minuteness of structural analysis that is customarily employed in modern physico-chemical investigations.

II.1 Methods of preparation

Prussian blue is, in essence, ferric ferrocyanide – or (to use IUPAC chemical nomenclature henceforth) iron(III) hexacyanoferrate(II). It may be conveniently precipitated from aqueous media by any of the following three types of reaction:

1 Iron(III) salts, $Fe^{3+}(aq)$, with hexacyanoferrate(II), $[Fe(CN)_6]^{4-}$.

2 Iron(II) salts, $Fe^{2+}(aq)$, with hexacyanoferrate(III), $[Fe(CN)_6]^{3-}$.
The product of this reaction was earlier thought to be a different substance, namely ferrous ferricyanide or iron(II) hexacyanoferrate(III), and was therefore distinguished by the name of Turnbull's Blue, after the manufacturing chemists of Glasgow. Recent studies, however, have unambiguously shown it to be essentially the same as Prussian blue. Nonetheless it is convenient to retain the name as an indication of the route by which it is prepared.

3 Iron(II) salts, $Fe^{2+}(aq)$, with hexacyanoferrate(II), $[Fe(CN)_6]^{4-}$.
This yields initially a precipitate of the colourless iron(II) hexacyanoferrate(II), known as Prussian white (or Berlin white, Williamson's salt or Everitt's salt). It is readily oxidised to Prussian blue, by oxidants such as air, hydrogen peroxide, dichromate, bromate, chlorate, hypochlorite, etc. When carried out in the presence of a large excess of ammonium ions, this is the industrial method for the manufacture, from commonly available materials, of the Prussian blue pigments of commerce:[601]

$$FeSO_4 + Na_4[Fe(CN)_6] + (NH_4)_2SO_4 \rightarrow (NH_4)_2Fe[Fe(CN)_6] + Na_2SO_4$$

$$(NH_4)_2Fe[Fe(CN)_6] + H_2SO_4 + NaClO_3 \rightarrow (NH_4)Fe[Fe(CN)_6] + NaCl + (NH_4)_2SO_4$$

The composition of Prussian blue depends on the relative proportions of the reactants used for its preparation: two formulations are usually defined, but blues of intermediate composition are also possible.[602] The extremes are conveniently, but inaccurately termed 'soluble' and 'insoluble' Prussian blue. Now, *all* forms of Prussian blue are highly insoluble in water, with a solubility product of *ca.* 10^{-40}, but the so-called 'soluble' form is, in fact, most readily peptized –*i.e.* dispersed as a blue colloidal suspension in water (a hydrosol)- thus giving the illusion of a true solution. This tendency to peptization of Prussian blue is of great importance to the blueprint process, where its occurrence during the wet treatment is most undesirable.

II.2 'Soluble' Prussian blue

This form is obtained when potassium hexacyanoferrate(II) and the iron(III) salt are reacted in 1:1 molar proportions, or when the hexacyanoferrate(II) is in excess. Its formula is usually written $KFe[Fe(CN)_6].H_2O$, although the water content is variable, and recent preparations have beeen reported to analyse as $KFe[Fe(CN)_6].5H_2O$.[603] Because single crystals of this variety have not yet been obtained, its proposed structure is based only on an early powder X-ray study by Keggin and Miles.[604] These authors found the powder pattern to be consistent with a face-centred cubic lattice, of probable space group Fm3m (O_h^5): the octahedral $[Fe(CN)_6]^{4-}$ units are centred on all the lattice sites, and all the octahedral holes (each surrounded by six N atoms of the cyanide groups) are occupied by Fe^{3+}; the centres of the octant cubes of the face-centred cubic unit cell (i.e. the sites of the formal 'tetrahedral holes' - although they are now cubically surrounded by Fe^{2+} and Fe^{3+} alternately) are thought to be occupied alternately by K^+ and H_2O. The lattice parameter is $a = 1016$ pm, and the number of formula units per unit cell, $Z = 4$. The unit cell of this idealised structure is illustrated in Fig 6. This is a very roomy crystal lattice, having a density of only 1.78 g/cm^3, which is quite low for an inorganic compound. It provides the simplest and most symmetrical model for discussing the structures of the metal hexacyanometallate family of compounds, many of which have been found to be derived from it.

The infrared spectrum of 'soluble' Prussian blue shows a single sharp peak at 2106 cm^{-1} in the ν(CN) stretching region, consistent with the single infrared-active, triply degenerate fundamental, species t_{1u}, for a regular octahedral O_h moiety $[Fe(CN)_6]^{4-}$. The Raman spectrum of electrodeposited Prussian blue[605] is reported to have peaks at 2089, 2123, and 2154 cm^{-1} which is not consistent with the regular octahedral structure, for which only two Raman-active fundamentals, $a_{1g} + e_g$, are predicted. Upon electroreduction these peaks are replaced by features at 2058, 2109, and 2140 cm^{-1} which are assigned to Prussian white.

Evidence from Mössbauer spectroscopy,[606,607] and photoelectron spectroscopy,[608] leave no doubt that all forms of Prussian blue and

Turnbull's blue are, essentially in terms of oxidation states, iron(III) hexacyanoferrate(II). The octahedrally-coordinated iron(II) is in the diamagnetic low-spin (t_{2g}^6) configuration, as would be expected for the very high ligand field of C-coordinated cyanide, while the octahedral iron(III) is in the high spin configuration ($t_{2g}^3e_g^2$), expected for the weak ligand field of the nitrogen donor atoms of the cyanide ligands, which is comparable with that of water in the spectrochemical series. These configurations account for the measured effective magnetic moment at room temperature, which corresponds to five unpaired electrons per two iron atoms.[609]

'Soluble' Prussian blues of formula $M^+Fe^{III}[Fe^{II}(CN)_6]^-$ can be prepared with other cations, M^+, as well as potassium, and many of these can be ion-exchanged because the the cubic cavity containing the cation is calculated to have an interior radius of 182 pm,[610] in comparison with the following radii due to Shannon and Prewitt:[611]

Li^+	Na^+	K^+	Rb^+	Cs^+	Tl^+	NH_4^+	
90	116	152	166	181	164	151 pm	(6-coordinate crystal radii)
	153	178	186	202	184		(12-coordinate crystal radii)

Thus, a soluble Prussian blue analogue may be obtained with Na^+, K^+, Rb^+, and NH_4^+ as cations in the lattice; Cs^+ is irreversibly trapped, and Li^+ cannot be incorporated at all because it is effectively much larger than the free-ion radius due to its firmly-bound primary hydration shell, $Li(OH_2)_4^+$. The preparation of Prussian blue using lithium salts yields the cation-free 'insoluble' form of Prussian blue (see below).[612] Moreover the sodium form can be irreversibly ion-exchanged for potassium, which is preferred.[613] When soluble Prussian blue is formed in the presence of acids, such as HCl, there is evidence that it incorporates some H_3O^+, which has a radius similar to NH_4^+.[614]

As mentioned above, this misnamed 'soluble' form is easily dispersed in water as nanoparticles (previously termed a colloid) – a tendency which is believed to be associated with the presence of the cations in the lattice. Replacement of K^+ by NH_4^+ diminishes the tendency to peptize. 'Soluble' Prussian blue may also be rendered less liable to peptization by treatment with a variety of multiply-charged cations, most notably Fe^{3+} and Ni^{2+}, which are also believed to be partially exchanged for the K^+ ions in the lattice. Rendering the Blue 'insoluble' is important, because it confers a greater degree of resistance to decomposition by alkalies.[615]

The toning of cyanotypes by Pb^{2+} or Tl^+ salts is very probably due to cation exchange in the cubic voids of the lattice. The incorporation of lead is improved in slightly alkaline conditions, which may suggest that it enters the lattice as $PbOH^+$. This ability of Prussian blue, which has a considerable affinity for Tl^+, has been exploited to provide a sensitive analytical electrode for determining thallium(I) ions in solution.[616] Reference has already been made in Chapter 3 to the effective use of Prussian blue as an antidote for absorbing toxic or dangerous cations such as thallium(I) or radiocaesium;[617] it has the benefit that no toxic effects of administering Prussian blue have been found either in animals or humans.[618]

II.3 'Insoluble' Prussian blue

This form results from preparations where the iron(III) salt is in large excess over the hexacyanoferrate(II), i.e. in molar proportions of 4:1 or more. It does not contain potassium ions in significant stoicheiometric amounts and, ideally, it has the composition $Fe_4[Fe(CN)_6]_3.14H_2O$, although the water content is variable, between 14 and 16 molecules. This form has been successfully grown as single crystals, which has enabled Ludi and co-workers to carry out a full 3-dimensional X-ray diffraction study,[619] and a neutron diffraction. study.[620] The structure determined by these authors can be conveniently described as a defect version of the ideal face-centred cubic lattice described above, in which one quarter of the $[Fe^{II}(CN)_6]$ groups are absent. Ludi et al. were able to carry out their least squares refinement in space group Pm3m (O_h^1), rather than in the Fm3m (O_h^5) of the ideal Keggin and Miles structure; the fact that the cubic cell, with a = 1017 pm, now appears primitive suggests at least a partial degree of ordering of the lattice vacancies. The cyanide sites thus emptied are reoccupied by extra water molecules to complete the octahedral coordination spheres about the remaining iron(III) centres, leading to an 'average' coordination sphere represented by $[Fe^{III}(NC)_{4\cdot5}(OH_2)_{1\cdot5}]$. If the $Fe^{II}(CN)_6$ vacancies are ordered, one per unit cell as is thought by Ludi et al, then one quarter of the iron(III) sites will remain as regular octahedral $[Fe^{III}(NC)_6]^{3-}$ and three-quarters will have the distorted octahedral coordination geometry trans-$[Fe^{III}(NC)_4(OH_2)_2]^-$. If, in writing the formula, we wish to emphasise the relationship to the ideal cubic lattice of $KFe^{III}[Fe^{II}(CN)_6]$, but with one quarter of the $[Fe^{II}(CN)_6]^{4-}$ sites vacant, the stoicheiometry may be appropriately represented as $Fe^{III}[Fe^{II}(CN)_6]_{¾}.3½H_2O$.[621]

It is possible that hydrolysis by proton loss can occur at the aquated iron(III) sites, effectively increasing the charge on the centres to

$[Fe^{III}(NC)_4(OH)(OH_2)]^{2-}$, or even $[Fe^{III}(NC)_4(OH)_2]^{3-}$. The extent of this hydrolysis will depend on the pH of the system. It is possible that the dramatic effect of gaseous ammonia on the colour, which is fully reversible, may be due to this deprotonation. It has been noted that the widths of peaks in both infrared spectra and powder X-ray patterns are significantly narrower for specimens of Prussian blue prepared in acidic media.[622] The presence of different iron(III) centres in this variety of Prussian blue is believed to be responsible for the broadening and splitting of the absorption band corresponding to the ν(CN) stretching vibrations, which are observable in the infra-red spectrum around 2080 cm^{-1}, compared with the single sharp peak at 2106 cm^{-1} in the 'soluble' form.[623]

If each octant cube centre in the unit cell were occupied by one water molecule, and the 'missing' cyanides each replaced by one water, there should be a total of 8 ('zeolytic') + 6 ('coordinated') = 14 water molecules in the unit cell. The neutron diffraction study confirms this, but with the additional proviso that some of the 'zeolytic' water may become hydrogen-bonded to the 'coordinated' water. A proton n.m.r. study of 'insoluble' Prussian blue demonstrates that there are, indeed, three different types of water molecule in the lattice, rather than two, and this is confirmed by thermogravimetric analysis of the thermal dehydration of the substance; but the quantitative findings are not fully in accord with the previous formulation: up to 65°C there is a continuous loss of six 'zeolytic' water molecules per unit cell; around 95°C there is a fairly abrupt loss of four 'lattice' waters (presumed to be hydrogen-bonded to the coordinated waters), and finally at 125°C there is another stepped loss of four water molecules (presumed to be coordinated in the primary coordination sphere around the iron(III) centres).[624] Prussian blue does not begin to decompose thermally until the temperature exceeds 200°C.[625] Dehydrated Prussian blue is extremely hygroscopic, taking up water from the atmosphere most readily. This form of Prussian blue can also take up suitably-sized cations from solution; indeed, there is evidence that it is somewhat more effective than the 'soluble' form as a detoxifying agent.[626]

II.4 Turnbull's blue

The blue precipitate obtained from the reaction of iron(II) salts with hexacyanoferrate(III) ions is definitely not iron(II) hexacyanoferrate(III), as was originally thought; instead, irreversible electron transfer between the two iron centres immediately gives an iron(III) hexacyanoferrate(II),[627] essentially the same as Prussian blue. However, it will be convenient to retain the historical name, Turnbull's blue, when it is important to emphasise the route by which this modification is prepared.

Wilde and co-workers have obtained infra-red spectra to suggest that Turnbull's blue can also exist in 'soluble' and 'insoluble' forms, with and without incorporated cation, respectively, but the evidence is indirect.[628] Turnbull's blue is the least well-investigated of the iron blues by analytical or spectroscopic means, but there is now some evidence emerging that it may differ significantly in composition from both the 'soluble' and 'insoluble' forms of Prussian blue previously described.

Recently, further light has been shed on the nature of Turnbull's blue by the Mössbauer spectroscopy of Reguera and co-workers,[629] who find that the relative intensities indicate that the two iron centres in the solid are in the stoicheiometric ratio Fe(III):Fe(II) = 3:2, rather than the 1:1 ratio of 'soluble' Prussian blue or the 4:3 ratio of the 'insoluble' variety. Accordingly, they postulate that an anion must be incorporated into the structure to restore charge neutrality, suggesting formulae for Turnbull's blue of the type $\mathrm{Fe^{III}_3[Fe(CN)_6]_2{}^+X^-}$ where $\mathrm{X^-}$ is a singly charged anion such as $\mathrm{OH^-}$ or $\frac{1}{2}(\mathrm{SO_4{}^{2-}})$. In keeping with the model based on a defect cubic lattice, this formula can be re-written as $\mathrm{Fe^{III}[Fe^{II}(CN)_6]_{2/3}X_{1/3}}$, showing that one third of the hexacyanoferrate(II) ions are absent from the perfect cubic structure, giving a lattice that resembles 'insoluble' Prussian blue, but with an even greater proportion of vacancies, probably re-occupied by foreign anions and water. The average coordination geometry of the iron(III) centres is $\mathrm{[Fe^{III}(NC)_4(OH_2)_2]}$, but this is only a mean of a statistical distribution over several coordination species. In support of this conjecture, the X-ray diffraction powder patterns for Turnbull's blue and 'insoluble' Prussian blue match rather closely, both having peaks much broader than those for 'soluble' Prussian blue, due to their disordered lattices. There is additional evidence for the incorporation of anions in Prussian blue from X-ray fluorescence element analysis, and infrared spectra.[630] The whole family of Prussian blue related compounds is compared in Table II.1, where f_r denotes the fraction of iron(III) sites occupied in the ideal cubic lattice.

Substance	**Formula**	**f_r**	**Oxidation States**
Soluble Prussian blue	$KFe[Fe(CN)_6]$	1	$KFe^{III}[Fe^{II}(CN)_6]$
Insoluble Prussian blue	$Fe_4[Fe(CN)_6]_3$	¾	$Fe^{III}[Fe^{II}(CN)_6]_{\frac{3}{4}}$
Turnbull's blue	$Fe_3[Fe(CN)_6]_2\ X$	⅔	$Fe^{III}[Fe^{II}(CN)_6]_{\frac{2}{3}}\ X_{\frac{1}{3}}$
Prussian white	$K_2Fe[Fe(CN)_6]$	1	$K_2Fe^{II}[Fe^{II}(CN)_6]$
Berlin green	$[Fe(CN)_6]_{\frac{2}{3}}$ $[Fe(CN)_6]⅓^{10/3-}$		$[Fe^{III}(CN)_6]_{\frac{2}{3}}$ $[Fe^{II}(CN)_6]_{\frac{1}{3}}^{10/3-}$
Prussian yellow	$Fe[Fe(CN)_6]$	1	$Fe^{III}[Fe^{III}(CN)_6]$

Table II.1 Varieties of Prussian blue and related compounds

II.5 Electronic spectrum of Prussian blue

The substance is a prototype for a whole class of 'mixed oxidation state' compounds, which are all characterised by intense colours. The absorption of light by Prussian blue is due to a strong broad band centred around 700 nm in the red region of the visible spectrum.[631] Different authors vary somewhat in the value they assign to the band maximum, λ_{max}, which may well be a reflection of the variability of the composition of the substance. Indeed, Mortimer and Rosseinsky have proposed that the value of λ_{max} can be used to characterise the type of Prussian blue, with the 'soluble' variety peaking at $\lambda_{max} = 690$ nm (14,500 cm^{-1}) and the 'insoluble' variety at $\lambda_{max} = 730$ nm (13,700 cm^{-1}).[632] This shift in λ_{max} could be attributed to the differing ligand field splittings in the Fe(III) centres, where N-bonded cyanide ligands are replaced partly by water in the latter compound. An alternative view has been put forward that the apparent shift may be due to partial oxidation of the hexacyanoferrate(II) centres (see below).

Values for the molar decadic extinction coefficient, $\mathcal{E}$[633] also range rather widely with different investigators; from 0.98×10^4 $dm^3mol^{-1}cm^{-1}$ to 2×10^4 $dm^3mol^{-1}cm^{-1}$. A value of 1.55×10^4 $dm^3mol^{-1}cm^{-1}$, measured for thin films of Prussian blue,[634] will be taken in this work as a mean value.

The interpretation of the electronic spectrum considers the visible bands to be due to charge transfer: the 700 nm absorption corresponds to the energy change arising from the transfer of an electron from the low-spin Fe(II) to the high-spin Fe(III) centre.[635,636] This transition corresponds to the change in one-electron configurations:

$$\{Fe^{III}(t_{2g}{}^3e_g{}^2)\ Fe^{II}(t_{2g}{}^6)\} \rightarrow \{Fe^{II}(t_{2g}{}^4e_g{}^2)\ Fe^{III}(t_{2g}{}^5)\}^*$$

where the star denotes an excited state. The transition is allowed because it involves transfer of an electron from a t_{2g} orbital on one centre to a similar orbital on the other, with no change in net spin.

There is also a weaker absorption band at 400 nm (25,000 cm^{-1}) in Prussian blue, corresponding to the transition arising from the configuration change:

$$\{Fe^{III}(t_{2g}{}^3e_g{}^2)\ Fe^{II}(t_{2g}{}^6)\} \rightarrow \{Fe^{II}(t_{2g}{}^3e_g{}^3)\ Fe^{III}(t_{2g}{}^5)\}^*$$

Here the electron is transferred from a t_{2g} orbital on one centre to an e_g orbital on the other, which is forbidden by local orthogonality. The difference in energy between the two bands can be seen to be equal to the ligand field splitting (10,500 cm^{-1}) for an $Fe^{II}N_6$ moiety, which is further evidence for the correct assignment of the iron oxidation states. More precisely expressed,[637] the permitted absorption corresponds to a transition from the totally symmetric ground state, $^6A_{1g}$, to two near-degenerate excited states of $^6T_{1u}$ symmetry.

II.6 Iron(III) aquapentacyanoferrate(II)

It has long been known that the monoaquopentacyanoferrate(II) complex anion can be obtained from hexacyanoferrate(II) by a photoaquation:[638]

$$h\nu + [Fe(CN)_6]^{4-} + H_2O \rightarrow [Fe(CN)_5(OH_2)]^{3-} + CN^-$$

and that this complex anion is also capable of yielding an ‘iron blue’ with iron(III). Only recently, however, has this corresponding ferric aquapentacyanoferrate(II) (FAPCF) been isolated in pure form, as $Fe^{III}[Fe^{II}(CN)_5(OH_2)]$, and characterised by X-ray diffraction of the powder.[639] The substance exhibits a moderate contraction, but no significant distortion of the cubic lattice. The visible absorption spectrum differs from that of Prussian blue in that the 680 nm band suffers a bathochromic shift to around 780 nm, due to the diminished average ligand field splitting at the aquated iron(II) centres. Visually, this corresponds to a more greenish blue. The electrochemical behaviour resembles that of Prussian blue, showing reversible oxidative and reductive waves at similar potentials.

The complex aquated anion $[Fe^{III}(CN)_5(OH_2)]^{2-}$ is likewise formed by hydrolysis of hexacyanoferrate(III), promoted by light, acids, or by ‘overoxidation’ of the hexacyanoferrate(III):

$$[Fe(CN)_6]^{3-} + Cl_2 + H_2O \rightarrow [Fe(CN)_5(OH_2)]^{2-} + Cl^- + ClCN$$

It is probably present in 'old' solutions of potassium hexacyanoferrate(III), which discolour from yellow to olive-brown. An early investigation of this problem also noted:

> 'Some crystals of potassium ferricyanide have a brownish-green tinge instead of the bright ruby-red colour...due to the presence of a small quantity of the violet aquopentacyanoferrate(III).'[640]

The potassium salts are isomorphous and can co-crystallise as the greenish-brown salt $3K_3[Fe(CN)_6].K_2[Fe(CN)_5(OH_2)]$. The presence of the aquated complex anion may be responsible for some of the colour differences observed between cyanotypes, especially the greener tones of older 19th century specimens made with impure hexacyanoferrate(III), which was often prepared by chlorine oxidation.

II.7 Investigation of cyanotype Prussian blue

The process of forming a traditional negative-working cyanotype, where an iron(II) photoproduct encounters hexacyanoferrate(III) in the sensitizer, corresponds in part to the preparative method for Turnbull's blue, with the hexacyanoferrate(III) always in excess; however it should also be born in mind that some of the image substance (that which has been 'solarized') will result from the re-oxidation of Prussian white by air, which is believed to yield the 'soluble' form of Prussian blue. The crucial question for the present investigation is: which of the forms of Prussian blue described above most nearly represents the pigment of a cyanotype? Or are the process and the substance so variable as to make this question meaningless? In situ analysis and spectroscopic investigation of the Prussian blue of a cyanotype are made difficult by the relatively small amounts of the substance present and the predominance of the cellulose substrate. Infrared spectroscopy usually provides a diagnostic 'fingerprint' for a substance; although the various types of Prussian blue are not very well differentiated by their infrared spectra, it is possible to distinguish the 'pure, undiluted' forms by the stretching vibrations of the cyanide groups, $\nu(CN)$, as indicated in Table 18.

In the case of the simple, non-defect, face-centred cubic lattice assumed for 'soluble' Prussian blue, Prussian white and Prussian brown, the site symmetry for the $Fe(CN)_6$ moities is regular octahedral, point group O_h. Vibrational theory leads us to expect a single feature in the $\nu(CN)$ region of the infrared: the triply degenerate infrared active t_{1u} normal mode. For the lattices having anion vacancies, the consequent lowering of site symmetries will give rise to broadening and splitting of this degenerate fundamental, as is seen in the spectra of ‘insoluble’ Prussian blue and Turnbull’s blue which have envelopes containing unresolved bands.

The infrared spectra of cyanotypes, prepared by various formulae, were obtained using a Matson ‘Genesis’ Fourier-transform infrared instrument with diffuse reflectance attachment, at the Chemistry Department of Manchester University.[641] Results were found to be essentially the same for all preparations involving the two-component sensitizers, regardless of their composition. All these cyanotype spectra showed a single ν(CN) absorption band peaking at 2090 cm^{-1} which was broad and had indications of a shoulder at *ca.* 2060 cm^{-1}; this pattern does not correspond exactly with any of the ‘control’ spectra.

Substance	**Formula**	**ν(CN)/cm^{-1}**	**Fe(II) Sites**
Soluble Prussian blue	$KFe^{III}[Fe^{II}(CN)_6].H_2O$	2106 vs sp	O_h
Insoluble Prussian blue	$Fe^{III}[Fe^{II}(CN)_6]_{\frac{3}{4}}.3\frac{1}{2}H_2O$	2106 m 2080 vs	O_h (¼) D_{4h} (¾)
Turnbull’s blue	$Fe^{III}[Fe^{II}(CN)_6]_{\frac{2}{3}}X_{\frac{1}{3}}.H_2O$ X = anion$^-$	2112 vs 2052 m	O_h (⅓) D_{4h} ?(⅔)
Prussian white	$K_2Fe^{II}[Fe^{II}(CN)_6]$	2085 vs sp	O_h
Berlin green	$K_{10/3}[Fe^{III}(CN)_6]_{\frac{2}{3}}[Fe^{II}(CN)_6]_{\frac{1}{3}}$	2074 2169	
Prussian brown	$Fe^{III}[Fe^{III}(CN)_6]$	2175 vs	O_h (Fe(III)
Cyanotype blue (Herschel)	$Fe^{III}[Fe^{II}(CN)_6]X.nH_2O$	2090 vs bd 2063 sh	
Proto-Cyanotype blue (Smee)	$Fe^{III}[Fe^{II}(CN)_5(OH_2)]$?	2071 vs bd	C_{4v}

Abbreviations: vs, very strong; m, medium; sp, sharp; bd, broad

Table Infrared spectra ν(CN) of Prussian blues and derivatives

The rather inconclusive inference to be made from these spectra is that ‘cyanotype Prussian blue’ is not identical with any one of the ‘established’ varieties, but it more nearly resembles ‘insoluble’ and Turnbull’s blue than ‘soluble’ Prussian blue. It does not have the regular crystalline structure, but is defective, possibly amorphous, and most of the iron(III) centres are likely to be aquated, and some partially hydrolysed. Prussian blue nanoparticles synthesised by the same photochemical method as used in new cyanotypes have been synthesised in emulsions and studied by electron microscopy, electron diffraction and energy-dispersive x-ray analysis.[642] The unit cell parameter was found to be 1013 pm and the TEM showed regular cubic Prussian blue nanoparticles, 12 nm in size. The visible absorption band was broad 680 nm and the infrared spectrum showed a peak at 2069 cm^{-1}.

The only cyanotypes that produced a significantly different infrared spectrum were those prepared from the single-component sensitizer of potassium hexacyanoferrate(III) alone: the peak here is at 2071 cm^{-1}. This lower frequency is an indication of an increase in the $t_{2g} \rightarrow \pi^*$ back-bonding from iron(II) d orbitals to the antibonding molecular orbitals of the cyanide, which would be consistent with the complex anion being aquated $[Fe(CN)_5(OH_2)]^{2-}$, as might be expected from the known photochemistry of hexacyanoferrate(III). Further evidence supporting this supposition comes from the visible spectra.

UV-Visible absorption spectra (220 - 880 nm) of these varieties of cyanotype were obtained using a Shimadzu UV-260 instrument in reflectance mode at the Chemistry Department of Manchester University.[643] There is little difference between the specimens prepared from the various two-component sensitizers, all show a broad absorption peaking at *ca.* 700 nm. But, once again the cyanotypes prepared from potassium hexacyanoferrate(III) alone are significantly different, in that the band maximum is shifted to 780 nm. Taken together with the infrared spectra, this evidence suggests that the form of Prussian blue produced by the 'proto-cyanotype' process is the variety with the aquated anion, FAPCF, $Fe^{III}[Fe^{II}(CN)_5(OH_2)]$.

II.8 Hydrolysis of Prussian blue

Prussian blue is stable in the presence of acids of moderate strength, down to pH 1 or 2, but is readily decomposed by alkalies at pH 10 and above, which hydrolyse the iron(III), and take the hexacyanoferrate(II) into solution, thus:

$$Fe[Fe(CN)_6]^- + 3OH^- \rightarrow \text{'}Fe(OH)_3\text{'} + [Fe(CN)_6]^{4-}$$

'Ferric hydroxide', which is more accurately described as a precipitated hydrous iron(III) oxide gel, only retains the capability of being dissolved by acids while freshly precipitated; immediate acidification can therefore reverse this hydrolysis reaction, regenerating

Prussian blue. However, ‘ferric hydroxide’ slowly transforms, over a period of a few days, to more highly polymerized crystalline forms, such as goethite, α-FeO(OH), which cannot be readily dissolved in dilute acids.[644] With time, therefore, the alkaline destruction of Prussian blue becomes permanent and irreversible.

This is an appropriate point to note that the ‘bleaching’ of Prussian blue by a concentrated solution of an oxalate is neither a hydrolysis nor a reduction, but a destruction of the Prussian blue lattice by the small oxalate ion penetrating it and complexing the iron(III); the products are completely soluble:

$$\mathrm{Fe[Fe(CN)_6]^-} + 3\mathrm{C_2O_4^{2-}} \rightarrow \mathrm{[Fe(C_2O_4)_3]^{3-}} + \mathrm{[Fe(CN)_6]^{4-}}$$

A 20% solution of potassium oxalate cleanly decomposes and dissolves Prussian blue, and can be used for stain-removal, title-writing on cyanotypes, or, at a lower concentration, for ‘reducing’ the blue density, provided the soluble products are removed afterwards by a brief wash in water.

II.9 Prussian white

The colourless, insoluble reduction product of Prussian blue is iron(II) hexacyanoferrate(II), otherwise known as Prussian white, Everitt’s salt or Williamson’s salt. If the two types of iron centre are equal in number, as is generally believed, the formula must incorporate two cationic charges for electroneutrality: $\mathrm{M_2Fe^{II}[Fe^{II}(CN)_6]}$, where M is a singly charged cation, usually $\mathrm{K^+}$ or $\mathrm{NH_4^+}$.

The substance is readily oxidised by air, in the presence of water molecules, to Prussian blue:

$$4\mathrm{Fe[Fe(CN)_6]^{2-}} + \mathrm{O_2} + 2\mathrm{H_2O} \rightarrow 4\mathrm{Fe[Fe(CN)_6]^-} + 4\mathrm{OH^-}$$

Many other oxidants will also effect this transformation, e.g. chlorate, bromate, dichromate, permanganate, and hydrogen peroxide. There is analytical evidence that the Prussian blue formed by oxidation of Prussian white is of the ‘soluble’ – i.e. cation-containing – variety. It should be especially noted that all these oxidations consume hydrogen ions, tending to make the system more alkaline, and this is supported by some analytical evidence for the formation of hydroxide in the system.[645] If hydrolysis of the resulting Prussian blue is to be avoided, such oxidations are best carried out under acidic conditions. The electrochemical reduction of Prussian blue by cyclic voltammetry (see below) shows that the process is fully reversible provided an adequate supply of suitable cations is available to diffuse in and out of the lattice to maintain charge neutrality.

The structure of Prussian white has not been fully determined, due to lack of single crystals, but Keggin and Miles reported observing a cubic X-ray diffraction pattern for the powder, similar to that of Prussian blue itself, and with a slightly larger lattice parameter, for which a value of 1036 pm has been proposed.[646] It is generally supposed, therefore, that the structure is regular face-centred cubic, like that proposed for 'soluble' Prussian blue, but with all the octant cube centres, which have a slightly larger radius of 192 pm, occupied by cations, usually K^+ or NH_4^+. The absence of colour in the substance is obviously due to the lack of any facile transition involving inter-valence electron charge transfer.

II.10 Berlin green

Oxidation of Prussian blue by nitric acid results in 'Berlin green' or 'Prussian green', which can also be obtained by heating iron(III) chloride and potassium hexacyanoferrate(III) in the dark, or by the action of chlorine on a boiling solution of potassium hexacyanoferrate(II).647 It was originally formulated as iron(III) hexacyanoferrate(III), $Fe[Fe(CN)6]$, but this presumption is now known to be incorrect. Keggin and Miles found its X-ray powder diffraction pattern to be cubic, with similar unit cell dimensions to Prussian blue, and presumed that the lattice was the same as that proposed for 'soluble' Prussian blue and Prussian white, but with no cations at all in the octant cube centres.

However, this green substance turns out to be an intermediate, which always contains some iron(II); from electrochemical studies the complex anion has been formulated as:[648]

$$[Fe^{III}(CN)_6]_{⅔}[Fe^{II}(CN)_6]_{⅓}{}^{10/3-}$$

although the extent of oxidation of Prussian blue has been shown to be cation dependent, and alternative formulations have been proposed.[649]

It was first pointed out by de Wet and Rolle that a mixture of iron(III) chloride and hexacyanoferrate(III) is evidently powerfully oxidising, because the chloride anion is oxidised with the evolution of chlorine[650]:

$$FeCl_3 + [Fe(CN)_6]^{3-} \rightarrow \text{Berlin Green} + Cl_2$$

which, with excess ferric chloride, leads to the formation of Prussian blue and more chlorine. For this reason, any inclusion of ferric ions in the developer for a cyanotype leads to blue fogging of the background, due to reaction with excess hexacyanoferrate(III).

II.11 Prussian brown or yellow

The brown mixture of iron(III) and hexacyanoferrate(III) also rapidly turns blue when spotted onto cellulose filter paper or any other oxidisable substrate.[651] Ferric ion in the presence of hexacyanoferrate(III) has a very high oxidising power, much stronger than either ion separately, because the insolubility of the reduction product, Prussian blue, drives the reaction and makes the redox potential about +1.5V, and so it forms in the presence of almost any oxidisable substance. This has provided the basis for a qualitative analytical spot-test[652] – a "classic reaction for the detection of H_2O_2",[653] but it must be a very non-specific unless H_2O_2 is the only oxidisable species present.

It has been suggested that in this system bound cyanide ions themselves may be oxidised, even in the solid state:

$$Fe^{3+} + [Fe(CN)_6]^{3-} + 2H_2O \rightarrow Fe^{2+} + [Fe(CN)_5]^{3-} + NH_4^+ + CO_2$$

accounting for the fact that solid iron(III) hexacyanoferrate(III) cannot be isolated from the aqueous system, and the product is always green.

Recently, the sophisticated techniques of cyclic scanning voltammetry (see below) have enabled the preparation of pure Prussian yellow, presumed to correspond to $Fe^{III}[Fe^{III}(CN)_6]$, on a platinum electrode surface when the potential reaches ca. +1.5 V on the Hydrogen Scale.[654] This potential is high enough to bring about the oxidation of water, which provides another reason why the substance cannot be isolated in pure form from aqueous solution:

$$4Fe[Fe(CN)_6] + 6H_2O \rightarrow 4(H_3O)Fe[Fe(CN)_6] + O_2$$

II.12 Electrochemical studies of redox behaviour

The standard redox potentials for iron(III)/iron(II) couples only have a limited utility when applied to the Prussian blue family of substances, owing to the large influence that insolubility has on the positions of equilibria. For instance, it was once argued that the formulation of Prussian blue itself as iron(III) hexacyanoferrate(II) was contrary to the standard redox potentials:

$E^0(Fe^{3+}/Fe^{2+}) = +0.771$ V

$E^0([Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}) = +0.356$ V

which would imply that Fe^{3+} will oxidise hexacyanoferrate(II), and that the stable form of the compound ought to be iron(II) hexacyanoferrate(III). Clearly the iron(III)/iron(II) redox potentials are considerably raised from their standard values by the formation of insoluble reaction products such as Berlin green and Prussian blue, so that a mixture of Fe^{3+} and $[Fe(CN)_6]^{3-}$ becomes capable of oxidising chloride ions:

$E^0(Cl_2/Cl^-) = +1.358$ V

or cellulose:

$E^0(RCHO, 2H^+/RCH_2OH) = +0.18$ V

The magnitude of this insolubility effect on the iron(III)/iron(II) redox couples is highlighted by the fact that the reverse reaction occurs under ‘standard’ conditions: hexacyanoferrate(III) may be prepared from hexacyanoferrate(II) by oxidation with chlorine gas:

$$Cl_2 + [Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-} + Cl^-$$

Owing to the high insolubility of Prussian blue (solubility product, $K_s \approx 10^{-40}$) modifying the standard potentials,[655] the electrochemistry has to be studied by cyclic voltammetry of the solid coated on an inert electrode surface dipped into suitable electrolytes. It was first shown by Neff in 1978 that a platinum electrode can be coated with Prussian blue.[656] Since then, thin films of the substance, prepared by reductive electrodeposition from an electrolyte solution containing iron(III) and hexacyanoferrate(III), have been extensively studied, because of the potential commercial applications for electrochromic display devices.[657] The thin films so deposited have coating weights comparable with those obtained in cyanotypes. The precise nature of the Prussian blue obtained electrochemically has been disputed, but it is now thought that the ‘insoluble’ variety is deposited initially for kinetic reasons connected with faster flocculation, but the process of reductive cycling of the electrode through a voltage range in a potassium ion electrolyte leads to its conversion to the ‘soluble’ form, incorporating potassium ions, which is the more thermodynamically stable,[658] although there is evidence from infra-red spectroscopy that this conversion may not be complete.[659] The voltammograms show anodic waves, occurring approximately at the following values, expressed on a scale relative to the Standard Hydrogen Electrode:

$E(Fe^{III}[Fe^{II}(CN)_6]^-/Fe^{II}[Fe^{II}(CN)_6]^{2-}) = +0.46$ V (White → Blue)

$E(\text{Berlin Green} / Fe^{III}[Fe^{II}(CN)_6]^-) = +1.17\ V$ (Blue → Green)

$E(Fe^{III}[Fe^{III}(CN)_6] / \text{Berlin Green}) \approx +1.5\ V$ (Green → Yellow)

The first two waves are fully reversible in an appropriate electrolyte, for instance the White → Blue transition has been cycled as many as 10^7 times in a single sample;[660] but the last oxidation wave to Prussian yellow is irreversible. Although these potentials are not strictly comparable with standard redox potentials, they do convey a qualitative idea of the redox chemistry, and explain why Prussian blue is the most stable member of this family of substances. The anodic oxidation wave occurring at a potential of ca. +0.46 V on the Standard Hydrogen Electrode scale implies that Prussian blue, in its ground-state, is not significantly oxidising in general chemical terms; it also explains why Prussian white is readily oxidised by air because $E^0(O_2, 4H^+/2H_2O) = +1.229$ V, and why, by the same token, Prussian yellow, with a potential of +1.5 V, can oxidise water to oxygen gas, as was noted above.

It has recently been shown that microcrystalline solid particles of Prussian blue or Turnbull's blue, prepared by conventional aqueous precipitation, can be mechanically attached to suitable electrodes and that they also display very similar redox properties to the thin films of Prussian blue generated electrochemically, so the observations summarised above also seem generally valid for the 'bulk material'.[661]

Appendix III Photochemistry of Cyanotype

The phenomenology of the cyanotype process has not yet received a full chemical explanation, nor has its mechanism been completely elucidated. Published accounts agree in outline that photo-induced reduction of iron(III) to iron(II) is the primary reaction, and the iron(II) then reacts with hexacyanoferrate(III) to give 'Turnbull's blue'; but this blue was long believed, mistakenly, to be iron(II) hexacyanoferrate(III).[662,663,664,665,666] It has not previously been pointed out that the photochemically-produced iron(II) is still coordinated by carboxylates, and must be divested of its ligands before it can be incorporated into the Turnbull's blue lattice. Furthermore, the extensive 'solarization', or tonal reversal which is observed when most cyanotype sensitizers are well-exposed, has received explanations which are neither in agreement with one another, nor photochemically plausible. None of the existing texts gives any account of the more recent commercial blueprint sensitizers, called Type B and Type C, which operate on chemical principles somewhat different to the traditional Type A.

It is the author's conviction that the solarization of cyanotypes observed during the printing exposure has a commonality with the photochemical fading of processed cyanotypes. Both phenomena become explicable on the basis that ***Prussian blue itself is a highly photoactive substance - but only when in intimate contact with an electron donor***. The eventual purpose of this Appendix is to offer some background to, and evidence for, this assertion, which will help remove apparent contradictions in the anecdotal evidence regarding the stability of Prussian blue and the fading and reversal of blueprints and cyanotypes. However, the appropriate point to begin this appendix is with a detailed account of the photochemistry underpinning the cyanotype sensitizers, as far as it is currently understood.

III.1 Light-sensitive iron(III) carboxylates

Photosensitivity has been noted in a number of salts or, more properly, complexes of iron(III) with the carboxylic acids which are listed in the Table III.1; many of these occur naturally in the plant kingdom, most notably oxalic, citric, and tartaric acids. On irradiating the iron(III) salts or complexes of these acids with light having some blue or ultra-violet content, electron charge is transferred from ligand to metal: the iron(III) is reduced to iron(II) and the ligand subsequently undergoes oxidative decarboxylation.

oxalic acid	$COOH.COOH$
glyoxylic acid	$CHO.COOH$
formic acid	$HCOOH$
pyruvic acid	$CH_3CO.COOH$
lactic acid	$CH_3CH(OH)COOH$
phenyllactic acid	$CH_3C(C_6H_5)(OH)COOH$
citric acid	$CH_2COOH.C(OH)COOH.CH_2COOH$
isocitric acid	$CH(OH)COOH.CHCOOH.CH_2COOH$
tartaric acid	$CH(OH)COOH.CH(OH)COOH$
malic acid	$CH(OH)COOH.CH_2COOH$
glycolic acid	$CH_2(OH)COOH$
mandelic acid	$C_6H_5CH(OH)COOH$
hydroxybutyric acid	$CH_3CH_2CH(OH)COOH$
malonic acid	$HOOCCH_2COOH$
succinic acid	$HOOCCH_2.CH_2COOH$
fumaric acid	$HOOCCH{=}CHCOOH$
aconitic acid	$HOOCCH_2C(COOH){=}CHCOOH$

Table III.1 Carboxylic acids having photosensitive iron(III) salts

It appears that one structural feature of such ligands that enhances photosensitivity, but is not essential for it in all cases, is the presence of an α-hydroxy group, which enables the oxidative decarboxylation to proceed without leaving behind an energetically unfavourable carbonium ion. Thus ferric acetate, by contrast, shows no evidence of photoactivity at all, and the succinate has only low sensitivity.

A general mechanism for the photochemistry of the α-hydroxycarboxylato-iron(III) salts was first proposed by Balzani and Carrassiti:[667]

$$h\nu + [Fe^{III}(RCH(OH)COO)]^{2+} \rightarrow [Fe^{II}(RCH(OH)COO\cdot)]^{2+}$$

$$Fe^{III} + [Fe^{II}(RCH(OH)COO\cdot)]^{2+} \rightarrow 2Fe^{II} + RCHO + CO_2 + H^+$$

In a number of cases for the acids listed above, the expected ketonic oxidation products have been identified. The primary photochemical reaction is assumed to be an intramolecular redox process in the complex caused by electron transfer from a coordinated anion to iron(III);

the radical formed in the primary process can then reduce an unexcited complex, leading to the formation of the final products with a theoretical quantum yield (in terms of Fe^{2+}) of $\phi = 2.0$, but ϕ is generally observed to be lower than this owing to competition from the reverse dark reaction.

III.2 Quantitative aspects of the photochemistry

The yield of photoproduct for an iron-based process has been calculated for typical parameters in a platinum/palladium sensitizer.668 To obtain a full scale image, exposure times in the order of two minutes were predicted for a UVA light source delivering a power flux of 50 W/m2 at a wavelength of 365 nm. This calculation is born out in practice. A similar approximate calculation for cyanotype, where the formation of the Prussian blue image is not so efficient, now follows.

The exposure, It, needed to bring about photochemical change in m moles of substance is given approximately by:

$$It = mNhc/A\lambda\phi f$$

Where:

I is the irradiance in W/m^2

t is the exposure time in s

m is the number of moles of substance transformed by light

N is Avogadro's number $= 6.023 \times 10^{23}\ mol^{-1}$

h is Planck's constant $= 6.626 \times 10^{-34}$ J s

c is the speed of light $= 2.998 \times 10^{8}$ m/s

A is the area of normal surface irradiated in m^2

λ is the wavelength of radiation in m (assumed monochromatic)

ϕ is the quantum efficiency of the photoactive species at wavelength λ

f is the fraction of the incident radiation absorbed by the photoactive substance at wavelength λ (f is assumed, for simplicity, to be independent of the exposure - an assumption that will only be good for small changes). For a two-component system, in which ε_P and C_P denote the molar absorptivity and concentration of the photoactive component, P, and ε_F and C_F denote the same for the inert filter, the fraction of light absorbed by P in the sensitized layer is given by:

$$f = (1-10^{-D})\varepsilon_P C_P d\ /D$$

where the optical density D of the layer, assuming the Beer-Lambert law holds,[669] is:

$$D = (\mathcal{E}_P C_P + \mathcal{E}_F C_F)d$$

where d is the layer thickness in cm.

In cyanotype sensitized layers, f is strongly wavelength-dependent owing to the intense absorption spectrum of the hexacyanoferrate(III) anion, which acts as an 'internal filter'. Knowing the absorption spectra of the two components, P (trisoxalatoferrate) and F (hexacyanoferrate) and the coating weight of the sensitizer, f can be calculated at various wavelengths. At 365 nm, for a typical cyanotype coating, $f = 0.65$, but this falls off rapidly with longer wavelengths as the absorption of hexacyanoferrate increases and that of trisoxalatoferrate decreases, so that at 420 nm, $f = 0.03$.

If the waveband of useful available actinic light is taken as 300-430 nm, a median value is $\lambda = 365$ nm, (corresponding with the atomic mercury line at the maximum emission of most UVA lamps).[670]

Then, inserting values for the physical constants:

$$Nhc/\lambda = 3.28 \times 10^5 \text{ J/mol}$$

We may estimate an 'order of magnitude' figure for the limiting maximum sensitivity to light of any photochemical system without amplification, if we assume optimum conditions for the photochemistry by setting $\phi = f = 1$, giving:

$$It = 3.28 \times 10^5\ m/A \text{ J/m}^2$$

If it is further assumed that all the photoproduct is converted into image pigment, and that a just-perceptible image ($D_{min} = 0.02$) is provided by a coating weight of pigment $m/A = 10^{-5}$ mol/m^2,[671] we arrive at a minimum exposure:

$$It = 3.28 \text{ J/m}^2$$

To obtain a tone of mid-density, would require about ten to twenty times this much exposure;[672] to obtain the maximum optical density, D_{max}, corresponding to an image coating weight of about $m/A = 10^{-3}$ mol/m^2,[673] would require about 300 J/m^2. These figures for the sensitivity at the limiting assumption of $\phi = f = 1$ may be compared with the calculations of Brinckman et al, who arrived at a typical figure of 82 J/m^2 for an image of maximum density.[674]

In the case of cyanotype, the molar coating weight, W, of Prussian blue needed to provide a maximum optical reflectance density ($D_{max} = 1.55$)

may be calculated from its molar extinction coefficient, or absorptivity, $\mathcal{E}$:[675]

$$W = 5D_{max}/\mathcal{E}$$

inserting the value of $\mathcal{E}$ for Prussian blue (Appendix II):

$$\mathcal{E} = 1.55 \times 10^4 \text{ dm}^3/\text{mol/cm}$$

the image coating weight for a typical $D_{max} = 1.55$ is found to be:

$$W = 5 \times 10^{-4} \text{ mol/m}^2$$

but we cannot identify this with the coating weight of the photoproduct, m/A, because the reaction forming Prussian blue from the iron(II) oxalato complex may be less than 100% efficient.

For a UVA source delivering 50 W/m^2, the time required in practice for a full exposure of such a cyanotype sensitizer is found to be about two minutes, corresponding to an exposure $It = 6000$ J/m^2. This would be sufficient to produce an approximate photoproduct coating weight of $m/A = 10^{-2}$ mol/m^2.

Clearly the performance of the sensitizer falls well short of the ideal in converting iron(II) photoproduct into pigment. Some of the light may be absorbed by the self-masking effect of the Prussian blue product as it is formed. It is also instructive to compare the coating weight of image pigment with the original coating weight of the sensitizer before exposure and processing. For a typical coating, experience shows that an appropriately-sized paper will absorb, per square meter, ca. 25 cm^3 of sensitizer solution, which has a concentration, typically, of 0.3 M, giving a sensitizer molar coating weight of 7.5×10^{-3} mol/m^2. Comparison with the value found for the coating weight, W, of Prussian blue actually formed shows that, even for the maximum densities, only about 6% of the sensitizer is converted into image substance.

III.3 Photochemistry of trisoxalatoferrate(III)

Of the several photosensitive carboxylato-complexes of iron(III), the trisoxalatoferrate(III) anion is well-characterised by the determination of its structure, both in the solid and in aqueous solution.[676] As the potassium or ammonium salt, its photochemistry has been by far the most extensively investigated,[677] and it provides the basis for a well-known chemical actinometer.[678] The stoicheiometry of the overall photochemistry is:

$$h\nu + 2[Fe(C_2O_4)_3]^{3-} \rightarrow 2[Fe(C_2O_4)_2]^{2-} + C_2O_4{}^{2-} + 2CO_2$$

The measured quantum yield per mole of iron(II) formed in aqueous solution is approximately 1.2 for radiation of wavelengths between 250 and 420 nm, falling slightly to 0.9 at 500 nm, but very sharply thereafter.[679] For the photolysis of the potassium salt in the crystalline solid state, however, the quantum yield is significantly lower,[680] and the iron(II) photoproduct does not appear to be the simple oxalate, FeC_2O_4, but may be a bridged dimer, $K_6[Fe^{II}_2(C_2O_4)_5]$.[681]

A mechanism for the photolysis in aqueous solution was first suggested by Hatchard and Parker; it proceeds from the initial formation of a radical anion by electron transfer from one oxalate ligand to the iron(III), reducing it to iron(II):[682]

$$h\nu + [Fe^{III}(C_2O_4)_3]^{3-} \rightarrow [Fe^{II}(C_2O_4)_2(\cdot C_2O_4)]^{3-}$$

The ligand radical will be in dissociative equilibrium with the complex:

$$[Fe^{II}(C_2O_4)_2(\cdot C_2O_4)]^{3-} = [Fe^{II}(C_2O_4)_2]^{2-} + \cdot C_2O_4{}^-$$

Reaction of the radical anion, $\cdot C_2O_4{}^-$, or even its partially coordinated complex, with a further molecule of the original iron(III) complex enables the transfer of the second electron from the ligand, which is then lost as two molecules of carbon dioxide, leaving another mole of the iron(II) oxalato complex:

$$[Fe^{III}(C_2O_4)_3]^{3-} + \cdot C_2O_4{}^- \rightarrow [Fe^{II}(C_2O_4)_2]^{2-} + C_2O_4{}^{2-} + 2CO_2$$

The quantum yield for ferrioxalate photoreduction in this process should ideally be $\phi = 2$; but the competing reverse dark reaction tends to diminish this. The quantum yield is found to be largely independent of pH. Under acidic conditions, ca. pH 2, the colour of a solution of trisoxalatoferrate(III) changes from emerald green to light yellow, corresponding to the formation, as the predominant species, of the hydrated complex ion $[Fe^{III}(C_2O_4)_2(H_2O)_2]^-$ which may be isolated as a crystalline solid with suitable large cations; it is still light-sensitive with approximately the same quantum yield.[683]

The iron(II) oxalato-complex photoproduct is a moderate reducing agent as can be seen from its redox potential:

$$E^0([Fe(C_2O_4)_3]^{3-}/[Fe(C_2O_4)_2]^{2-}) = +0.02\ V$$

and it is capable of liberating ‘noble’ metals from their complexes, kinetic factors permitting, thus:

$$[MX_4]^{2-} + 2[Fe^{II}(C_2O_4)_2]^{2-} + 2H_2O \rightarrow M + 4X^- + 2[Fe^{III}(C_2O_4)_2(H_2O)_2]^-$$

That the noble metal complexes or salts are reducible thermodynamically is evident from their large positive redox potentials:

$E(PtCl_4^{2-}/Pt) = +0.73$ V
$E(PdCl_4^{2-}/Pd) = +0.62$ V
$E(Ag^+/Ag) = +0.80$ V
$E(Hg^{2+}/Hg) = +0.85$ V
$E(AuCl^{4-}/Au) = +1.00$ V

Photographic images have been printed by this means in platinum, palladium, silver, mercury and gold. In principle, complexes of ruthenium, rhodium, rhenium, osmium, and iridium are also reducible, but their use for imaging is inhibited by kinetic factors in some cases, and by sheer expense in others.

III.4 Composition of ammonium iron(III) citrate

This substance has been available since the 1840s in a variety of ill-characterised forms. The pharmacopoeias listed it traditionally as *Ferri et Ammoniae Citras* and recognised that the '...want of chemical compactness, the loose state in which the iron is combined, precludes their recognition as well-defined chemical compounds.'[684] As a convenient source of biologically assimilable iron, it has been used extensively in iron-deficiency therapy.[685] It is usually obtained as glassy amorphous flakes – the 'scale salts' of iron – which can have an iron content ranging from 14% to 28%, the colour varying correspondingly from a light green to a deep red-brown as the iron:citrate ratio increases. All cyanotypes prior to 1897 were made with varieties of the 'brown' scale salt, for which Valenta gave the analysis shown in Table III.2. The so-called 'green' salt was first prepared in 1897 by Valenta,[686] who gave the analysis as conforming to the composition shown in Table III.2, in which cit^{4-} represents the fully deprotonated citrate anion $C_6H_4O_7^{4-}$, and $Hcit^{3-}$ denotes the tribasic anion $C_6H_5O_7^{3-}$. L.P. Clerc, in a later publication (1937), gives somewhat different formulations of the two varieties,[687] but in a subsequent edition of his manual (1954) he declines to offer any formulae at all, implying just how "ill-characterised" these salts must be. Most present-day catalogues of the chemical supply houses offer a product described as the 'green' salt which contains rather more than 14% iron – commonly up to about 18% – and this product frequently does not appear green at all, but light brown. However, it appears to perform well enough as a sensitizer, especially if excess citric acid is added to redress the ratio in the composition. Many present-day varieties of the 'brown' salt likewise offered in the chemical catalogues are stated to contain much more iron than 19% – even up to 28% in one instance. The variety used in the experimental work described in §9 had an iron content of 19% like that of the 19th century product.

Formula	FW	Fe %	FW per Fe	Mole Fe:cit
Brown form (Valenta) $4Fe(Hcit).3(NH_4)_3(Hcit).3Fe(OH)_3$	2030	19.26	290	7 : 7
Green form (Valenta) $5Fe(Hcit).2(NH_4)_3(Hcit).NH_4(H_3cit).2H_2O$	1956	14.27	391	5 : 8
Brown form (Clerc) $Fe(Hcit).(NH_4)(H_3cit).Fe(OH)_3.3H_2O$	615	18.16	308	2 : 2
Green form (Clerc) $2Fe(Hcit).(NH_4)_3(Hcit)$	733	15.29	367	2 : 3

Table III.2 Analyses of ammonium ferric citrates
$cit^{4-} = C_6H_4O_7^{4-}$ $Hcit^{3-} = C_6H_5O_7^{3-}$

The only structural information available on these ill-characterised salts is an investigation by electron paramagnetic resonance spectroscopy, which has revealed that the 'green' and 'brown' varieties differ profoundly.[688] The spectrum of the green salt shows specific resonances close to the values found in ferric citrate, indicating a definite complex or mixture of oligomeric complexes, with a specific stoichiometry. On the other hand, the brown salt exhibits a broad featureless resonance of the same character as that seen in hydrated ferric oxide. It is reasonable to assume that the brown salt is the more highly polymerized species, consisting of large aggregates of hydrated iron(III) oxide gel, bound with citrate ligands only on the exterior. Solution studies on the alkaline hydrolysis of ferric citrate have shown that the simple anions present at low pH begin to polymerise in the region of pH 8 to 9, and finally result in a polymer consisting of nanometer-sized particles containing around 1200 iron atoms linked by hydroxy and oxy bridges.[689] It seems likely that these extensively hydrolysed forms of the substance will have a much greater tendency to leave residues of hydrated ferric oxide in the paper, with consequences both for the colour and the stability of the resulting cyanotypes.

III.5 Photochemistry of citratoferrate(III)

Studies of the speciation of the iron(III)/citrate system in aqueous solution have shown that a photo-inactive monomer predominates between pH 0.5 and 1.5, but a photo-active dimer is formed above pH 2.[690] The quantum yield at 365 nm has a maximum value of 0.45 at pH 4, but then tends to drop with increasing pH, possibly owing to hydrolysis of the iron(III) and further oligomerization. Previous studies have shown that the rates of attainment of equilibrium become slow above pH 3.[691]

The existence of dimeric iron(III)/citrate species in solution has recently received confirmation from the successful isolation of two crystalline dinuclear citratoferrate(III) complexes with suitable cations, and the determination of their structures by X-Ray diffraction.[692] One dimeric anion is $[Fe_2cit_2(OH_2)_2]^{2-}$, which has a centrosymmetric structure, and the other $[Fe_2(Hcit)_3]^{3-}$, where cit^{4-} represents the fully deprotonated citrate anion, $C_6H_4O_7^{4-}$. In both complex anions the iron(III) centres are octahedrally coordinated, and they are oxy-bridged by the two or three available alkoxide groups of the ligands, respectively. The carboxylate groups coordinate in a monodentate fashion. The ability to crystallise either anion selectively from an aqueous solution containing excess citric acid suggests that these two species are present in equilibrium. It is likely that they play an important role in the complex biochemistry of iron transport within living cells.

The initial photochemical reaction product of citratoferrate(III) has been identified as acetone dicarboxylic acid, but the nature of the iron(II) photoproduct remains unknown:[693]

$$h\nu + [Fe_2(C_6H_4O_7)_2(OH_2)_2]^{2-} \rightarrow 2[Fe^{II}] + CO(CH_2COOH)_2 + CO_2$$

The acetone dicarboxylic acid may suffer further decarboxylation to yield acetone finally:

$$CO(CH_2COOH)_2 \rightarrow CO(CH_3)_2 + 2CO_2$$

The quantum yield of 0.45 at 365 nm drops to a value of 0.28 at 436 nm. Photolysis by sunlight of iron(III) polycarboxylates occurring naturally in surface waters has important effects on the complex speciation of iron, with consequences for its availability in numerous biogeochemical processes.[694]

III.6 Photochemistry of hexacyanoferrate(III)

It has long been known that the photochemical decomposition of the hexacyanoferrate(III) anion is complicated, with several possible reaction products, including Prussian blue as first observed by Herschel. The reaction scheme is summarised in the monograph by Balzani and Carassiti;[695] although the reaction paths are not yet fully mapped out, it is well-established that the first step is a photoaquation with the formation of aquapentacyanoferrate(III):

$$h\nu + [Fe^{III}(CN)_6]^{3-} + 2H_2O \rightarrow [Fe^{III}(CN)_5(OH_2)]^{2-} + HCN + OH^-$$

Due to the weakness of hydrocyanic acid, the pH tends to rise during irradiation. At high pH, a protolytic reaction yields the corresponding hydroxo complex anion:

$$[Fe^{III}(CN)_5(OH_2)]^{2-} + OH^- \rightarrow [Fe^{III}(CN)_5(OH)]^{3-} + H_2O$$

A stepwise continuance of this reaction can ultimately produce a precipitate of ferric hydroxide. The aquapentacyanoferrate(III) ion has also been shown to undergo a facile reduction to aquapentacyanoferrate(II), which can ultimately yield iron(II) by hydrolysis, so the ingredients are available to form Prussian blue, or its aquated analogue, iron(III) aquapentacyanoferrate(II), $Fe^{III}[Fe^{II}(CN)_5H_2O]$.

It has also been shown that the free cyanide ion released in the photoaquation is photo-oxidised by iron(III) species:[696]

$$h\nu + 2[Fe(CN)_6]^{3-} + CN^- + H_2O \rightarrow 2[Fe(CN)_6]^{4-} + OCN^- + 2H^+$$

The resulting hexacyanoferrate(II) is then available to form Prussian blue with any liberated iron(III). Quantum yields are very low for all these photolysis reactions of hexacyanoferrate(III); reported values for the aquation and reduction reactions are in the order of f = 0.01, which explains why Herschel's first method, the 'proto-cyanotype', using hexacyanoferrate(III) by itself, is very 'slow' compared with the method employing ferricitrate, where the quantum yield is around f = 0.4.

III.7 Photochemistry of the blueprint process –1

In the usual negative-working process, the sensitizer consists of a mixture of potassium hexacyanoferrate(III) with a photosensitive iron(III) salt – ammonium iron(III) citrate in Herschel's original recipe, which is replaced by ammonium trisoxalatoferrate(III) in later commercial blueprint papers. Upon exposure to ultraviolet light, the iron(II) salt is formed photochemically in situ as described above:

$$h\nu + 2[\mathrm{Fe^{III}(C_2O_4)_3}]^{3-} \rightarrow 2[\mathrm{Fe^{II}(C_2O_4)_2}]^{2-} + \mathrm{C_2O_4}^{2-} + 2\mathrm{CO_2}$$

In the case of the citrate system the precise identity of the iron(II) photoproduct is not known, but it is likely to be a citrato- complex.

Prussian blue is then supposed to be formed via the Turnbull's blue route, presumably by an overall reaction such as:[697]

$$[\mathrm{Fe^{II}(C_2O_4)_2}]^{2-} + [\mathrm{Fe^{III}(CN)_6}]^{3-} \rightarrow \mathrm{Fe^{III}[Fe^{II}(CN)_6]^{-}} + 2\mathrm{C_2O_4}^{2-}$$

However, this complex reaction cannot occur in one concerted step, because the carboxylate ligands must be stripped off the iron(II) before it can be incorporated in the Prussian blue lattice.[698] There is a simple piece of experimental evidence to show that this overall reaction does not take place readily: if a solution of trisoxalatoferrate(III) is irradiated with UV light then added to a solution of hexacyanoferrate(III), little or no Prussian blue is formed. It is more probable that the initial reaction is direct reduction of the hexacyanoferrate(III):

$$[\mathrm{Fe^{II}(C_2O_4)_2}]^{2-} + [\mathrm{Fe^{III}(CN)_6}]^{3-} \rightarrow [\mathrm{Fe^{III}(C_2O_4)_2}]^{-} + [\mathrm{Fe^{II}(CN)_6}]^{4-}$$

which is a simple electron transfer, favoured by the relevant redox potentials:

$$E([\mathrm{Fe^{III}(CN)_6}]^{3-}/[\mathrm{Fe^{II}(CN)_6}]^{4-}) = +0.356\ \mathrm{V}$$

$$E([\mathrm{Fe^{III}(C_2O_4)_3}]^{3-}/[\mathrm{Fe^{II}(C_2O_4)_2}]^{2-}) = +0.02\ \mathrm{V}$$

The production of more iron(II) during the on-going exposure then provides the material to form the pigment after the attendant ligands are removed. Iron(II) does not bind oxalate very strongly, as may be seen from the overall dissociation constant:

$$[\mathrm{Fe^{II}(C_2O_4)_2}]^{2-} = \mathrm{Fe}^{2+} + 2\mathrm{C_2O_4}^{2-} \qquad \beta_2 = 4 \times 10^{-7}$$

Removal of oxalate will be promoted by the presence of hydrogen ions, which compete with the metal to form undissociated oxalic acid, for which the overall equilibrium constant is:

$$\mathrm{C_2O_4}^{2-} + 2\mathrm{H}^+ = \mathrm{H_2C_2O_4} \qquad K_a = 3.24 \times 10^5$$

Accordingly, the equilibrium:

$$[\mathrm{Fe^{II}(C_2O_4)_2}]^{2-} + 4\mathrm{H}^+ = \mathrm{Fe}^{2+}(aq) + 2\mathrm{H_2C_2O_4}$$

lies to the right hand side, with $K = K_a^2\beta_2 = 4.2 \times 10^4$.

The development of the image from such a sensitizer is strongly promoted by initial treatment in a bath of dilute acid, rather than water, as may be seen from the D/logH curves in Fig (Chapter 6). Dissociation of the iron(II) oxalato complex thus releases ferrous ions, which will be competed for by both hexacyanoferrate(III) and hexacyanoferrate(II), to form both Prussian blue and Prussian white:

$$Fe^{2+}(aq) + [Fe^{III}(CN)_6]^{3-} \rightarrow Fe^{III}[Fe^{II}(CN)_6]^{-}$$

$$Fe^{2+}(aq) + [Fe^{II}(CN)_6]^{4-} \rightarrow Fe^{II}[Fe^{II}(CN)_6]^{2-}$$

The relative proportions of the two products will depend on the hexacyanoferrate concentrations: in regions of very low exposure, hexacyanoferrate(III) will predominate, producing Prussian blue; in regions of heavy exposure the main species present will be hexacyanoferrate(II), and Prussian white will result. Thus, we are led to an explanation of the phenomenon of cyanotype ‘solarization’ i.e. the reversal of the tonal scale in the shadow areas, which fade to a pale bluish-grey as the exposure proceeds.

Previously, two different explanations have been put forward for this effect. One, due to Suzuki maintains that it is the direct photoreduction of hexacyanoferrate(III) on prolonged exposure that provides the hexacyanoferrate(II) which reacts with the iron(II) oxalato photoproduct to give Prussian white:[699,700]

$$h\nu + [Fe^{III}(CN)_6]^{3-} \rightarrow [Fe^{II}(CN)_6]^{4-}$$

$$[Fe^{II}(C_2O_4)_2]^{2-} + [Fe^{II}(CN)_6]^{4-} \rightarrow Fe^{II}[Fe^{II}(CN)_6]^{2-} + 2C_2O_4^{2-}$$

The low value of the quantum yield for hexacyanoferrate(III) photoreduction, mentioned previously, would seem to disallow this mechanism as a significant contributor to blueprint ‘solarization’. Moreover, there is no explanation of how this addition of a small proportion of white pigment to the image can be responsible for the extensive solarization that is actually observed, in which Prussian blue already formed is seen to be reduced. The other explanation, offered by Murray, is more plausible: the heavy exposure in the shadow areas forms excess iron(II) oxalato complex, which reduces the Prussian blue already-formed to Prussian white:[701]

$$[Fe^{II}(C_2O_4)_2]^{2-} + Fe^{III}[Fe^{II}(CN)_6]^{-} \rightarrow [Fe^{III}(C_2O_4)_2]^{-} + Fe^{II}[Fe^{II}(CN)_6]^{2-}$$

This explanation is also supported by the values of the relevant redox potentials:

$$E([Fe(C_2O_4)_3]^{3-}/[Fe(C_2O_4)_2]^{2-}) = +0.02\ V$$

$$E(Fe^{III}[Fe^{II}(CN)_6]^{-}/Fe^{II}[Fe^{II}(CN)_6]^{2-}) = +0.46\ V$$

It should be noted that, in order to bring about this reduction, the iron(II) complex does not have to be divested of its ligands. Furthermore, it has been shown that ‘soluble’ Prussian blue has a high ionic mobility and can perform electrochemistry even in the absence of a liquid electrolyte.[702]

The partial correctness of Murray’s explanation was confirmed experimentally by irradiating a solution of pure ammonium trisoxalatoferrate(III) under a UV lamp for ten minutes, then immersing a washed and processed cyanotype step test in the solution for five minutes. The test strip was partially bleached, in comparison with a control strip that was immersed in an identical, but unirradiated, solution for the same length of time, and suffered little or no loss. Evidently the photoproduct is capable of reducing Prussian blue. After washing and drying this test, it slowly re-oxidised in the air to Prussian blue, demonstrating that the bleaching reaction had indeed been a reduction to Prussian white and not a hydrolysis or peptization. An identical experiment was also made using a solution of ammonium iron(III) citrate, with the same result. This mechanism may therefore contribute to the solarization.

However, a further experiment demonstrated that the simple thermal reaction between the iron(II) photoproducts and Prussian blue does not fully account for the phenomenon. Solutions identical to those in the previous experiment were irradiated with a test strip of processed Prussian blue immersed *in situ* and exposed to the UV lamp. In these circumstances the reduction to Prussian white was observed to be much faster and more complete even in the regions of high density. It may be inferred that the Prussian blue itself becomes photochemically activated, making it easier to reduce:

$$h\nu + Fe^{III}[Fe^{II}(CN)_6]^{-} \rightarrow \{Fe^{II}[Fe^{III}(CN)_6]^{-}\}^{*}$$

$$[Fe^{II}(C_2O_4)_2]^{2-} + \{Fe^{II}[Fe^{III}(CN)_6]^{-}\}^{*} \rightarrow [Fe^{III}(C_2O_4)_2]^{-} + Fe^{II}[Fe^{II}(CN)_6]^{2-}$$

where the formulation $\{Fe^{II}[Fe^{III}(CN)_6]^{-}\}^{*}$ represents an electronically excited charge-transfer state of Prussian blue – essentially, iron(II) hexacyanoferrate(III).

It has been shown that Prussian white can reduce molecular oxygen to water in aqueous acidic electrolytes.[703] The Prussian white in the ‘solarized’ regions of a cyanotype is therefore re-oxidised to Prussian blue by the oxygen of the air during processing and drying, so the shadow values slowly regain their density over a period of several hours, because the oxygen molecule is small enough to diffuse through the pores in the lattice:

$$4Fe^{II}[Fe^{II}(CN)_6]^{2-} + O_2 + 2H_2O \rightarrow 4Fe^{III}[Fe^{II}(CN)_6]^- + 4OH^-$$

Alternatively, for a rapid result, re-oxidation may be accomplished by a bath of dilute (0.3%) hydrogen peroxide:

$$2Fe^{II}[Fe^{II}(CN)_6]^{2-} + H_2O_2 \rightarrow 2Fe^{III}[Fe^{II}(CN)_6]^- + 2OH^-$$

In the past, a bath of potassium dichromate (ca. 5% to 10%) was commonly employed as the oxidant:

$$6Fe^{II}[Fe^{II}(CN)_6]^{2-} + Cr_2O_7^{2-} + 7H^+ \rightarrow 6Fe^{III}[Fe^{II}(CN)_6]^- + 2Cr^{3+} + 6OH^-$$

but its high toxicity now discourages this practice.

It should be noted that each of these oxidations consumes protons, so generating hydroxyl ions, which may build up sufficiently to cause some hydrolysis of the Prussian blue. The oxidations should therefore be carried out for preference under acidic conditions.

III.8 Photochemistry of the blueprint process -2

In the mid-1930s a number of patents were granted claiming improvements in blueprint sensitizers which operated on a rather different principle from the traditional mixtures. The photosensitive component was still, almost universally, ammonium trisoxalatoferrate(III), but the hexacyanoferrate(III) was replaced, partially or wholly, by potassium hexacyanoferrate(II).[704] It might be expected that mixing these two compounds would instantly lead to the precipitation of Prussian blue, but this is not so: the stability constants of the iron(III) oxalato complex are so high, that there is very little free ferric iron present, especially if the solution is neutral or slightly alkaline, or if the equilibrium is suppressed by the presence of excess oxalate ligand. The overall dissociation constants for the complex species are:[705]

$$[Fe(C_2O_4)_3]^{3-} = Fe^{3+} + 3C_2O_4^{2-} \qquad \beta_3 = 4 \times 10^{-21}$$

$$[Fe(C_2O_4)_2]^{-} = Fe^{3+} + 2C_2O_4^{2-} \qquad \beta_2 = 6.3 \times 10^{-17}$$

$$[Fe(C_2O_4)]^{+} = Fe^{3+} + C_2O_4^{2-} \qquad \beta_1 = 4 \times 10^{-10}$$

These very small values governing the concentration of free ferric iron explain why only a trace of Prussian blue is formed when the sensitizer components are mixed. The dissociation of the iron(III) citrato complexes is slightly greater ($\beta = 6.3 \times 10^{-14}$), but in either case only sufficient colloidal Prussian blue is formed at equilibrium to impart a blue colour to the sensitizer solution, and the equilibrium lies well to the left hand side in the reaction:

$$[Fe^{III}(C_2O_4)_3]^{3-} + [Fe^{II}(CN)_6]^{4-} \text{ -/-> Prussian blue}$$

Upon irradiation, such a sensitizer will form Prussian white directly when the iron(II) photoproduct reacts with hexacyanoferrate(II) according to the overall equation:

$$h\nu + [Fe^{III}(C_2O_4)_3]^{3-} + [Fe^{II}(CN)_6]^{4-} \rightarrow Fe^{II}[Fe^{II}(CN)_6]^{2-} + 2C_2O_4^{2-} + 2CO_2$$

The dissociation constants listed above show that the displacement of oxalate ligands from iron(II) is much easier than from iron(III), as might be expected. The Prussian white image is subsequently oxidised to Prussian blue during wet processing. This procedure for making blueprints offers the possibility of achieving a higher Dmax than the traditional method, while maintaining high printing speeds, for two reasons:

1. Hexacyanoferrate(II) has a much lower optical absorbance in the blue and near ultraviolet regions of the spectrum, so it offers less of an internal filter effect than hexacyanoferrate(III), which absorbs strongly, as described above. Hexacyanoferrate(II) may therefore be used in higher, even equimolar, concentrations without greatly diminishing the speed.

2. The colourless Prussian white photoproduct offers less self-masking to the incident light, which is altogether more efficiently used for the photochemistry, and not wastefully absorbed by the photo-inactive components in the system.

Sensitized papers using hexacyanoferrate(II) are referred to in the industry as ‘blue layers’, or ‘latitude papers’ to distinguish them from the ‘yellow layers’ of the traditional hexacyanoferrate(III) papers (see Chapter 4). Because the unexposed paper has a blue background that is bleached by light, the exposure initially gives a positive-working image, which is gradually transformed into a negative-working image by the wet processing and action of air. The greatest problem with ‘blue layer’ papers is that the background fog of Prussian blue pigment must be completely washed out of the highlights before the bulk of the Prussian white is oxidized. This ‘wash-out’ is assisted by dispersing agents such as sodium hexametaphosphate, $(NaPO_3)_6$.[706] It appears that this whole procedure is feasible because Prussian blue is readily peptized whereas Prussian white is not; the latter does not easily form a colloid, but immediately flocculates when precipitated.[707] To suppress excessive Prussian blue formation in the sensitizer, extra quantities of alkali-metal oxalates, citrates, or phosphates can be added, but in moderation, otherwise they impair the quality of colour and reduce the speed.[708]

These two different types of blueprint sensitizer have been termed Type A (‘yellow layer’) and Type B (‘blue layer’). Mixtures, Type AB, were also recommended in the patent literature.[709] There is additionally a Type C sensitizer, also ‘blue layer’ in appearance, but differing in its constituents: it uses a mixture of iron(II) oxalate or the bisoxalatoiron(II) complex with hexacyanoferrate(III).[710] Again it may seem surprising that the equilibria do not allow the instant formation of Prussian blue in copious amounts from these two components, but excess oxalate is added to suppress the free ferrous iron concentration. Although the mixture does become quite strongly coloured, the amount of colloidal Prussian blue formed is still quite small. Redox potential data (see the values quoted above) suggest that substantial electron transfer should take place between these two components to give a mixture of an iron(III) oxalato complex (which will be photosensitive) and hexacyanoferrate(II):

$$[Fe^{II}(C_2O_4)_2]^{2-} + [Fe^{III}(CN)_6]^{3-} \rightarrow [Fe^{III}(C_2O_4)_2]^{-} + [Fe^{II}(CN)_6]^{4-}$$

so that one ends up with a light-sensitive mixture essentially resembling Type B. The printing characteristics of Types B and C are indeed similar, and a mixture of the two, Type BC, has also been recommended.

III.9 Photochemical reduction of Prussian blue

In spite of the well-known tendency of blueprints to fade in light, it is important to acknowledge that there is good evidence for pure Prussian blue being photochemically inert to a high degree. Thus, the Colour Index lists its lightfastness as ‘excellent’.[711] Recent studies of an aqueous suspension of pure ‘insoluble’ Prussian blue by Harriman and co-workers found that irradiation with visible light causes no perceptible photodecomposition, which would be marked by loss of optical density and/or the evolution of oxygen, due to the oxidation of water.[712]

The early reports by Desmortiers and Chevreul that prolonged exposure to sunlight causes bleaching of Prussian blue and the formation of some cyanogen, and a shift of colour to a greener hue on re-oxidation, suggests that very high exposures (ca. 50 Mlux hr) to light with some ultraviolet content (the sun) may bring about oxidation of some of the cyanide ligands, with formation of the aquopentacyano complex, possibly by reactions such as:

$$h\nu + 2Fe^{III}[Fe^{II}(CN)_6]^- + 2H_2O \rightarrow 2Fe^{II}[Fe^{II}(CN)_5(OH_2)]^{2-} + (CN)_2$$

However, Harriman et al further observed that the introduction of trisbipyridylruthenium(II) cation into the system of the aqueous Prussian blue sol renders it photochemically active and enables rapid photoreduction of the Prussian blue to Prussian white, and the concomitant oxidation of water. This is a complex system because the trisbipyridylruthenium(II) cation is itself highly photoactive, but one of the reactions considered is:

$$h\nu + [bipy_3Ru]^{2+} + Fe^{III}[Fe^{II}(CN)_6]^- \rightarrow [bipy_3Ru]^{3+} + Fe^{II}[Fe^{II}(CN)_6]^{2-}$$

in which photoexcitation of Prussian blue as well as the ruthenium complex may play a part. In another recent experiment, methanol was the chosen electron donor, but the electron transfer was mediated by the presence of titanium dioxide, which is photoactive in generating electron/hole pairs under irradiation; its presence facilitated rapid photobleaching to Prussian white under visible light.[713] These two experiments were carried out in rather complex systems, differing from the cyanotype environment, but they do show that the photoreduction of Prussian blue is critically dependent on the presence of other electron-donating species.

Absorption of light at 400 or 700 nm by the ligand-to-metal charge transfer transitions in the Prussian blue (see Appendix II.5) leads to an excited state which can be described approximately as iron(II) hexacyanoferrate(III), $\{Fe^{II}[Fe^{III}(CN)_6]^-\}^*$, and which is a more powerful oxidising agent than Prussian blue in its ground state. Such enhancement of redox activity in electronically excited states by the absorption of visible light has been extensively studied in some inorganic complexes such as the trisbipyridylruthenium(II) cation,[714] but there has been little report of the phenomenon in Prussian blue, whose excited electronic states have not been fully characterised.

If there is an oxidisable species accessible to the photoexcited Prussian blue, electron transfer could occur to bring about bleaching of the blue to Prussian white and oxidation of the electron donor. However, this mechanism is critically dependent on the half-life of the electronically-excited state of Prussian blue, which must be long enough to permit chemical reaction to occur more rapidly than thermal relaxation to the grond state. In view of the insolubility of Prussian blue, this reaction would have to proceed in the solid state, and it could only be facile if the Prussian blue and its electron donor were in close contact. This becomes possible if the reducing agent is incorporated into the zeolitic cavities or the anion vacancies of the Prussian blue lattice. Surface adsorption onto colloidal Prussian blue is also a possibility, because of the high surface area and the fact that Prussian blue has been shown to be a photoconductive material. In view of the increased negative charge in the Prussian white lattice, neutrality must be maintained by the migration of cations into the lattice on reduction, as described in Appendix II; so a supply of appropriately-sized cations is also necessary for photo-reduction to take place.

The reaction is easily demonstrated experimentally, and effective reducing agents can be readily identified, as follows. The potential reducing agent is applied in solution (concentration *ca* 5-10%), under subdued lighting, to half of a small area of paper coated with Prussian blue, which may be prepared either by exposing and processing cyanotype paper, or by chemical metathesis and precipitation. The two areas are compared, still under subdued illumination, for any signs of a 'dark' thermal reduction reaction. If there is none, the dry sheet is then irradiated with visible light, for an exposure of about one kilolux hour (*i.e.* 15 minutes exposure to a 4 kilolux artificial daylight source, provided by four standard daylight fluorescent tubes). Fading of the coated area versus the uncoated control area should be apparent in this time. Substances which have been found to promote such photochemically-induced bleaching of Prussian blue include alkali metal or ammonium citrates and oxalates, and the iron(II) oxalato complex as demonstrated above. This reaction would appear to offer a possible mechanism to explain the fading of cyanotypes, by reactions such as:

$$h\nu + \mathrm{Fe^{III}[Fe^{II}(CN)_6]^-} \rightarrow \{\mathrm{Fe^{II}[Fe^{III}(CN)_6]^-}\}^*$$

$$2\{\mathrm{Fe^{II}[Fe^{III}(CN)_6]^-}\}^* + \mathrm{C_2O_4^{2-}} \rightarrow 2\mathrm{Fe^{II}[Fe^{II}(CN)_6]^{2-}} + 2\mathrm{CO_2}$$

where the oxalate may be replaced by other oxidisable species, e.g. citrate. The implications of this type of photochemical sensitization of Prussian blue for the conservation of cyanotypes are discussed in §9.1.

Appendix IV Units of Concentration

The concentration of a solution can be specified in a variety of different ways, the choice of which may depend on whether the user is a chemist or a lay person. Those who have worked with or researched early photographic processes will be aware of this diversity and the occasional difficulty in making comparisons. Reconciling or interconverting these different modes of expressing concentration is not altogether trivial, and sometimes even impossible with complete exactness. Fortunately, high precision is not usually a prerequisite in this area. The usual measures of concentration that need be considered are as follows.

IV.1 Concentration as weight percent volume (% w/v)

If a solution is said to have a concentration of C % w/v, this implies that C grams (g) of the solute are contained in 100 cubic centimeters (cc) of the solution. This measure of concentration only has meaning if the units are appropriately chosen – usually as grams per decilitre.

(1 decilitre = 0.1 litre = 100 millilitres or 100 cubic centimeters)[715]

The convenience of this mode of expression is obvious, because solutions are most easily dispensed by liquid volume, and the measured volume in decilitres multiplied by the concentration in these units provides an exact statement of the weight of solute that is present in the volume dispensed.

IV.2 Concentration as molarity

This is the ‘chemist’s unit’ of concentration. A molarity of M, implies that the solution contains M gram molecular weights (or ‘moles’) of the solute in one litre (= 1000 cc = 1 cubic decimeter) of the solution.

A knowledge of molarities enables the chemist to predict exactly the equivalent combining volumes of solutions of reacting substances. Molarity is the basis for all analytical chemistry in solution, especially titrations.[716] Although its use is not necessary in everyday photographic practice, it is desirable to be able to calculate concentrations as molarities when devising new formulations, or reviewing old ones in which the level of chemical understanding may not have been accurate.

It is easy to convert the expression for concentration as C % w/v into the molarity, M, by multiplying by 10 and dividing by the gram molecular weight, R, (also called the relative molecular mass):[717]

$$M = 10\ C/R \text{ moles/litre}$$

R is found by summing the atomic weights of the component elements in the molecular formula.

IV.3 Concentration as weight percent weight (% w/w)

If a solution is specified as having a concentration of C_w % w/w, then C_w grams of the solute are contained in 100 grams of the solution (and likewise for any other unit of weight). Since it is much less convenient to measure and deliver samples of solutions by weight, rather than by liquid volume (a balance is much more costly than a measuring cylinder or pipette), this is a less practical mode of expression. The only advantage is its independence of the units of weight used, provided they are both the same; i.e. no units need to be specified.

IV.4 Concentration as volume percent volume (% v/v)

If a solution is specified as having a concentration of C_v % v/v, then a volume C_v cc of the solute is contained in 100 cc of the solution. This is obviously a useful measure when the solute is commonly obtained in liquid form.

IV.5 Early formulations and recipes

Most of the older formulations and recipes for making-up historic photographic preparations usually prescribe a procedure of the form:

'X parts (by weight) of solute are dissolved in V parts (by volume) of water (or other solvent).'

While it is easy to specify and carry out the making-up of a solution in this way, it also creates a quantitative difficulty, because the dissolution of the solute in the solvent changes the total volume, so that the solution finally obtained no longer has a volume equal to V, but one that has been increased by an unspecified and unpredictable amount that depends on the individual chemical identity of the solute. Only for very dilute solutions, say 1% or less, is it a reasonable approximation to assume that V remains unchanged, and that the concentration may therefore be taken as % w/v, once the units have been converted to g/100cc.

The concentration of a solution made up in such a way can be calculated exactly as C_w % w/w by:

$$C_w = 100\ X/(X + V\ d)$$

where d is the density (or specific gravity) of the solvent in appropriate units. If the solvent is water at room temperature, the assumption that d = 1 g/cc is generally accurate enough, so the expression may be simplified to:

$$C_w = 100\ X/(X + V)$$

provided that X is expressed in g and V in cc.

Unfortunately, if a solution is made up in this way it becomes impossible to relate its concentration accurately to the more useful, rational, and chemically significant units of C % w/v, unless further information – the density – is available (see below).

IV.6 Modern formulations and recipes

Most practising photographers have some experience in making up solutions for darkroom work,718 and will be aware that the instructions in modern formularies now tend to take the form:

‘Dissolve X g of the substance in water (an approximate volume may be indicated as a guide) and make up the solution with water, with thorough mixing, to a final volume of V cc.’

It is obvious that this way of making up solutions can be accurately expressed by a concentration of C % w/v simply defined by:

$$C = 100\ X/V \text{ g/decilitre}$$

This method is greatly to be preferred, especially if quantitative chemical reasoning is to be employed, and it is also the way of working that is natural for any trained chemist.

IV.7 Interconversion of C_w and C

The information needed to relate values of C_w and C is the specific gravity or density, D, of the solution in appropriate units:

$$D = C/C_w \text{ g/cc}$$

In general, information regarding the density, D, of a solution of any particular strength is not readily available (although it has been tabulated for aqueous solutions of a limited number of common chemicals in the CRC Handbook,[719] for example)

However, tables of *solubility* in the Merck Handbook[720] do provide values of C, C_w, and D for *saturated* solutions of quite a large number of substances, at room temperature. By making an assumption concerning the effect of the solute in modifying the final volume of solution, it is possible to derive a factor, called f, for any substance, which may then be used to make an approximate conversion between C and C_w for any value of the concentration. This assumption is that the 'effective volume' occupied by unit mass of dissolved solute is independent of the concentration. Given this, it can be shown that:

$$1/C = 1/C_w - f$$

and this formula can be used to find a value for C, given C_w, where the incremental factor f is conveniently defined by either:

$$f = (D^{sat} - 1)/C^{sat}$$

or:

$$f = 1/C_w^{sat} - 1/C^{sat}$$

in which D^{sat} , C_w^{sat} , and C^{sat} are the density and concentrations of the saturated solution, at the same temperature. The factor, f, for a variety of chemicals important to alternative photography, has been calculated from the Merck Tables as shown in Table 21

Substance	D^{sat} g/cc	C^{sat} % w/v	C_w^{sat} % w/w	f	V_g 1–100f
Ammonium dichromate	1.18	33	27.9	0.00545	0.455
Potassium dichromate	1.092	14.2	13.0	0.00648	0.352
Ammonium ferric citrate	1.43	97	67.7	0.00443	0.557
Ammonium ferric oxalate	1.26	65	51.5	0.00400	0.600
Potassium ferricyanide	1.187	38.1	32.1	0.00491	0.509
Potassium ferrocyanide	1.173	28.2	24.0	0.00613	0.387
Silver nitrate	2.29	164	71.5	0.00787	0.213
Citric acid	1.311	88.6	67.5	0.00351	0.649
Trisodium citrate	1.272	61.2	48.1	0.00445	0.555
Sodium chloride	1.198	31.7	26.5	0.00625	0.375
Potassium bromide	1.380	56	40.6	0.00679	0.321
Potassium iodide	1.721	103.2	59.8	0.00699	0.301
Potassium oxalate	1.20	34	28.3	0.00592	0.408

Table 21. Solubility data for relevant chemicals

V_g is the effective volume in cc 'occupied' by the solute per gram of its weight dissolved, and can be useful for estimating the final volume of the solution, knowing the volume of solvent taken.

IV.8 Conversion of units in obsolete formulae

When working with ‘historic’ formulations, it is advisable to convert all units of weight to grams, and all volumes to cubic centimeters. To assist this, the following conversions may be useful.

Apothecaries’ measure was used by early scientists for weighing out solids and making up formulae:

1 grain		= 0.0648 g
1 scruple	= 20 grains	= 1.296 g
1 drachm	= 3 scruples (60 grains)	= 3.888 g
1 ounce	= 8 drachms (480 grains)	= 31.104 g
1 pound	= 12 ounces (5760 grains)	= 373.242 g

Troy weight has the same basis as Apothecaries measure, the grain, and was always used for weighing precious materials such as gold and silver metal:

1 grain Troy	= 1 grain Apothecaries	= 0.0648 g
1 pennyweight	= 24 grains	= 1.555 g
1 ounce	= 20 pennyweight (480 grains)	= 31.104 g
1 pound	= 12 ounces (5760 grains)	= 373.242 g

Avoirdupois measure was the common system for weighing and selling solids; it was adopted by the British Pharmacopoeia in 1864:

1 grain	= 1 grain Troy	= 0.0648 g
1 ounce	= 437.5 grains	= 28.35 g
1 pound	= 16 ounces (7000 grains)	= 453.59 g

Texts do not always make clear which system their ‘ounces’ (abbreviated ‘oz.’) refer to, but they are more likely to be avoirdupois.

British fluid measure was used for making up volumes of solutions:

1 minim	(*ca.* 1 drop)	= 0.0592 cc
1 fluid drachm	= 60 minims	= 3.552 cc
1 fluid ounce	= 8 fluid drachms	= 28.413 cc
1 gill	= 5 fluid ounces	= 142.065 cc
1 pint	= 20 fluid ounces	= 568.261 cc
1 quart	= 2 pints	= 1136.522 cc
1 gallon	= 8 pints	= 4546.087 cc

1 fluid ounce of water weighs approximately 1 ounce avoirdupois
A concentration of 1 grain/fluid ounce = 2.28 g/l = 0.228 % w/v

US volume measurement differs from that used in Britain:

1 minim (USA)			=	0.0616 cc
1 fluid dram (USA)	=	60 minims	=	3.697 cc
1 fluid ounce (USA)	=	8 fluid drams	=	29.574 cc
1 pint (USA)	=	16 fluid ounces (USA)	=	473.176 cc
1 gallon (USA)	=	8 pints (USA)	=	3785.412 cc

Specific gravity was commonly used to indicate the strength of some concentrated solutions, because these could be readily determined with a hydrometer or areometer. Unfortunately the scale often employed was the now long-obsolete (and ambiguous):

Beaumé hydrometer scale.

For liquids denser than water, the number on the Beaumé scale, 0, 1, 2, 3, etc., denotes the specific gravity of an aqueous solution containing 0, 1, 2, 3, etc., % w/w of sodium chloride (common salt). If B represents the Beaumé number, and D is the specific gravity (or density in g/cc) as above, the relationships between them are:[721]

$$D = 1/(1 - B/m)$$

or, conversely:

$$B = m(1 - 1/D)$$

where the parameter, m, has been assigned various values between 144 and 147 on slightly differing definitions of the scale, but may be taken approximately as m = 145 for nineteenth century measurements at 20°C.

Twaddell's Hydrometer Scale.

If T represents the reading on the Twaddell scale, the specific gravity D is given by:

$$D = 1 + 0.005\,T$$

Notes and References

Notes and references

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[26] For readers in the USA, the blueberry is, of course, the exception that proves the rule.

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[27] The intensity of the Rayleigh scattering is inversely proportional to the fourth power of the wavelength. Thus, blue light with its smaller wavelength is scattered most by the atmosphere. This is also responsible for the yellowness of direct sunlight; our sun is actually a blue-white star. The effect is most marked at sunset, when the path length of light through the atmosphere is greatest.

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[46] In the eighteenth century the price of ultramarine was as high as five guineas an ounce. Following the discovery by Guimet in 1828 of a method for preparing it synthetically from materials as common as clay, sulphur, and soda, the price fell to about a shilling per pound.

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[51] The English language is full of metaphors involving 'blue' in this context. It is a moot point whether the language determines the visual connotation or derives from it.

[52] Komar, V, and Melamid, A, *Painting by Numbers: Komar and Melamid's Scientific Guide to Art*, edited by J Wypijewski, (New York: Farrar, Straus & Giroux, 1997)
See also reviews of this book in *The Guardian*, (Friday, 16 January, 1998); *The New York Times*, (4 January, 1998); *Bookforum*, (Winter 1997), p37.

[53] The scientific system for the measurement of colour is based in the recommendations of the *Commission Internationale de l'Eclairage* (CIE) and is expressed as three coordinates, L*a*b*, in a defined colour space. However, this system conveys little or nothing to the general reader, and for a visual reference one of the preferred industry standards is the Munsell system of *hue*, *value* and *chroma*, which is embodied in a colour atlas, which is however a rather expensive reference work. *Munsell Book of Color*, Munsell Color, Macbeth Division of Kollmorgen Corporation (Baltimore: 1976)

[54] Kornerup, A, and Wanscher, J H, *Methuen Handbook of Colour*, (London: Eyre Methuen Ltd., 1978)

[55] Lyons, John, 'Colour in Language', in Lamb, Trevor, and Bourriau, Janine, (eds.), *Colour: Art & Science*, (Cambridge: the University Press, 1995), pp195-224

[56] Zajonc, A, *Catching the Light,* (London: Bantam Press, 1993), pp13-15

[57] Regrettably, Bismarck was *not* referring to the manufacture of a pigment at the time. (The fact that the only dyestuff to be named after him should be brown, can be considered an 'irony'.)

[58] Kirby, J, 'Fading and Colour Change of Prussian Blue: Occurrences and Early Reports', *National Gallery Technical Bulletin*, **14** (1993), pp63-70

[59] Roscoe, H E, and Schorlemmer, C, *A Treatise on Chemistry* (London: Macmillan and Co., 1881), pp104, 655-6; Coleby, L J M, 'A History of Prussian Blue', *Annals of Science*, **4** (1939), pp206-211

[60] A decisive experiment in 1828 was F Wöhler's simple conversion by heat of the inorganic salt, ammonium cyanate NH_4NCO, into its

isomer, the organic animal natural product, urea $(NH_2)_2CO$. See: *Poggendorff's Annalen*, **12** (1828), p253.

[61] The name "Prussian Blue" has been reappropriated in the early 21st century by a young duo of female pop singers – whose fascist lyrics prove to be far from 'politically correct'. Internet searchers beware!

[62] There was a school of rabbinical thought that identified the dyestuff called *tekhelet* in the Bible, which was prescribed for the woollen yarn of priestly apparel, as Prussian blue, but this has been disqualified; see: Ziderman, I I, 'Blue Thread of the Tzitzit: Was the Ancient Dye a Prussian Blue or Tyrian Purple?' *Journal of the Society of Dyers and Colourists*, **97** (1981), pp362-4

[63] Egyptian blue must take the title of the earliest synthetic pigment, but its formula was lost for many centuries.

[64] Bartoll, Jens and Jackisch, Bärbel, "Prussian Blue: A Chronology of the Early Years," *Zeitschrift für Kunsttechnologie und Konservierung*, **24**, No. 1, 2010

[65] Orna, M V. *Archaeological Chemistry;* Fitzhugh, E, *Artists Pigments*, OUP 1997; Butler and Gash, *Chemistry in Britain*, 952, 1993.

[66] Lapis lazuli is probably the same blue gemstone referred to as '*Kyanos*' by writers of classical antiquity such as Dioscorides, Theophrastus, and Pliny. See: Stillman, J M, *The Story of Early Chemistry*, (New York: Appleton and Company, 1924), pp19, 44. The mineral has been mined in the mountains of the Hindu Kush for 6000 years. Ultramarine was used by the Ancient Egyptians to decorate the death mask of King Tutankamun.

[67] Wall, A H, *A Manual of Artistic Colouring, as applied to Photographs: A Practical Guide to Artists and Photographers* (London: Thomas Piper, 1861), pp46-7

[68] Kraft, Alexander, 'On the Discovery and History of Prussian Blue', *Bulletin for the History of Chemistry*, vol. 33, no. 2, 2008, pp. 61-67; *idem,* 'On Two Letters from Caspar Neumann to John Woodward Revealing the Secret Method for Preparation of Prussian Blue', *ibid.,* vol. 34, no. 2, 2009, pp. 134-140; *idem,* ' "Notitia Cœrulei Berolinensis Nuper Inventi" on the 300th Anniversary of the First Publication on Prussian Blue', *ibid.*, vol. 36, no. 1, 2011, pp. 3-9.

[69] 'Notitia Coerulei Berolinensis nuper inventi', *Miscellanea Berolinensia ad incrementum scientiarum*, **1** (1710), pp377-8.
An English translation of the Latin original by Jo Kirby and Raymond White may be found in the Appendix to Kirby, J, 'Fading and Colour Change of Prussian Blue: Occurrences and Early Reports', *National Gallery Technical Bulletin*, **14** (1993), pp63-70.

[70] Woodward, J, 'Praeparatio Caerulei Prussiaci ex Germania Missa ad Johannem Woodward', *Philosophical Transactions of the Royal Society*, **33**, 381 (January-February 1724), pp15-17.
An English translation of Woodward's Latin paper can be found in: Powell, H M, 'The Beginnings of Co-ordination Chemistry', *Proceedings of the Chemical Society,* (March 1959), pp73-5

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[71] Stahl, G E, *Experimenta, Observationes, Animadversiones*, (Berlin: 1731) p281

[72] Johann Konrad Dippel was born in Castle Frankenstein in 1673. Having failed to make gold, he launched an 'animal oil' upon the public in 1700. It was hailed as a panacea, presumably on the widely-held premise that anything so obnoxious must be beneficial.

[73] A mixture of alkyl cyanides and nitrogenous organic bases, such as pyrrole, quinoline and pyridine, obtained by the destructive distillation of blood, bones and offal. It was also used by Niépce as a solvent for bitumen.

[74] Campbell, A, 'Keep on taking the oil', *Chemistry in Britain*, **33** 6 (June 1997), p54.

[75] McKenzie, C, *One Thousand Experiments in Chemistry; with Illustrations of Natural Phenomena and Practical Observations on the Manufacturing and Chemical Processes Pursued in the Useful Arts* (London: 1821 and 1825), p161; for an alternative account see: *The Mirror of Literature, Amusement and Instruction*, **33**, 951 (1 June 1839) p347

[76] The French name for the pigment was *Bleu de Prusse*. An alternative German name was *Preussiches Ultra-Marin.*

[77] There is a dangerous inconsistency here in the early nomenclature: although 'prussic acid' is unambiguously hydrogen cyanide (or hydrocyanic acid); 'prussiate of potash' does *not* generally signify potassium cyanide (also highly toxic), but potassium ferrocyanide (which is relatively innocuous). This possibly lethal ambiguity is resolved by some authors, who refer to the latter as 'yellow prussiate of potash' or 'ferroprussiate of potash'. The German name for this salt was *Blutlaugensaltz* – 'blood residue salt' – acknowledging one method of its preparation.

[78] Macquer, P-J, 'Examen chymique du bleu de Prusse', *Mémoire de mathématique et de physique de l'Académie Royale des Sciences,* (1756), pp60-77

[79] Scheele, *Traite de l'Air et du feu*

[80] Nitrogen had meanwhile been identified by Daniel Rutherford in 1772 as 'dephlogisticated air'.

[81] Gay-Lussac, *Annales de Chimie*, **77** (18??), p128; **95** (18??), p136

[82] In Homeric Greek there is evidence that *kyanos* did not in fact mean 'blue' but simply 'dark'; see Chapter 1.

[83] Prussian blue can also claim the more arcane chemical distinction of being the first coordination compound, or 'complex' of a metal to be synthesised. See Powell, *loc cit.*

[84] The bond here between the atoms of carbon and nitrogen is very strong – a 'triple bond' in chemists' parlance – so the two bound atoms tend to act as a single entity, the cyanide radical.

[85] Hunt, R, (ed), *Ure's Dictionary of Arts, Manufactures and Mines* (London: Longman, 1860), p545

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[86] Their ‘Pyroligneous acid’ works were at 100 Camlachie Street, see Royal Commission on the Ancient and Historical Monuments of Scotland, John Hume Collection

[87] *The New Statistical Account of Scotland (1845)*, Volume VI – Lanark, City of Glasgow. I thank Dr. Sara Stevenson for this reference.

[88] Brückle, I, ‘The Historical Manufacture of Blue-coloured Paper’, *The Paper Conservator*, **17** (1993), pp20-31; Bower, Peter, *The Quarterly*, **31**, (August 1999), pp11-17

[89] Eder, J M, *History of Photography*, Epstean, E (trans.) (New York: Dover Publications Inc., 1978), pp56, 101

[90] Döbereiner, J F, ‘Chemische Thätigkeit des Lichts und Erzeugung des (neutralen) Humboldtits auf chemischem Wege’, *Jahrbuche für Chemie und Physik von Schweigger-Seidel,* **62** (1831) pp86-90; this paper was also summarised in *Pharmaceutiches Centralblatt*, **2** (August 1831), p383-5; See also Eder, *op cit*, p177.

[91] Parnell, E, *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 Milligan 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 oxidisable material.

[92] His later contributions are summarised in Parnell, *op cit*, 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 Maritime Museum, Liverpool.

[93] Talbot, W H F, *Notebook M, Folio 34*, (before March 1835). ‘Paper wetted with common mur. acid, & then with Pruss. Potash, turns blue owing to the presence of iron in the acid.’
I am indebted to Michael Gray, curator of the Fox Talbot Museum, Lacock, for this transcription from Talbot’s notes.

[94] Talbot, W H F, ‘On Photography without the Use of Silver’, *The British Journal of Photography*, **9** (9 December 1864), pp495-6

[95] Schaaf, L J, *Out of the Shadows: Herschel, Talbot and the Invention of Photography* (New Haven & London: Yale University Press, 1992)

[96] I am grateful to the Harry Ransom Humanities Research Center, University of Texas at Austin for supplying photocopies and for permission to quote from this material.

[97] Sir John F.W. Herschel, ‘On the Chemical Action of the Rays of the Solar Spectrum on Preparations of Silver and other Substances, both metallic and non-metallic, and on some Photographic Processes’, *Philosophical Transactions of the Royal Society*, vol. 131, 1840, pp. 1-59.

[98] In the Museum of the History of Science, Oxford, and at the Harry Ransom Center, University of Texas at Austin.

[99] Somerville, Mary, 'On the Action of the Rays of the Spectrum on Vegetable Juices. Extract of a Letter from Mrs. M. Somerville to Sir J.F.W. Herschel, Bart. dated Rome, September 20, 1845.

Communicated by Sir J. Herschel', *Philosophical Transactions of the Royal Society,* vol. 136, 1846, pp. 111-120.

[100] Fabbri, Malin, *Anthotypes* (Stockholm: Alternativephotography.com, 2012).

[101] Herschel, Sir J F W, *MS Notebook*, vol. III, Science Museum Library, London

[102] 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.

[103] Letter, Herschel to Talbot, 21 April 1842. NMPFT 1937-4900. See Schaaf, L J (ed.), *Selected correspondence of William Henry Fox Talbot 1823-1874,* (London: Science Museum and National Museum of Photography, Film & Television, 1994), p36, and Schaaf, *op. cit.*, p126

[104] '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), p40

[105] Herschel, Sir J F W, '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), pp181-215

[106] Schaaf, *op cit*, p127

[107] Smee, A, *Elements of Electro-metallurgy*, see also: Smee, A, '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 Smee-Odling, E M, *Memoir of the Late Alfred Smee, FRS*, (London: George Bell and Sons, 1878)

[108] Gore, G, 'Electro-Metallurgy' in *The Circle of the Sciences*, **VII**, *Practical Chemistry*, (London: Griffin, Bohn, and Co., 1856), pp4, 7-100

[109] See note 15. The 'sesqui-' prefix in the first of these names arose through a misconception at the time of the chemical formulation of this salt.

[110] The name, 'potassium ferricyanide' does not conform to the most recent international (IUPAC) recommendations for chemical nomenclature, 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. *Caveat lector!*

[111] Smee, A, 'On the Ferrosesquicyanuret of Potassium', *Philosophical Magazine*, series 3, **17**, 109 (September 1840), pp193-201

[112] Gmelin, L, *Schweigger's Journal,* **34** (1822), p325

[113] Potassium ferrocyanide was then prepared, as a first step in the manufacture of the important pigment Prussian blue, by an obnoxious process of heating potash with animal residues such as

blood and offal or parings of hoof and horn; hence its original German name *Blutlaugensaltz* ('blood-residue salt').

[114] '$F^3/_2CP$' is the personal abbreviation that Herschel commonly used in his notes for 'ferrosesquicyanuret of potash' as potassium ferricyanide was then known.

[115] Herschel, Sir J F W, *Memoranda*, Manuscript Library, Harry Ransom Humanities Research Center, in the University of Texas at Austin

[116] Herschel first coined the word 'cyanotype' in his *Memoranda* for 16 August 1842; and used it in print in a postscript to his 1842 paper

[117] Herschel, Sir J F W, *Diary 1833 to 1864*, Transcript in the Library of the Royal Society, MS583-585.

[118] The pathways of photochemical decomposition of potassium ferricyanide are complex, and have not been fully mapped out even today – see Appendix III.

[119] Herschel, Sir J F W, *Memoranda*, HRC, ref 109

[120] Letter, Smee to Herschel, 25 April 1842. Royal Society Library.

[121] Letter, Smee to Herschel, 10 May 1842. Royal Society Library.

[122] Smee, A, 'Photogenic Drawing', *Literary Gazette* (18 May 1839), pp314-16

[123] Letter, Smee to Herschel, Royal Society Library

[124] Christison, R, *A Dispensatory, or Commentary on the Pharmacopoeias of Great Britain* (Edinburgh: Adam and Charles Black, 1848), p975

[125] The adjective 'chalybeate' derives from the tribe of Chalybes, metallurgists of Anatolia, living on the east coast of the Black Sea, who are credited with the first extraction of metallic iron from its ores, some time around 1500 BCE.

[126] Taniguchi, M, Imamura, H, Shirota, T,, Okamatsu, H, Fujii, Y, Toba, M, and Hashimoto, F, '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), pp161-171

[127] Herschel's personal diary entry for 17 June 1846 records that he was prescribed ACI for his stomach complaints. An irony indeed!

[128] 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)

[129] Draft of a letter, Herschel to Smee, 15 June 1842. Royal Society Library.

[130] Although Herschel also thought of platinum as an ideal image substance, he was unable to make it work with the chemicals available. Much later, in 1873, in the hands of William Willis, a successful platinum printing process was achieved. See: Mike Ware, 'The Eighth Metal: the Rise of the Platinotype Process', in Julie Lawson, Ray McKenzie and A.D. Morrison-Low (eds.), *Photography 1900: The Edinburgh Symposium* (Edinburgh: National Museums of Scotland and National Galleries of Scotland, 1992), pp. 98-111.

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[131] The word is proposed by Herschel himself in a footnote to *The London, Edinburgh and Dublin Philosophical Magazine and Journal of Science*, series 3, vol. 21, 1842, p. 227. This neologism is also attributed to Herschel by the editor, Sir David Brewster, in 'Drawing by the Agency of Light', *The Edinburgh Review*, vol. 76, no. 154, January 1842, p. 339:

> "Hence Sir J. Herschel considers the name *siderotype,* taken from the *iron* employed in one of the solutions, as preferable ..."

The same article is reprinted in *The Penny Mechanic and Chemist*, no. 146 3rd series, 29 July 1843, pp. 236-8. Brewster again uses the word in *The North British Review*, vol. 7, no. 14, 1847, p. 474. The word "siderotype" entered the scientific canon in Henry Watts, *A Dictionary of Chemistry*, vol. 5 (London: Longmans, Green & Co., 1868), p. 240.

[132] Herschel's chrysotype (Greek: χρυσος = 'gold') furnished permanent, deep red images made of nanoparticle gold (the 'Purple of Cassius' used by ceramicists and stained glass artists), but it failed to gain acceptance into the photographic repertoire - partly owing to its obvious expense, but partly also on account of chemical difficulties over controlling the colour, tonality and contrast of the image. Only in the last two decades of the 20th century have the photochemical problems of chrysotype been resolved, see:
Mike Ware, *Gold in Photography: the history and art of Chrysotype* (Brighton: ffotoffilm publishing, 2006). See also: Mike Ware, 'Herschel's Chrysotype: A Golden Legend Re-told', *History of Photography*, **30**, 1, (Spring 2006), pp. 1-24.

[133] The later platinum & palladium printing processes due to William Willis used ferric oxalate.

[134] Towards the end of the nineteenth century, Herschel's argentotype process suddenly fathered a whole family of derivative iron-silver processes: Van Dyke Brown; Kallitype (Greek: καλλι = beautiful); Sepiaprint; and Brownprint are the self-descriptive names for these essentially similar processes. Unfortunately they did not enjoy a high reputation for permanence, unless toned with gold or platinum, but some are still practised today by the devotees of the hand-made photograph, see: Christopher James, *The Book of Alternative Photographic Processes,* 2nd edn. (New York: Delmar Cengage Learning, 2008).

[135] See, for example: Eder, J M, *Ausführliches Handbuch der Photographie*, Part 13, 'Die Lichtpausverfahren, die Platinotypie und verschiedene Copirverfahren ohne Silbersalze', (Halle: Wilhelm Knapp, 1899), p203-4; Pizzighelli, G, and Hübl, Baron A, *Platinotype*, Iselin, J F, (trans.), (London: Harrison and Sons, 1886), p35; Abney, Capt. W de W, and Clark, L, *Platinotype, its Preparation and Manipulation*, (London: Sampson Low, Marston & Co. 1895), p156; Chapman Jones, *The Science and Practice of Photography*, (London: Iliffe and Sons, 1904)

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[136] The application of some modern chemistry, 150 years later, has enabled me to devise a latter-day version of the chrysotype process that is less profligate in its consumption of gold, and is capable of providing images as fine and permanent even as those obtained by platinotype, but of a more remarkable range of colours. See: Ware, M J, 'Prints of Gold: The Chrysotype Process Re-invented', *Scottish Photography Bulletin,* No 1, (1991), pp6-8; *idem*, 'Photographic Printing in Colloidal Gold', *Journal of Photographic Science*, **42**, 5 (1994), pp157-161

[137] Ware, Mike, 'On Proto-photography and the Shroud of Turin', *History of Photography*, vol. 21, no. 4, Winter 1997, pp. 261-9. See also: http://www.usask.ca/lists/alt-photo-process-l/200609/msg00420.html

[138] Herschel, Sir John F W, '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*, **133**, (1842), pp. 181-221.

[139] Now in the photographic collection of the Harry Ransom Center of the University of Texas at Austin. The items are listed in the Center's Photographic Collections Database, with the engraving title and year of publication: http://norman.hrc.utexas.edu/photoPublic/fullDisplay.cfm?CollID=73

[140] 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. The first paper, written in 1839, was withdrawn before publication, and was long thought lost until the MS copy was discovered by Schaaf. See: Schaaf, L J, 'Sir John Herschel's 1839 Royal Society paper on photography', *History of Photography*, **3**, 1 (1979), pp47-60.
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.

[141] Herschel, Sir J F W, '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), pp181-215

[142] The *other* solution referred to here by Herschel, is the subject of his preceding articles §202 to §205, *viz* Smee's potassium ferricyanide.

[143] Herschel, Sir J F W, *loc. Cit.*

[144] 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 ±'. It seems likely that Herschel forgot to allocate a prepared paper number to it at the time.

[145] After the Greek for "dark" kelaino = κελαινο

[146] Herschel, *op. cit.*, p214

[147] Herschel made strenuous efforts in trying to secure a viable mercury-printing process, which he had christened 'kelainotype' or

'celaenotype'. At Talbot's suggestion this was temporarily re-named '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 43 indexed Herschel specimens at HRHRC are completely blank.

[148] Herschel, Sir J F W, '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)

[149] Herschel, *op. ci.t*, p210

[150] Nadeau, L, *Encyclopedia of Printing, Photographic, and Photomechanical Processes*, (Fredericton: Atelier Luis Nadeau, 1989), p80.

[151] Letter, Smee to Herschel, 29 September 1842. Royal Society Library.

[152] Fisher, George Thomas, *Photogenic Manipulation*, (London: George Knight and Sons, 1843), p36

[153] Thornthwaite, W H, *Photogenic Manipulation*, (London: Edward Palmer, 1843), p43

[154] Hunt, Robert, *A Manual of Photography*, 5th edn., (London: Richard Griffin and Company, 1857), p140.

[155] "A Practical Chemist and Photographist", *A Practical Manual of Photography*, (London: E. Mackenzie, 1845), p58

[156] Bingham, Robert J, *Photogenic Manipulation*, 9th edn., (London: George Knight and Sons, 1852), p66

[157] Snelling, Henry H, *History and Practice of Photography*, (New York: 1845), p

[158] Humphrey, S D, *A System of Photography*, (Albany: C. van Benthuysen, 1849), p121

[159] Towler, John, *The Silver Sunbeam*, (New York: Joseph H. Ladd, 1864), p273

[160] Sutton, Thomas, and Dawson, George, *A Dictionary of Photography*, (London: Sampson Low, Son & Marston, 1867), p79-80

[161] Maunder, M, 'Testing Herschel', *The PhotoHistorian*, 149, (January, 2007), pp 14-21

[162] Maunder, M, 'Herschel's Genius', *Ag 41*, (Autumn, 2005), p56

[163] Mrhar, Peter, *Cyanotype: Historical and Alternative Photography*, 2013.
http://www.petermrhar.com/alternative

[164] Döbereiner, J W, 'Chemische Thätigkeit des Lichts und Erzeugung des (neutralen) Humboldtits auf Chemischem Wege', *Schweigger's Jahrbuch*, **62** (1831), p86, pp90-96.
An abstract of this paper was published in *Pharmaceutisches Central Blatt,* **2** (August 1831), pp383-5. It was subsequently translated into French as 'Influence chimique de la lumière et formation de la humboldtite neutre par un moyen photomètrique' [sic], *Journal de*

Pharmacie et des Sciences Accessoires, **18,** 3 (March, 1832), pp117-123

[165] Herschel, Sir J F W, *The Photographic News*, **8**, 278 (12 February 1864), p82

[166] Hunt, R, *Researches on Light*, (London: Longman, Brown, Green and Longmans, 1844), p147

[167] Most importantly, it formed the basis for Willis's Platinotype (1873) and Nicol's Kallitype (1889) processes.

[168] The circumstances of this discovery and its future significance have been described by Schaaf. The substance is now more correctly described as calcium hexahydroxyplatinate(IV).

[169] 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: Herschel, Sir J F W, 'On the Action of Light in determining the Precipitation of Muriate of Platinum by Lime-water', *London, Edinburgh, and Dublin Philosophical Magazine*, **1** (July, 1832), pp58-60

[170] Herschel's paper, *op. cit.,* was translated and published in German: Herschel, John F W, 'Ueber die Wirkung des Lichts als Ursache der Präcipitation des salzauren Platins durch Kalkwasser', *Annalen der Pharmacie*, **3**, 3 (1832), pp337-341.
This transcript carries a long editorial footnote (signed only 'Br.') referring to 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.'

[171] Döbereiner, J W, 'Chemische Eigenschaften und physische Natur des auf nassem Wege reducirten Platins', *Annalen der Pharmacie*, **14** (1835), pp10-21

[172] Letter, Herschel to Talbot, 31 March 1843. National Museum of Photography, Film & Television.

[173] This application was finally accomplished in 1898 in a tri-colour printing method due to Brewerton.

[174] The prepared paper numbers in the Memoranda referring 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.

[175] Delamotte, P H, Diamond, H W, Hardwich, T F, Malone, T A, Percy, J, Pollock, H, and Shadbolt, G, *Journal of the Photographic Society*, **2** (1855), p251

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[176] Ware, M, *Mechanisms of Image Deterioration in Early Photographs*, (London: Science Museum and National Museum of Photography, Film & Television, 1994)

[177] The process is not unlike the tanning of leather, and uses the same chemical agents – dichromates. The pigmented gelatin is rendered insoluble where the light falls; the unexposed regions remain soluble and are washed away with water to develop the image.

[178] Ware, M J, 'Photographic Printing in Colloidal Gold', *Journal of Photographic Science*, **42**, 5 (1994), pp157-161

[179] Ware, M, 'The Eighth Metal: The Rise of the Platinotype Process', in *Photography 1900: The Edinburgh Symposium*, (National Museums of Scotland and National Galleries of Scotland, 1994), pp99-111.

[180] Liesegang, P, 'Positive Printing without Silver', *The Photographic News*, **283** (5 February 1864), pp66-7

[181] 'The Late Sir John F W Herschel FRS : his Discoveries in Photography', *British Journal of Photography*, **18**, 576 (19 May 1871), pp229-231

[182] Marion and Co., *Practical Guide to Photography*, (London: Marion and Co., 1887), p215-7

[183] Tronquoy, C, 'Reproductions photographiques par le Papier au Ferro-Prussiate de M. Marion', *Annales du Génie civil*, (Paris: Eugène Lacroix, 1872). An English translation of this paper was published as 'Photographic Printing by means of Marion's Ferro-prussiate Paper', *The Photographic News*, **16**, 739 (1 November 1872) pp526-527; continued in 740 (8 November 1872) p536

[184] 'The Cyanotype Process',*The Photographic News,* **21** (22 June 1877), p289; *ibid* (24 August 1877), p401

[185] Whitaker, C, 'Apparatus for Printing by the Blue Process', *The Photographic News*, (8 June 1883) pp358-9

[186] In modern nomenclature: iron(III) hexacyanoferrate(II)

[187] When iron (symbol Fe, from the Latin *Ferrum*) is chemically combined with other elements, its atoms acquire a positive electric charge by transferring two or three of their (negatively charged) electrons onto atoms of other elements. (It is a law of nature that electric charge has to balance. Electrons are the fundamental particles of negative electricity, and form the outer cloud of every atom, surrounding a positively-charged nucleus). So each iron atom ends up in one of two states:
'ferrous' iron – also called iron(II), denoted by Fe^{2+} for short,
or 'ferric' iron – also called iron(III), denoted by Fe^{3+}.
The superscripted number, 2+ or 3+, is called the *oxidation state* of the iron, and signifies the positive electric charge that the iron atom has acquired in the reaction. Electrically charged atoms are given the general name of *ions*: *cations* are positive, *anions* are negative.

[188] As an example of the 'mixed valence' iron minerals that occur naturally, one of the best-known is the 'lodestone', magnetite, Fe_3O_4, which is so intensely coloured that it often appears black. Special magnetic properties are often a characteristic of mixed-valence compounds.

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[189] It is a consequence of the quantum theory of Max Planck, that the smaller the energy needed to promote such a transition, then the longer is the wavelength of light absorbed. Prussian blue absorbs long-wavelength light in the red region of the spectrum (around 700 nm).

[190] Bader, A, 'Out of the blue', *Chemistry in Britain*, **33**, 11 (November 1997), pp24-6. http://digicoll.library.wisc.edu/cgi-bin/WI/WI-idx?type=HTML&rgn=div1&byte=1658105294&q1=Prussian%20blue Dr Bader offered a £1000 reward for evidence leading to the identification of the author of his painting, which was awarded to Dee Cook in 2001 for naming him as Thomas Phillips; see *Chemistry in Britain*, **37**, 7, (July 2001) p99.

[191] Brande, W T, *A Manual of Chemistry*, (London: John W Parker, 1845, 5th edn), pp754-7. Brande's famous text was the standard chemistry reference book for Talbot and Herschel, and was first published in 1819. Faraday's copy is in the Wellcome Institute Library.

[192] Ware, Mike, 'Prussian Blue: Artists' Pigment and Chemists' Sponge', *Journal of Chemical Education*, **85**, 5, (May 2008), pp612-621

[193] After Thomas Everitt (1805-1845), English chemistry teacher and founder member of the Chemical Society of London. Everitt, T., "On the Reaction which takes place when Ferrocyanuret of Potassium is distilled with dilute Sulphuric Acid", *The London and Edinburgh Philosophical Magazine and Journal of Science,* **6**, series 3, (February 1835), pp97-103. See: Kraft, Alexander, "On the History of Prussian Blue: Thomas Everitt (1805-1845) and Everitt's Salt", *Bulletin for the History of Chemistry*, vol. 3?, no. ??, 20??, pp.??

[194] Williamson, Alexander W., "On the Blue Compounds of Cyanogen and Iron", *Chemical Society Memoranda*, **3**, (1846), pp125-140

[195] Maunder, M, 'Herschel's Genius and Testing Herschel', *The PhotoHistorian*, **149**, (January 2007), pp 14-21:

"What you get is the first fallacy - it's not Prussian blue but Turnbull's blue. Something I learnt in the 1950s for my A-Levels. Thus, anyone who says you get Prussian blue is wrong. This piece of evidence was more than enough for me to stick to scientific method and protocol and not use modern historians' documents."

[196] Chadwick, B M, and Sharpe, A G, *Advances in Inorganic Chemistry and Radiochemistry*, **8** (1966), p119; Sharpe, A G, *The Chemistry of Cyano Complexes of the Transition Metals*, (Academic Press, 1976), pp121-126

[197] Some idea of the difficulties that this topic presented to nineteenth-century chemists can be obtained from: Williamson, A W, 'On the Blue Compounds of Cyanogen and Iron', *Chemical Society Memoirs*, **3** (1846), pp125-140; and Williams, H E, *Cyanogen Compounds*, (London: Edward Arnold, 1948), pp191-200, 226-228

[198] Formula $Fe_4[Fe(CN)_6]_3.15H_2O$.

[199] Formula $KFe[Fe(CN)_6].H_2O$.

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[200] Buser, H J, Schwarzenbach, D, Petter, W, and Ludi, A, 'The Crystal Structure of Prussian Blue: $Fe_4[Fe(CN)_6]_3.xH_2O$', *Inorganic Chemistry*, **16** (1977), p2704 and references cited therein.

[201] The etymology of *peptise*, from the Greek 'to digest', is appropriate.

[202] The technical definition of a *colloid* is determined by the size of its particles, which lie within a range intermediate between molecular dimensions and the crystals of a normal solid. The usual criterion is that the particles should be smaller than the wavelengths of visible light, so that they cannot be discerned under a normal optical microscope. The name 'nanoparticles' is now preferred to colloid because the latter no longer necessarily implies (as its Greek root might suggest) that the material is 'gluey' – although substances such as gum and gelatin do indeed constitute another class of colloid, different in physical properties from colloids such as Prussian blue.

[203] Having the formula $NH_4Fe[Fe(CN)_6].H_2O$.

[204] Holtzman, H, 'Alkali Resistance of the Iron Blues', *Industrial and Engineering Chemistry*, **37** (1945), p855

[205] The cations of caesium and thallium, Cs^+ and Tl^+, are both singly-charged, and of similar size to potassium, K^+.

[206] Pearce, J, 'Studies of any Toxicological Effects of Prussian-Blue Compounds in Mammals – A Review', *Food and Chemical Toxicology*, **32**, 6 (1994), pp577-582

[207] Brewer, K, *New Scientist*, **138** (1993), p10

[208] International Atomic Energy Authority. *http://f40.iaea.org/worldatom/Press/Focus/Chernobyl-15/caesium.pdf*

[209] http://www.utexas.edu/courses/sami/dieda/socio/chernobyl.htm

[210] BBC News. *http://news.bbc.co.uk/1/hi/world/europe/1086547.stm* University of Texas, Sociology Department. *http://www.utexas.edu/courses/sami/dieda/socio/chernobyl.htm*

[211] Giese, W, 'The use of ammonium-ferric(III)-cyano-ferrate(II) in pigs fed with radiocesium contaminated whey powder', *Wiener Tierarztliche Monatsschrift*, **82**, 10 (1995), pp310-315

[212] Center for Disease Control. *http://www.bt.cdc.gov/radiation/prussianblue.asp*

[213] Emsley, John, *Molecules at an Exhibition*, Oxford: OUP, 1998, 222-4, and *The Elements of Murder: the History of Poison*, 2005. Thallium poisoning features in the crime novels of Agatha Christie (*The Pale Horse*, 1961) and Ngaio Marsh (*Final Curtain*, 1947).

[214] Kravzov, J, Rios, C, Altagracia, M, Monroynoyola, A, and Lopez, F, 'Relationship between Physicochemical Properties of Prussian Blue and its Efficacy as Antidote against Thallium Poisoning', *Journal of Applied Toxicology*, **13**, 3 (1993), pp213-216

[215] Hoffman, R S, *Toxicolog. Rev.* **22**, (2003), pp29-40

[216] Mortimer, R J, and Rosseinsky, D R, "Electrochemical Polychromicity in Iron Hexacyanoferrate Films and a New Film Form of Ferric Ferricyanide", *Journal of Electroanalytical Chemistry*, **151** (1983),

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pp133-147; Mortimer, R J, "Electrochromic Materials", *Chemical Society Reviews*, **26**, 3, (1997), pp147-156

[217] Thompson, C J S, *The Lure and Romance of Alchemy*, (London: G G Harrap, 1932)

[218] The yellow solution of ferric chloride is rendered colourless by sunlight, corresponding to the reduction of iron(III) to iron(II); some of the organic component is correspondingly oxidised.

[219] Wittstein, G C, *Practical Pharmaceutical Chemistry*, (Darby, S, trans. of 2nd German edn.), (London: John Churchill, 1853) p132.

[220] Eder, J M, *History of Photography*, Epstean, E., (trans.), (New York: Dover Publications Inc., 1978), p159

[221] Lathrop, A K, 'The Provenance and Preservation of Architectural Records', *The American Archivist*, **43**, 3 (1980), p331

[222] Oxidation is the process of making atoms or molecules more positive (or less negative) in the electrical sense. So when iron forms compounds, it is oxidized. Reduction is the converse: making atoms or molecules less positive (or more negative), e.g. oxygen gas, which consists of molecules containing two linked atoms of oxygen, O_2, is reduced to form oxides, which contain the O^{2-} anion. Both processes involve the transfer of electrons. Oxidation is the removal of electrons, reduction is their addition. When iron(III) is transformed to iron(II), it is reduced.

[223] These organic acids, originally referred to as 'vegetable acids' by Herschel, are all familiar 'household chemicals' - even the poisonous oxalic acid, which occurs (in small amounts) in the leaves of rhubarb, spinach and sorrel.

[224] For more details of the chemistry of 'precious metal' printing see Ware, M J, 'Noble Metals for Common Images', in *Photochemistry and Polymeric Systems*, Kelly, J M, McArdle, C B, and Maunder, M J de F, (eds.), Special Publication No. 125 (Cambridge: Royal Society of Chemistry, 1993), pp250-265

[225] For introductory texts on photochemistry at the undergraduate level see: Cox, A, and Kemp,T J, *Introductory Photochemistry*, (London: McGraw-Hill, 1971); Wayne, R P, *Photochemistry*, (London: Butterworths, 1970). The comprehensive research manual is: Calvert, J G, and Pitts, J N Jr, *Photochemistry*, (New York: John Wiley & Sons Inc, 1966)

[226] For biographical background on the scientists, see: Roger Jones and Mike Ware, *What's Who?*, (Leicester: Troubador Publishing Ltd, 2010)

[227] The quantum yield (defined as number of molecules changed divided by number of photons absorbed) is then said to be equal to one. Departures from this value significantly greater than one can apparently arise when the light triggers a chain reaction, but this is not the case in iron-based photographic processes. The quantum yield can quite commonly appear to be less than 1.0, however, due to competing reactions which diminish the efficiency of the photochemical process.

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[228] A 'print-out' material acquires its image by the action of light alone; there is no chemical amplification of the effect by development with added chemicals.

[229] The ISO (arithmetic) speed is defined as 0.8/exposure in lux-seconds to give a just-perceptible image. A minimal exposure of one second to the sun's illumination (on average, say, 80,000 lux) gives a speed of about 1/100,000 = 10^{-5} ISO.

[230] Review of 5th Exhibition of the 'Photographic Society',*The Athenæum*, 1582, (20 February 1858), p246.

[231] Hydrogen cyanide is recognisable by a smell of 'bitter almonds'. It is highly toxic.

[232] A mixture of ferric and ferricyanide ions is powerful enough to oxidise the cellulose of paper, forming Prussian blue. Further explanation for the chemistry can be found in Appendix II.

[233] Hunt, R, *Researches on Light*, (London: Longman, Brown, Green, and Longmans, 1844), p142;
idem, A Manual of Photography, (London: John Joseph Griffin & Co., 1853), p52

[234] Bird, G, *The Elements of Natural Philosophy*, (London: John Churchill, 1854), 4th edn., p576

[235] Wilson, J L, 'The Cyanotype', in Pritchard, M, (ed.) *Technology and Art: the Birth and Early Years of Photography*, Proceedings of the Royal Photographic Society Historical Group conference, September 1989 (Bath: Royal Photographic Society, 1990), p19

[236] Sutton, Thomas, and Dawson, George, (eds.), *A Dictionary of Photography*, (London: Sampson Low, Son, & Marston, 2nd edn., 1867), p79

[237] 'Employment of Ferricyanide of Potassium for Photographic Purposes', *The Photographic News*, (15 March 1872), p124

[238] Herschel Memoranda, HRHRC, Austin, Texas.

[239] This represents yet another enduring contribution by Herschel to the vocabulary of photography, joining his better-known usage of the terms 'negative', 'positive' and, indeed, the invention of the word 'photography' itself. Herschel did not, unfortunately, use the word 'solarising' in his publications, so he has not been accorded the credit for coining it. Prof. John W. Draper also used the word in 1840 to describe the overexposure of daguerreotypes: *Philosophical Magazine*, **17**, (1840), p217

[240] Herschel Memoranda, HRHRC, Austin, Texas

[241] Herschel, Sir J F W, '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), pp203-4

[242] Prof. Alexander Herschel's account of his father's recipe (according to the "London Photo News") is cited by Ernst Lietze, *Modern Heliographic Processes*, (New York: D. Van Nostrand, 1888), p56

[243] This problem is fully discussed in: Ware, M, *Mechanisms of Image Deterioration in Early Photographs*, (London: Science Museum and National Museum of Photography, Film & Television, 1994)

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[244] Hunt, R, *Researches on Light*, (London: Longman, Brown, Green, and Longmans, 1844) pp139–144. The 'hydrargyrocyanotype' is one of the seven cyanotype processes that Hunt lists as 'the most interesting of this class'. It is remarkable that he does not list, in its own right, Herschel's standard negative-working method (a), except as a preliminary to this process. The making of negative images may have seemed less important to him.

[245] Mercury(I) nitrate, $Hg_2(NO_3)_2$.

[246] 'Corrosive sublimate' is the alchemical name for mercuric chloride, or mercury(II) chloride, $HgCl_2$; it is an extremely toxic salt: ingestion of only 0.05 g can be fatal.

[247] Herschel, Sir J F W, '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)

[248] Maunder, M, 'Herschel's Genius', *Ag 41*, (Autumn 2005), p62, and 'Testing Herschel', *The PhotoHistorian*, 149 (January, 2007) pp14–21

[249] Herschel, Sir John, 'On Certain Photographic Effects', Letter dated 10 August 1842 to *The Athenæum*, **773**, (20 August 1842), p748. I am indebted to Roger Taylor for bringing this letter to my attention.

[250] Pellet, H, *British Patent no. 4632,* (6 December 1877)

[251] Pellet, H, *French Patent,* (23 November, 1877)

[252] Henri Pellet, assigned to Clarisse Zoe Joltrain, *US Patent* no. 241713 (17 May 1881)

[253] Eder, J M, 'Modern Cyanotype Printing', *The Photographic News*, **25**, 1181 (22 April 1881), p186

[254] Pellet, H, *US Patent no 241713*, (17 May 1881), as quoted in Lietze, E, *Modern Heliographic Processes*, (New York: van Nostrand, 1888) pp65–69

[255] Lietze, E, *Modern Heliographic Processes*, (New York: van Nostrand, 1888), p69

[256] Nadeau, L, *Encyclopedia of Printing, Photographic, and Photomechanical Processes*, (Fredericton: Atelier Luis Nadeau, 1990), p360

[257] Duchochois, P C, *Photographic Reproduction Processes*, (London: Hampton Judd, 1892) p33: 'We have used Pellet's paper imported from Paris, which it was impossible to work satisfactorily …'

[258] Tritton, F J, 'Photography in the Drawing Office', *The Photographic Journal*, (September 1943), p329

[259] See Eder, *loc cit*; Lietze, *loc cit*; Duchochois, *loc cit*; Brown, *op cit*, pp53–55

[260] Obtained by diluting the concentrated acid 10 times: always adding 100 cc of the acid to 1 litre of water, not vice versa.

[261] Waterhouse, Col. J, 'The Positive Cyanotype Process', *The Photographic News*, **32**, 1566 (7 September 1888), pp562–566; *idem.*, *General Report on the Operations of the Survey of India Department during 1887–1888*, (Calcutta: Government Printing Office, 1889), pp18–21

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[262] Fisch, A, *La Photocopie, ou Procédés de reproductions Industrielles par la lumière*, (Paris: Michelet, 1886)

[263] Duchochois, *op cit*, p29

[264] This is a solution of 45° Baumé = SG 1.453 = 50% $FeCl_3$ w/w – see Appendix IV.

[265] I am grateful to John Falconer, Keeper of the Oriental and India Office Collections of the British Library for providing information concerning Waterhouse.

[266] Price, Lois Alcott, *Line, Shade and Shadow: The Fabriction and Preservation of Architectural Drawings*, (Wilmington DE: Oak Knoll Press, 2010)

[267] Valenta, E, *Photographisches Correspondenz* (1897), p74

[268] Eder, J M, *Jahrbuch für Photographie*, (1898), p448

[269] J Merk in Darmstadt, and Dr. Theodor Schuchardt, Chemische Fabrik, in Goerlitz.

[270] It is an oversimplification to suggest that there are just two varieties of this substance. In fact, ammonium ferric citrate is an 'ill-characterised' compound whose composition depends on the method of preparation, and it may vary in iron content from 14% to 28%, corresponding to a colour shift from green to brown.

[271] The main bibliographic sources of the cyanotype formulations in this survey were:

Brothers, A, *A Manual of Photography,* (London: Charles Griffin and Co, 1899)

Brown, G E, *Ferric and Heliographic Processes,* (London: Dawbarn and Ward, 1902)

Burbank, Rev W H, *Photographic Printing Methods*, (New York: Scovill and Adams Co, 1891)

Burton, W K, *Practical Guide to Photographic and Photo-mechanical Printing Processes*, (London: Marion & Co, 1892)

Clerc, L P, *Photography, Theory and Practice*, (London: Sir Isaac Pitman and Sons, 1954)

Duchochois, P C, *Photographic Reproduction Processes*, (London: Hampton Judd, 1892)

Eder, J M, *Die Lichtpausverfahren*, from *Ausführliches Handbuch der Photographie*, (Halle: Wilhelm Knapp, 1899)

Jones B E, (ed.), *Cassell's Cyclopaedia of Photography*, (London: Cassell and Co, 1911)

Kosar, J, *Light Sensitive Systems*, (New York: John Wiley and Sons, 1965)

Lietze, E, *Modern Heliographic Processes*, (New York: Van Nostrand, 1888)

Neblette, C B, *Photography: its Materials and Processes*, (London: Macmillan and Co, 1952)

Tennant, J A, (ed.), *The Photominiature*, **1**, (10) (London: Dawbarn and Ward, 1900)

Wall, E J, *Dictionary of Photography*, (London: Hazell, Watson and Viney, 1895)

Wall, E J, and Jordan, F I, *Photographic Facts and Formulas*, (Boston: American Photographic Publishing Co, 1947)
Ward, H S, *Figures, Facts and Formulae of Photography*, (London: Dawbarn and Ward, 1903)
Watts, W A, *The Photographic Reference Book*, (London: Iliffe and Son, 1896)

[272] A concentration of X % w/v (read as 'X weight per cent volume') means that a weight, X grams (g), of the solute is contained in a volume, 100 cubic centimeters (cc), of the solution. For further details of the various means of expressing concentration see Appendix IV.

[273] Whitaker, C, 'Apparatus for Printing by the Blue Process', *The Photographic News*, (8 June 1883) pp358-9

[274] Hunt, R, 'Chromo-Cyanotype, a new Photographic Process', *Philosophical Magazine*, (June, 1844), pp435-9

[275] Hunt, Robert, *A Manual of Photography*, (London: Richard Griffin and Company, 1854) 4th edn.

[276] *Analytica Chimica Acta*, **318**, 1 (1995), pp71-76

[277] 'Early Photographs by Robert Hunt', *The Year-Book of Photography and Photographic News Almanac*, (1890), pp193-4

[278] Letter, Mercer to Playfair, December 1847. Quoted in:
Parnell, E A, *The Life and Labours of John Mercer*, (London: Longmans, Green & Co., 1886), p222

[279] Mercer, J, 'On Chromatic Photographs', *Report of the Meeting of the British Association for the Advancement of Science, Transactions of the Sections,* (Leeds: 1858), p57. An account of cyanotype on cloth was, however, pre-published by R. Smith, *Journal of the Society of Arts*, (4 February 1853), p121

[280] But see, for an account of mordanting by iron: Mercer, John, *The British Journal of Photography*, **42** (1895), p557

[281] Parnell, E A, *The Life and Labours of John Mercer*, (London: Longmans, Green & Co., 1886), pp220-230, 328-337

[282] The standard histories of photography make no mention of John Mercer. His contributions to photography were only brought to public knowledge recently, by Dr. Stella Butler, curator of the North West Museum of Science and Industry in a lecture to the Historical Group of the Royal Society of Chemistry, at Liverpool in June 1987.

[283] http://archivecat.lancashire.gov.uk/CalmView/record.aspx?src=CalmView.Catalog&id=UDCL/8/19

[284] Letter, Burnett to Church, dated 1 September 1855. I am indebted to Sara Stevenson for bringing this letter to my attention.

[285] 'Ferridcyanide' is an obsolete alternative for ferricyanide. It had the merit of amplifying the difference between this, and ferrocyanide.

[286] Catalogue of the exhibition of Glasgow Photographic Association, staged for the British Association meeting in Glasgow, September, 1855. I am indebted to Roger Taylor for producing this catalogue entry from his database.

[287] Burnett, C J, "On the application of Uranium and other matters to Photography", *Photographic Notes*, **23** (1857), pp97-101

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[288] Sodium nitroprusside is now corrrectly called sodium nitrosylpentacyanoferrate, $Na_2Fe(NO)(CN)_5$

[289] "Description of Mr. Burnett's Pictures in the Photographic Exhibition, Suffolk Street", *Journal of the Photographic Society*, (5 February, 1859), p182

[290] West, Redfield B., "Photosensitive Composition", *US patent no.* 625,527, 23 May 1899.

[291] Maddox, R L, 'A Cyanotype Process', *The British Journal Photographic Almanac*, (1892) pp544-6

[292] Lumiére, A, and Lumiére, L, 'New Photographic Iron Printing Process', *The British Journal of Photography*, **47**, 2121 (1900), p820

[293] Valenta, E, 'Ferro-Prussiate Sensitizers', *The British Journal of Photography*, (9 February 1917), p70

[294] Halleur, G.C. Hermann, *The Art of Photography*, (G.L. Strauss, trans.), (London: John Weale, 1854), p57

[295] Editorial, *Popular Science Review*, **3** (1864), p131; C. Guillou, "Blue Photographs", *Photographic Notes*, **9**, 186, (1 January 1864), p10

[296] Traill-Taylor, 'Iron Printing', *The British Journal Photographic Almanac, and Photographer's Daily Companion*, (1889), pp357-360

[297] Valenta, E, 'Verwendung von Ferrialkalioxalat als Ersatz für Ferriammoniumzitrat beim Zyanotypverfahren', *Photographische Korrespondenz*, 728 (May 1921), p107

[298] The guanidinium cation has the formula $C(NH_2)_3^+$

[299] Barnes, Robert Bowling, 'Ferric guanidine oxalate and a process of making it', *U.S. Patent* no. 2,265,934, (9 December 1941). http://www.freepatentsonline.com/2265934.pdf

[300] http://thecarbonworks.com/blog/?p=1286

[301] Hnatek, A, 'Uber die Steigerung der Lichtempfindlichkeit von braunem Ferriammoniumcitrat durch Beimengung verschiedener organischer Säuren', *Photographische Korrespondenz*, **91**, 7 (1955), pp111-5

[302] King, Terry, 'Changing the Blueprint', *British Journal of Photography*, **151**, 7490, (21 July 2004), pp31-33.

[303] "Printing with Salts of Iron", *The British Journal of Photography*, **21**, 718, (6 February, 1874), pp72

[304] Sullivan, Richard, "Ferric Oxalate: its Care and Feeding": http://www.bostick-sullivan.com/techart.php

[305] King, Terry, 'The Cyanotype Rex: a *Hands-On Pictures* manual: http://www.hands-on-pictures.com/Tutorials/Rex.html

[306] King, Terry, 'Changing the Blueprint', *op. cit.*

[307] Maunder, Michael, 'Ironing Wrinkles', *Ag 40*, (Summer 2005), pp78-83

[308] King, Terry, "Chrysotype Rex and Cyanotype Rex: A Revolution in Iron Based Processes", *View Camera*, (November/December, 2005), pp40-43

[309] Of all the incident light scattered by a photographic subject, only a small fraction (*ca.* one hundredth to one thousandth) is captured by a camera lens and projected onto the photographically sensitized surface. It follows from the law of reciprocity that direct exposure of the same sensitized surface to the incident rays of the sun, to make

a contact exposure, will take only about one hundredth to one thousandth of the camera exposure time, to provide a clear outline of any object placed upon it. Such 'photograms' or prints are therefore much easier to make by direct contact than are camera photographs, see:
Ware, Mike, ‘On Proto-photography and the Shroud of Turin’, *History of Photography*, **21**, 4, (Winter 1997), pp261-9. See also:
http://www.usask.ca/lists/alt-photo-process-l/200609/msg00420.html

[310] King, Terry, *op. cit.*

[311] http://www.alternativephotography.com/wp/processes/cyanotype/making-cyanotypes-in-camera

[312] https://www.facebook.com/groups/68142897748/permalink/10151454186012749/?comment_id=10151454267582749&offset=0&total_comments=6

[313] Townsend, N, and Ware, M J, *unpublished observations*, 1990

[314] Burnett, C J, *Photographic Notes*, (1857), p99

[315] http://unblinkingeye.com/Articles/Uranium/uranium.html

[316] http://www.youtube.com/watch?v=AeDK6byP2tk&feature=youtu.be

[317] http://periodictable.com/Elements/092/

[318] Neblette, C B, *Photography: Its Principles and Practice*, (London: Chapman & Hall, 1942), 4th edn., pp657-8

[319] Ware, Mike, *Platinomicon: The History, Science and Art of Photographic Printing in Platinum and Palladium,* 2013.

[320] McCorkle, James, "On the Uranium Toning of Platinum Paper", *Camera Notes*, **6**, 2, (1902), p90; John A, Tennant, (ed.), "Platinotype Processes", *The Photo-Miniature*, **1**, 7, (October 1899), pp319-355; "Platinotype Modifications", *The Photo-Miniature*, **4**, 40, (July 1902), pp153-193, 605-9; "Platinum Printing", *The Photo-Miniature*, **10**, 115, (May 1911), pp305-342.

[321] Benecke, R, ‘Transparencies in Prussian Blue’, *The Year-Book of Photography and Photographic News Almanac*, (1890), p194

[322] Raess, H F, ‘How to Make Blue Lantern Slides and Transparencies’, *The International Annual of Anthony’s Photographic Bulletin and American Process Year-Book*, **10,** (1898), pp175-177

[323] Brown, G E, *Ferric and Heliographic Processes,* (London: Dawbarn and Ward, 1902), pp20-24

[324] http://www.alternativephotography.com/wp/processes/platinum/carrier-clear-coating-for-printing-platinumpaladiumgold-and-pigment-on-glass

[325] http://www.apug.org/forums/archive/index.php/t-93695.html

[326] http://www.glithero.com/blueware-tiles

[327] http://www.glithero.com/blueware-vases

[328] Muspratt, S, *Chemistry, Theoretical, Practical and Analytical, as Applied and Relating to the Arts and Manufactures*, (Glasgow: William Mackenzie, 1860), pp647-9

[329] Stieglitz, Mary, “Historic Photographs on Cloth”, *History of Photography*, **1**, 2, (April 1977), pp105-110

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[330] Arnow, J, *Handbook of Alternative Photographic Processes*, (New York: Van Nostrand Reinhold, 1982)

[331] Wilson, W, *private communication*, Royal College of Art, 1998.

[332] Lucas, A D, 'Health Hazards Associated with the Cyanotype Printing Process', *Journal of Environmental Pathology, Toxicology and Oncology*, **11**, 1 (1992), pp18-20

[333] *Amateur Photographer Booklet No. 9.* Nashua Pillow Co., Manufacturers of Silkdown™ Specialities, Pillows, Cushions, and Photographic Blue Print Covers. 6-18 Pearsons Avenue, Nashua NH, (1900).
I am indebted to the late Peter Palmquist, curator of the *Women in Photography International Archive*, for supplying me with a photocopy of this catalogue.

[334] I thank Hazel McKenzie and Ann Thomas of the NGC for making this item available to me.

[335] Hewitt, Barbara, *Blueprints on Fabric*, (Colorado: Interweave Press, 1995)

[336] http://www.alternativephotography.com/wp/photographers/linda-stemers-cyanotype-business
http://www.blueprintsonfabric.com/

[337] http://www.stonecreeksilk.co.uk/

[338] Brown, Ruth, *Cyanotypes on Fabric*, (Sunk Island: SC Publications, 2006)

[339] Stieglitz, Mary, "Photography & Fabric: A Long-Term Relationship", *Surface Design*, (Fall, 2006), pp6-7; Malarcher, Patricia, "Picturing the World in Blue Cyanotype", *ibid.*, pp8-11

[340] Tellkampf, A, and Traube, A, *German Patent* no 201968, (10 August, 1905)

[341] Nadeau, L, *Encyclopedia of Printing, Photographic, and Photomechanical Processes*, (Fredericton: Atelier Luis Nadeau, 1990), p453 and references cited therein.

[342] Dorel, Felix, *US patent no 1,386,995* (filed 1918, awarded 1921)

[343] Priseman, C, 'Iron Printing Processes', *The British Journal of Photography*, (19 July 1918), pp324-5

[344] Brown, E, 'Some Notes on the True-to-scale Gelatine Process', *British Journal of Photography*, **86** (8 December 1939), pp719-721

[345] Price, Lois Olcott, *Line, Shade and Shadow: the Fabrication and Preservation of Architectural Drawings,* (Wilmington DE: Oak Knoll Press, 2010), pp211-214

[346] Spencer, D A, 'A New Application of the Ferro-Gelatin Process', *Seventh International Congress of Photography*, pp354-8

[347] Farnham, Roger, "Gel Lithography", in *Blueprint: Photography and Engineering*, Roger Farnham and Harry Magee (eds.), (Glasgow: Print Studio and Street Level Photoworks, 2013)
http://www.blueprint2013.com

[348] Schömmer, F, *Photographische Rundschau und Mitteilungen*, **62,** (1925), p46, as reported in *American Photography*, (1926), p331. I

am grateful to Richard Farber for bringing this process to my attention.

[349] Kissell, Eléonore, and Vigneau, Erin, *Architectural Photoreproductions: a Manual for Identification and Care*, (New York: Oak Knoll Press & New York Botanical Library, 1999); see also Price, Lois Olcott, *loc.cit.*

[350] Crowley, C A, and Goodyear, G H, *US Patent no. 2,350,991* (13 June 1944)

[351] Kwech, R E, 'Commercial Blue-print Papers', *The British Journal of Photography*, **71** (15 August 1924), pp491-3; this is a reprint of an article first published in *American Photography*.

[352] Willcock, K, *British Journal of Photography*, **82** (19 July 1935), p458

[353] Neblette, *op cit*, pp697-700

[354] Kosar, J, *Light Sensitive Systems: Chemistry and Application of Non Silver Halide Photographic Processes*, (New York: John Wiley and Sons, 1965), pp28-37

[355] Priseman, C, 'Iron Printing Processes', *The British Journal of Photography*, (19 July 1918), p324

[356] Reichert, J S, *US Patent* no 1,998,883 (23 April 1935)

[357] Kwech, R E, *US Patent* no 1,877,246 (13 September 1932);
Crowley, C A, and Goodyear, G H, *US Patent* no 2,093,421 (21 September 1937)

[358] Holden, J, *British Patent* no 418,369 (24 October 1934)

[359] Reynolds, A P, *US Patent* no 2,093,738 (21 September, 1937)

[360] *Andrews Reproduction Paper Coating*, (New York: Andrews Paper & Chemical Co. Inc., 1964), p20. I am indebted to Reg Heron for this reference.
Jahoda, E, *US Patent* no 2,517,111 (1 August 1950)

[361] Heron, R, 'Blueprint into Blackprint', *Afterimage*, **1**, 9 (December 1973), pp4-7, 12

[362] I am indebted to Reginald Heron for information on this paper and the loan of specimen prints.

[363] *Andrews Reproduction Paper Coating*, (New York: Andrews Paper & Chemical Co. Inc., 1964), pp49, 53

[364] *Reproduction Bulletin*, (Andrews Paper & Chemical Co. Inc., 1972).

[365] By the Huey Company of Chicago, and the Universal Blueprint Paper Company of Denver and Fort Worth.

[366] The paper may be obtained from NaturePrint™, P.O.Box 314 Moraga, California 94556, USA.

[367] The only camera negatives known to have been made by John Herschel are views of his father's 40-foot telescope at Slough. Specimens of these negatives are in the collections of the Museum of the History of Science, in Oxford, and the National Museum of Photography, Film & Television.

[368] Talbot, W H F, 'An account of some recent improvements in photography', *Proceedings of the Royal Society*, **4**, 48 (1841), pp312-16

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[369] Herschel recorded in his diary on 14 February 1839: '...pursued without intermission the Photographic transfer of engravings. Prepared and set going a lot sent me by P. Stew^{t}...'

[370] Beck, H, *Victorian Engravings*, (London: Victoria & Albert Museum, 1973), pp19–23

[371] Herschel, Sir J F W, *MS Notebooks*, vol III, Science Museum Library, London.

[372] I shall use the terms 'correct' and 'reversed' to denote the chirality (handedness) of an image with respect to the original object. A spatially 'reversed' photograph depicts the mirror image of the original, when viewed from the recto. Herschel also used this word, but rather than 'correct' he used 'direct' – which I shall avoid because it might be taken today to imply a different meaning. These adjectives will be used in conjunction with the nouns 'positive' or 'negative' to denote the tonality of the image. This should be carefully distinguished from a third characteristic: the intrinsic response of the process itself, which may be inherently either positive-working or negative-working.

[373] This he first did on 31 January 1839, and showed the result to Talbot on 1 February 1839.

[374] Thus, the result of making a negative of a negative is a positive, just as $-1 \times -1 = +1$; while a negative of a positive is still a negative: $-1 \times +1 = -1$, and a positive of a positive is a positive: $+1 \times +1 = +1$. The analogy could also be argued that the 'sum' of a negative and a positive is blank, i.e. zero: $-1+1 = 0$.

[375] Schaaf, L, 'Sir John Herschel's 1839 Royal Society Paper on Photography', *History of Photography*, **3**, 1 (January 1979), pp47–60

[376] Herschel, Sir J F W, 'On the Chemical Action of the Rays of the Solar Spectrum on Preparations of Silver and other Substances, both metallic and non-metallic, and on some Photographic Processes', *Philosophical Transactions of the Royal Society*, (1840) pp3, 7–8

[377] The concepts of optical densitometry and the characteristic curve of a photosensitive layer lay several decades into the future.

[378] There is just one engraving diaphane in the NMPFT collection, and it has not been completely cropped, so the partly excised title can be matched to one of Herschel's titles: *Rosolia*. There are frequent references to this title in the *Memoranda*; one of Herschel's positive cyanotypes of this image has been published by Schaaf.

[379] I am indebted to Dr Sara Stevenson, Chief Curator of Photographs at the Scottish National Portrait Gallery, for her invaluable help in searching for and identifying these two engravings.

[380] *Art Libraries Association Portrait Index*, p1377

[381] Pringle, T, (ed.), *Friendship's Offering; and Winter's Wreath: A Christmas and New Year's Present for MCCCCXXXVI*, (London: Smith, Elder & Co., 1836), Plate III, facing p36

[382] Renier, A, *Friendship's Offering: An Essay on the Annuals and Gift Books of the 19th Century*, (London: Private Libraries Association, 1964)

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[383] *British Museum Catalogue of Engraved British Portraits*, p553

[384] Pringle, T, (ed.), *Friendship's Offering; and Winter's Wreath: A Christmas and New Year's Present for MCCCCXXXVIII*, (London: Smith, Elder & Co., 1838), Plate IV, facing p73

[385] A postcard reproduction of a negative cyanotype made by Herschel from this engraving is obtainable from the Museum of the History of Science at Oxford.

[386] Many of the library holdings of *Friendship's Offering* are incomplete. The National Arts Library, the British Library, the Bodleian Library, Oxford, and Birmingham Public Library have almost complete runs.

[387] In the archive at the Museum of the History of Science, at Oxford, on a packet labelled '1 Cyanotype, 2 Amphitypes' there is a note in Herschel's hand which reads: 'Dr. Sir, when done with...sent to care of Mr Stewart, 65 Cornhill. They will come safe to hand.'

[388] Simcock, A V, *Photography 150: Images from the First Generation*, (Oxford: Museum of the History of Science, 1989), p22

[389] Britton, J, *Modern Athens! Displayed in a Series of Views: or Edinburgh in the Nineteenth Century, from original drawings by Thomas H. Shepherd*, (London: Jones & Co., 1831), reissued (New York: Benjamin Blom, Inc., 1969)

[390] Simcock, A V, 'An ark for the history of science', *International Association of Technological University Libraries Quarterly*, **1**, 3, (1987), pp196-215

[391] http://norman.hrc.utexas.edu/photoPublic/fullDisplay.cfm?CollID=73

[392] Schultze, R S, 'Re-discovery and Description of Original Material on the Photographic Researches of Sir John F. W. Herschel, 1839-1844', *Journal of Photographic Science*, **13** (1965), pp57-68.

[393] Simcock, A V, *Photography 150: Images from the First Generation*, (Oxford: Museum of the History of Science, 1989)

[394] For a transcription of this MS see: Helmut Gernsheim, *Julia Margaret Cameron*, (London: The Fountain Press, 1948), p71, Plates 4 and 51

[395] Schultze, *loc. cit.*

[396] The validity of these arguments rests on two assumptions, which are justified by the generally sharp quality of the resulting images: namely, that Herschel did not make more than two successive derivative contact prints from an engraving, and that he did not print through the *verso* of an engraving to obtain an image of the same chirality in one step.

[397] Cat. no. 1943-39/72

[398] Schaaf, L J, *Out of the Shadows: Herschel, Talbot & the Invention of Photography*, (New Haven: Yale University Press, 1992), fig 82, p128.

[399] The original engraving diaphane of *Rosolia* is also in the NMPFT. It comes from *Friendship's Offering* for 1837, Plate X, p289.

[400] These four sheets of specimens are now in the Harry Ransom Humanities Research Centre, at Austin, Texas.

[401] http://norman.hrc.utexas.edu/photoPublic/fullDisplay.cfm?CollID=73

[402] The 'coating weight' is defined as the weight of a specified component per unit area of the surface.

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[403] Which corresponds typically to a volume of 1.4 cc applied to an A4 sheet.

[404] Schaaf, L J, *Sun Gardens. Victorian Photograms by Anna Atkins*, (New York: Aperture, 1985)

[405] Children, J G, 'Lamarck's Genera of Shells', *The Quarterly Journal of Science, Literature and the Arts*, **16**, 31 (1823)

[406] Schaaf, *o.p cit.*, p24

[407] 'Fac-simile of a Photogenic Drawing', *The Mirror of Literature, Amusement, and Instruction*, **33**, 945 (20 April 1839), p241

[408] Hervey, W H, *A Manual of British Algae*, (London: John van Voorst, 1841)

[409] A. A. [Atkins, Anna], *Photographs of British Algae. Cyanotype Impressions.,* (Halstead Place, Sevenoaks: privately published, 1843-53)

[410] Hunt, R, 'On the Application of Science to the Fine and Useful Arts. Photography – second part.' *The Art-Union Monthly Journal*, **10,** (1 August 1848), pp237-8

[411] Talbot, H F, 'On Photography without the Use of Silver', *The British Journal of Photography*, **9,** (9 December 1864), pp495-6

[412] Hunt's and Lang's copy passed through Christie's sale rooms in 2004: http://www.christies.com/LotFinder/lot_details.aspx?intObjectID=4278518

[413] Lang, W, 'The Cyanotype Reproduction of Sea-Weeds', *The Photographic News*, **34**, 1683 (5 December 1890), p948

[414] Lang, W, 'The Cyanotype Reproduction of Seaweeds', *Proceedings of the Philosophical Society of Glasgow*, **21**, (1889-90), p155; *idem., Photographic News*, **34**, (5 December 1890), p948; *idem., British Journal of Photography*, (25 October 1889), p702.

[415] http://digitalgallery.nypl.org/nypldigital/dgtitle_tree.cfm?title_id=100174&level=1&parent_id=288165&word=&s=&notword=&d=&c=&f=&k=0&sScope=&sLevel=&sLabel=&lword=&lfield=&imgs=20&snum=0

[416] *The Anna Atkins Volumes*, Auction Catalogue on CD-ROM (London: Bonhams of Knightsbridge, 1996)

[417] *The Guardian*, (Wednesday 19 June 1996), p5; *The Observer*, (Sunday 23 June 1996), p20-23

[418] As with most claims to be 'first', this can be disputed – depending on the precise interpretation that is placed on the expression 'photographically illustrated book'. The debate does not detract one scintilla from Anna Atkins's achievement, however.

[419] Anne Dixon (1799-1864) was born Anne Austen (a second cousin to the novelist); she married Henry Dixon, the vicar of Ferring, Sussex, in 1837; the couples spent much time together, including botanising on the Sussex seashores.

[420] Atkins, A, *Memoir of John George Children, Esq., Including Some Unpublished Poetry by His father and Himself*, (London: John Bowyer Nichols & Sons, 1853)

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[421] Wilson, J L, *Some aspects of the photographically illustrated book*, a lecture delivered to the Historical Group of the Royal Photographic Society, (20 January 1988).

[422] Wilson, J L, 'The Cyanotype', in Pritchard, M, (ed.), *Technology and Art: the Birth and Early Years of Photography*, (Bath: Royal Photographic Society Historical Group, 1990), pp19-25

[423] Johnstone, W G, and Croall, A, *The Nature-Printed British Seaweeds: a History, accompanied by Figures and Dissections of the Algae of the British Isles*, Nature-Printed by Henry Bradbury. (London: Bradbury and Evans, 1859), vol I, p77; *ibid* vol II, p143

[424] *The Athenaeum*, 1657, (30 July 1859), pp149-150

[425] *The Athenaeum Review Database*, III, 1713, (25 August 1860), 293; *ibid.,* IV, 1714, (1 September 1860), 262

[426] This album, lent from the collection of Hans Kraus Jnr., was displayed in the exhibition 'Photography in Science: Beauty of Another Order' at the National Gallery of Canada, Ottawa, in 1997. I am indebted to Hans Kraus for kindly affording me the opportunity to examine it.

[427] *The Photographic Journal*, **137**, 7 (September 1997), p281. See also *ibid.* **135**, 10 (November 1995), pp418-420

[428] Schaaf, L J, *Sun Gardens; an Exhibition of Victorian Photograms by Anna Atkins*, Crawford Centre for the Arts, The University of St. Andrews, 1988

[429] For the 'Meteorological Observations' for these months, see, for example, *The Philosophical Magazine*, **22**, 146 and 148, (May and June 1843), pp415 and 503 respectively.

[430] The question is further complicated by the fact that some of the author's pencilled annotations refer to 'modifications of the Herschel formula', labelled by the author as A, B, and C. There is no obvious difference between the resulting prints so labelled, and despite the coincidence, this notation cannot be identified with Herschel's own 'varieties (a), (b), and (c)', because (b) and (c) were positive-working processes, as has been deduced earlier, but all the cyanotypes in *Dried Ferns* were obviously made by a negative-working process. It seems likely that these 'modifications' A, B, and C, were only minor variants in the processing, because they have not given rise to any sensible difference in the final images.

[431] Armstrong, Carol, and de Zegher, Catherine, (eds.), *Ocean Flowers: Impressions from Nature*, (New York: The Drawing Center & Princeton University Press, 2004)

[432] I am indebted to John Sullivan, curator of the photographic archive of the National Library of New Zealand, for this information. See also: Sampson, F B, *Early New Zealand Botanical Art*, (Reed Methuen, 1985), pp109-110

[433] DiNoto, Andrea, and Winter, David, *The Pressed Plant: The Art of Botanical Specimens, Nature Prints, and Sun Pictures*, (New York: Stewart, Tabori & Chang, 1999), pp126-7

[434] Hamilton, A, *Four Flowers: Cyanotypes,* Catalogue for a touring exhibition, (Edinburgh: Fotofeis Ltd., 1995)

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[435] Janis, E P, and Sartre, J, *Henri Le Secq: Photograph de 1850 à 1860*, (Paris: Musée des Arts Décoratifs/Flammarion, 1986)

[436] Jammes, A, and Janis, E P, *The Art of the French Calotype,* (Princeton, NJ: Princeton University Press), pp206-210

[437] Le Secq's negatives were made exclusively by the waxed paper process.

[438] Janis, E P and Sartre, J, *op. cit.*, p39

[439] Musée d'Orsay, exhibition 1996-7: *Paul B. Haviland (1880-1950): a photographer*:
http://www.musee-orsay.fr/en/events/exhibitions/in-the-musee-dorsay/exhibitions-in-the-musee-dorsay/article/paul-b-haviland-1880-1950-a-photographer-4449.html?cHash=4edb944c85

[440] Heilbrun, F, and Bajac Q, *Paul Burty Haviland (1880-1950), photographe*, (Paris: Editions de la Réunion des musées nationaux, 1996), p84. I am indebted to Roger Wilson and Pamela Roberts for first bringing this work to my attention.

[441] Heilbrun, F, and Bajac Q, *op cit.,* p66

[442] I thank the owner of the album, John Moran and his family, for the kind provision of information on this work.

[443] Fairbrother, Trevor, *Ipswich Days: Arthur Wesley Dow and his hometown,* (Andover: Addison Gallery of American Art, 2007).

[444] http://www.mhs.ox.ac.uk/collections/imu-search-page/results/?query=Teasdale&thumbnails=on&querytype=basic
http://www.mhs.ox.ac.uk/cameras/index.htm?item75

[445] http://www.mhs.ox.ac.uk/collections/search/display-narrative/?irn=14216&index=1

[446] http://www.luminous-lint.com/app/photographer/Washington__Teasdale/A/

[447] Jacobson, K, *Études d'après Nature*, (Petches Bridge: Ken & Jenny Jacobson, 1996), pp135, 162

[448] Many of the Rijksmuseum's 611 cyanotypes may be viewed online:
https://www.rijksmuseum.nl/en/search?p=1&ps=12&technique=cyanotypie&ii=3
I thank Photograph Conservator, Martin Jürgens for this information.

[449] Braun, Marta, 'Muybridge's *Animal Locomotion*: The Director's Cut', *History of Photography*, **24**, 1, (Spring 2000), pp52-54:
http://www.flickr.com/photos/publicresourceorg/sets/72157600215529969/with/493890432/

[450] Information posted to the PhotoHistory List of the Internet by Debbie Griggs Carter. One such strip was exhibited at the Cinema's Centennial Exhibition in 1995.

[451] Bartholomew, E, Curator, Photographic & Film Collection, National Railway Museum, York, *a private communication*.

[452] Ware, Mike, *Annual Annan Lecture, 2013*, of The Scottish Society for the History of Photography, "Cyanotype: a Blueprint for Visual Vandalism?", *Studies in Photography*, (2013), pp24-44

[453] Stevenson, S, *Light from the Dark Room*, (Edinburgh: National Galleries of Scotland, 1995), p113

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[454] Album, *Forth Bridge*, Canadian Centre for Architecture, Montreal: http://www.cca.qc.ca/en/collection/504-forth-bridge-scotland
see also: Phyllis Lambert, *Casabella*, October 2000: http://www.cca.qc.ca/en/collection/660-queensferry-cantilever-as-seen-from-the-south-approach

[455] Grey, Michael, and Maggi, Angelo, *Evelyn George Carey: Forth Bridge* (Milan: Federico Motta Editore, 2009).

[456] Album of cyanotypes, *Percement du Canal de Panama*, (1888-ca.1903), (Canberra:National Library of Australia,) http://catalogue.nla.gov.au/Record/3044425

[457] I am indebted to Philip Jackson of the National Library of Australia for this information.

[458] Neuzil, Mark, *Views on the Mississippi: The Photographs of Henry Peter Bosse* (Minneapolis: University of Minnesota press, 2001).

[459] Pullis, Pierre, cyanotypes of New York City Subway construction 1901-09:
http://catalogue.swanngalleries.com/asp/fullCatalogue.asp?salelot=2298++++++69+&refno=++659886&saletype
http://tinyurl.com/q6ps8md

[460] http://www.luminous-lint.com/app/home/?action=ACT_VEX&p1=_PROCESS_Cyanotype_01&p2=1&p3=0&p4=0

[461] Goldblatt, R, ‘The Mafeking Blues’, *The South African Philatelist*, (March 1978), pp62-79

[462] The account is slightly obscured by the common error of transposing ferrocyanide for ferricyanide.

[463] Bensusan, A D, *Silver Images: History of Photography in Africa*, (Cape Town: H Timmons, 1966)

[464] *The Dictionary of National Biography* has his forename as “Edwin”.

[465] I thank Julia Findlater, Curator of Leighton House, for showing me this material.

[466] Roberts, M A, ‘Edward Linley Sambourne (1844-1910)’, *History of Photography*, **17**, 2 (1993), pp207-213; Rimmer, R W, ‘A Note on Linley Sambourne (1844-1910)’, *The Photohistorian*, 110 (January 1996), pp13-15; Gent, M, *The Cyanotype*, Materials and Techniques Essay, Royal College of Art MA course in conservation, 1992

[467] Simon, Robin, (ed.), *Public Artist, Private Passions*, Exhibition catalogue, (London: Kensington and Chelsea Libraries and Arts Service, 2001); Grant, Lucille, “Salacious and Satirical”, *Journal of the Royal Photographic Society*, (October 2001), pp376-7

[468] https://www.facebook.com/groups/13488949283/

[469] http://www.flickr.com/photos/tags/cyanotype/
http://www.flickr.com/groups/61907246@N00/

[470] http://www.alternativephotography.com/wp/category/gallery-by-process/cyanotype-photographers

[471] http://www.alternativephotography.com/wp/essays/cyanotypes-a-new-look-at-an-old-technique-thesis

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[472] http://www.angela-easterling.co.uk/angela-easterling.co.uk/blueprint_for_living.html
http://www.angela-easterling.co.uk/angela-easterling.co.uk/Workshops.html

[473] http://www.nickveasey.blogspot.co.uk/2012/05/from-rocks-and-reefs.html

[474] http://www.dcfineart.net/

[475] Farnham, Roger, and Magee, Harry, (eds.), *Blueprint* : *photography and engineering,* (Glasgow Print Studio, 2013) http://www.blueprint2013.com

[476] Fabbri, Malin, *Alternative Photography: Art and Artists, Edition I*, (Stockholm: AlternativePhotography.com, 2006); Fabbri, Malin, and Fabbri, Gary, *Blueprint to Cyanotypes: Exploring a historical alternative photographic process*, (Stockholm: AlternativePhotography.com, 2004)

[477] http://www.schaeferphoto.com/

[478] http://www.photographydealers.com/artists/john-dugdale/
http://www.holdenluntz.com/artists/john-dugdale

[479] http://www.ciurejlochmanphoto.com/naturalhistory/nathist01.html

[480] http://www.museumofmemory.com/

[481] http://alternativeimpressions.wordpress.com/category/cyanotypes/
http://lightimpressions.blogspot.co.uk/search/label/Cyanotypes?zx=521ae47e508555a1

[482] Wood, John, "The Art of the Cyanotype and the Vandalous Dreams of John Metoyer", in *The Photographic Arts*, (Iowa: University of Iowa Press, 1997)

[483] http://www.brentonhamiltonstudio.net/main.html

[484] http://peternappi.squarespace.com/cyanotypes/

[485] Crawford, W, *The Keepers of Light*, (New York: Morgan & Morgan, 1979); Farber, R, *Historic Photographic Processes: A Guide to Creating Handmade Photographic Images*, (Allworth Press, 1998); James, Christopher, *Alternative Photographic Processes*, (New York: Delmar Cengage Learning, 2009); Enfield, Jill, *Jill Enfield's Guide to Photographic Alternative Processes*, (New York: Focal Press, 2013; Anderson, Christina Z.,

[486] An exception to this was the solar microscope, which harnessed the sun's rays to project an enlarged image with sufficient intensity to be printable on the very insensitive papers of the time. A primitive enlarger employing the sun's light was also described by John Stewart, the brother-in-law of Sir John Herschel, in the *Journal of the Photographic Society,* **1**, 8 (22 August 1853), pp101-3.

[487] Herschel is generally acknowledged as the author of the word *photograph*: he first used it in his diary on 13 February 1839; on 28 February 1839 he commended it to Talbot, and on 14 March he made the first use of it publicly. Many of his initial specimens are annotated 'J.F.W.H. Photogr.', the earliest of these being dated 10 February, 1839. Simcock has pointed out that it is not clear exactly what Herschel intended by this abbreviation, *i.e.*, 'Photograph', 'Photographer' or 'Photographsit', analogous to the 'pinxit' of

painters. The word ‘photograph’ first appeared in print on 25 February, 1839.

[488] Batchen, G, ‘Photogenics’, *History of Photography*, **22**, 1 (1998), pp18-26

[489] Talbot originally named such images *skiagraphs*, which translates as ‘shadow-writings’, but he later changed the name to *photogenic drawings*.

[490] A cyanotype made from this anatomical specimen in the 1960s was exhibited at the National Gallery of Canada, Ottawa, in 1997 in *Photography in Science: Beauty of Another Order* .

[491] The paucity of our language in this respect is highlighted by the fact that, just to describe the simple concept of a shadow-cast image, we have had to enlist the surname of a Frenchman, M. Étienne de Silhouette (1709-1767). Duchochois (*op cit,* p22) offers us another French word, ‘Cliché’, explaining in a footnote, ‘*Cliché* is the term applied by photographers to the negatives and diapositives, and by extension to any drawing or print on transparent materials, employed in the photo-mechanical and other photographic printing methods.’ The OED definition of *cliché* as ‘a metal stereotype of a wood engraving used to print from’ implies that this is a rather inappropriate usage. However the word was also used by Waterhouse to describe Schulze’s cut-out letters, as if it were then current parlance. See *The Photographic Journal,* (June 30 1903), p166.

[492] The Shorter Oxford English Dictionary: ‘*Diaphane*. 1. A transparent body or substance; a transparency 1840. 2. A silk stuff having transparent coloured figures 1824.’
The well-known adjective ‘diaphanous’ derives from it and was used by Herschel in his 1839 paper, but it has now degenerated to a rather hackneyed stock-in-trade of the romantic novelist!

[493] It may be objected that *diaphane* is inappropriate for totally opaque objects - in which case *skiaphane* or *scotophane* might be considered.

[494] Jones, B E, (ed.) *Cassell’s Cyclopaedia of Photography,* (London: Cassell and Company, 1911), p181

[495] *The British Journal of Photography*, (15 September 1863), pp371-2.

[496] *Elegant Arts for Ladies*, (London: Ward and Lock, nd, 1861?), pp154-5. Among the several techniques of ‘diaphanie’, one describes the application of engravings to glass with ‘washable varnish’ followed by treatment with a ‘clearing liquid’. The special solutions for this purpose were available commercially from Jabez Barnard, an artists’ colourman of Oxford Street. I am grateful to Roger Taylor for discovering this reference.

[497] Kemp, Martin, *The Science of Art*, New Haven and London: Yale University Press, 1990.

[498] Puckett, R. Campbell, *Sciography or Radial Projection of Shadows,* London: Chapman & Hall, 1871; Fred Dubery and John Willats,

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Perspective and other drawing systems, London: The Herbert Press, 1983, see chapter 9 on ‘Sciography’.

[499] Ware, Mike, 'Prolegomena to a Skiology of Photogenic Drawing', *History of Photography*, **28**, 3, (Autumn 2004), pp237-246; *idem.*, ‘On Proto-photography and the Shroud of Turin’, *History of Photography*, **21**, 4, (Winter 1997), pp261-9.

[500] Vision under high illuminance, which is photopic rather than scotopic.

[501] An angle is defined in radians as the ratio of the length of the subtended arc of a circle to its radius. Since the circumference of a circle is, by definition, 2π times its radius, it follows that the conversion between the two systems of angular measurement is given by: 360 degrees ≡ 2π radians, whence 1 radian ≡ 180/π = 57.296° (degrees of arc). When angles are small (in the order of 25° or less), the length of the short arc of the circle’s circumference is closely approximated (with a precision better than 1%) by the (slightly shorter) straight line spanning the same arc (called in geometry, the ‘chord’), and we shall make frequent use of this approximation to determine small angular measures easily.

[502] Pirenne, M H, *Optics, Painting & Photography*, (Cambridge: Cambridge University Press, 1970). The light sensitive receptors in the most sensitive region of the retina, the fovea, are the cones, packed together and each subtending an angle of 0.5 minutes of arc at the pupil - *i.e.* the critical limit of angular resolution by the eye is twice this: about 1 minute of arc or ca. 1/3420 radian.

[503] The reader can easily test these figures personally, by viewing the millimeter scale of a ruler (preferably one of white plastic with black calibrations) in a good light, at distances measured with a tape, to determine the distance (in mm) at which the mm calibrations just become discernable; the reciprocal of this distance gives the angular resolution of vision in radians.

[504] Jacobson, Ralph E, (ed.), *The Manual of Photography*, (London: Focal Press, 7th edition, 1978).

[505] Or 1/100th of an inch at a distance of 10 inches.

[506] The sun's diameter is about 864,000 miles (1,391,000 kilometers). The Earth orbits the sun at an average distance of about 92,960,000 miles (149,600,000 kilometers).
The angular diameter is therefore 864,000/92,960,000 = 1/108 rad or 0.533 degrees. Data from: R. C. Weast, (ed.), *CRC Handbook of Chemistry and Physics*, (Boca Raton: CRC Press, 1980).

[507] Lynch, David K, and Livingston, William, *Color and Light in Nature*, (Cambridge: Cambridge University Press, 1995).

[508] The umbra and penumbra are most conspicuous at the time of a solar eclipse.

[509] Likewise, any diffusion of the sunlight by clouds would also have blurred a projected image by increasing the effective size of the light source.

[510] The new cyanotype process used for these photograms requires shorter exposures: one minute suffices in the Aegean sun.

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[511] Is there a case for coining a neologism here – a *tenebrogram*?

[512] See also: DiNoto, Andrea, and Winter, David, *The Pressed Plant*, (New York: Stewart, Tabori & Chang, 1999).

[513] These conditions are often agreeably met with in a Mediterranean climate!

[514] http://www.mikeware.co.uk/mikeware/HellenImp.html

[515] Roberts, J C, *The Chemistry of Paper*, (Cambridge: The Royal Society of Chemistry, 1996), pp109-110.

[516] Ware, M, 'A Handmade Paper for Alternative Processes', *Ag+ Photographic*, **7,** (1995), pp34-9

[517] UVB lies below 320 nm, at which point ordinary glass begins to absorb strongly, and UVC lies below 280 nm.

[518] http://www.pictorico.eu/productsshop/?no_cache=1&L=2 http://www.permajet.com/ProductGrp/PermaJet-Digital-Transfer-Negative-Film-165u

[519] Fabbri, Malin, and Fabbri, Gary, *Blueprint to cyanotypes: exploring a historical alternative photographic process*,

[520] Ware, M, 'A New Blueprint for Cyanotypes', *Ag+ Photographic*, **7** (1995), pp74-80; Barnier, J, 'The New Cyanotype', *Photo Techniques*, **18**, 1 (Jan/Feb 1997), pp12-15

[521] Tennant, J A, 'The Blue Print Process', *The Photo-miniature*, **8**, 81 (1906), pp432-7

[522] One well-respected practitioner complained of having to reject three bottles of the chemical before finding a satisfactory one: Judy Seigel, *World Journal of Post-Factory Photography*.

[523] *i.e. ca.* 10% *w/v* potassiumn ferricyanide, corresponding to 0.3 molar

[524] The solubility of potassium ferric oxalate is 6.6 g per 100 cc of water at 15 °C.

[525] If ammonium ferricyanide were available, making up the sensitizer would be very easy: dissolve 8 g of it in ca. 70 cc of water; add 17 g of ammonium ferric oxalate, dissolve it, and make up to 100 cc.

[526] Ware, M J, 'A New Blueprint for Cyanotypes', *Ag+ Photographic*, **7** (1995), pp74-80; Barnier, J, 'The New Cyanotype', *Photo Techniques*, **18**, 1 (1997), pp12-15

[527] called a "graduate" in the USA

[528] The chemical explanation is given in Appendix III, where it is shown why, for ferrioxalate sensitizers, acid conditions greatly promote the formation of Prussian blue after exposure.

[529] The Materials Safety Data Sheets can be found on the World Wide Web at http://www.enviro-net.com/technical/msds/

[530] Lucas, A D, 'Health Hazards Associated with the Cyanotype Printing Process', *Journal of Environmental Pathology, Toxicology and Oncology*, **11**, 1 (1992), pp18-20

[531] Dating from 1901, when Andrew Greig Barr of Glasgow adopted ammonium ferric citrate as the essential active ingredient for Scotland's *other* national drink: *Irn-Bru*. This beverage contains 0.002% ammonium ferric citrate – regrettably too dilute for making cyanotypes!

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[532] See the texts cited in ref 15

[533] Young, W Russell III, "Traditional Cyanotype", in Barnier, John, (ed.), *Coming into Focus: A Step-by-Step Guide to Alternative Photographic Printing Processes*, (San Francisco: Chronicle Books, 2000)

[534] Mrhar, Peter, *Cyanotype: Historical and Alternative Photography*, 2013.
Inspection of the works of the Cyanotype Group on Facebook: https://www.facebook.com/groups/13488949283/ suggests that about 50% of them are toned.

[535] Gent, M, *The Cyanotype*, (Materials and Techniques Essay, MA Joint Course in Conservation, RCA and V&A, November, 1992)

[536] Hewitt, Barbara, *Blueprints on Fabric: innovative uses for cyanotype*, (Loveland CO: Interweave Press, 1995), p64.

[537] It is conjectured that this effect may be due to ammonia causing a reversible deprotonation of water coordinated to Fe(III); transformation of the ligands from OH_2 to OH^- would affect the energy of the electron charge-transfer transition between Fe(III) and Fe(II), and change the colour.

[538] These deeply coloured iron complexes, when prepared directly from iron salts and an infusion of oak-galls, have provided the basis for iron-gall writing inks since medieval times.

[539] Seigel, Judy, *e-mail communication to the Alternative Photographic Process Internet List*, 1996.

[540] Many examples may be viewed on the Facebook Cyanotype group, *loc. cit.,* and similar forums.

[541] Mrhar, Peter, *Cyanotype: Historical and Alternative Photography*, 2013

[542] I acknowledge the late Harry Milligan FRPS, former Curator of Photographs at the Greater Manchester Museum of Science and Industry, for first drawing my attention in 1984 to the unpublished endeavours of John Mercer.

[543] One of Mercer's ferric processes was based on the formation of insoluble cuprous thiocyanate, which could then be toned in various ways, such as conversion to the brown cuprous ferricyanide. Mercer's work therefore antedates the process attributed to J B Obernetter, which was published in 1864.

[544] 'Box of Experiments in Chromatic Photography by John Mercer', UDCL-8/19, Lancashire County Record Office, Bow Lane, Preston.

[545] I thank Jenny Wetton, curator at the Museum of Science and Industry in Manchester, for access to this item.

[546] 'Photographic Images in Dyes', *The British Journal of Photography*, (8 July 1898), p445

[547] Eder, J M, *Rezepte Tabellen und Arbeitsvorschriften für Photographie und Reproduktionstechnik*, (Halle: Wilhelm Knapp, 1933), p220

[548] Planchon, V, *French Patent* no 639,189 (13 January 1927)

[549] Heron, R, 'Blueprint into Blackprint', *Afterimage*, **1**, 9 (December 1973), pp4-7, 12

[550] Heron, Reginald, *private communication to the author*, 1998

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[551] The presence of lead in the image substance has been detected by X-ray Fluorescence Spectrometry.

[552] http://en.wikipedia.org/wiki/Lead_poisoning#History

[553] Holtzman, H, 'Alkali Resistance of the Iron Blues', *Industrial and Engineering Chemistry*, **37**, 9 (1945), pp855-861

[554] Whiting, Harold, 'Process of toning blue prints', U.S. patent no. 397,480, (5 February 1889).

[555] Hammond, A, *How to Tone Prints*, (Boston: American Photographic Publishing Co., 1940), pp60-63

[556] Somerville, C W, *Toning Bromides and Lantern Slides*, (London: Hazell, Watson & Viney, Ltd., 1907), pp53-58; Ward, H S, *The Figures, Facts and Formulae of Photography*, (London: Dawbarn and Ward Ltd., 1903), p1

[557] Planchon, V, 'Le gélatino-prussiate', *Bulletin de la Société Française de Photographie*, 2 (February 1927), pp50-3

[558] Kirby, J, 'Fading and Colour Change of Prussian Blue: Occurrences and Early Reports', *National Gallery Technical Bulletin*, **14** (1993), pp63-70

[559] 'Lead white' is a basic lead carbonate, $PbCO_3.Pb(OH)_2$. It is possible that the basic nature of this pigment may contribute to the deterioration of Prussian blue by causing alkaline hydrolysis.

[560] Kirby, J, and Saunders, D, to be published

[561] See Eder, J M, *History of Photography*, Epstean, E, (trans.), (New York: Dover Publications Inc., 1978), p130, for an account of Desmortiers' investigations and references to his original publications.

[562] *Ibid,* p190-192

[563] Brande, W T, *A Manual of Chemistry*, (London: John W Parker, 1841), p755. Eder's date of 1849, given in reference 4, for Chevreul's finding cannot be correct.

[564] Turner, E, *Elements of Chemistry*, (London: Taylor and Walton, 1847), p751

[565] Reilly, J M, *Care and Identification of 19th Century Photographic Prints*, (Rochester: Eastman Kodak Company, 1986), p43

[566] Lathrop, A K, 'The Provenance and Preservation of Architectural Records', *The Americal Archivist*, **43**,3 (1980), pp325-338

[567] Moor I L, and Moor A H, 'The Conservation of Anna Atkins' British Algae', *Symposium on the 150th Anniversary of Photography,* Vevey, Switzerland, 29 June-2 July, 1989, (Vevey: European Society for the History of Photography, 1997)

[568] McElhone, J P, 'Determining Responsible Display Conditions for Photographs', *Topics in Photographic Preservation*, **5** (1993), pp60-72; American Institute for Conservation, Meeting of the Photographic Materials Group, Austin, Texas 1993.

[569] I am indebted to John McElhone and the National Gallery of Canada for permission to quote these findings in advance of publication.

[570] Moor, I and Moor, A, 'Atlantis Silversafe Photostore – a suitable paper for photographic conservation' *Library Conservation News*, **30** (1990), pp4-5

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[571] I am grateful to Peter Bower, paper historian, for advice and for supplying the samples of these historic papers.

[572] I am indebted to Judy Seigel for supplying me with these useful step tablets.

[573] Since exposure is defined as the product of illumination and time, these two parameters must be combined in reciprocal proportion to achieve the same result, i.e. if the illumination is halved, the time must be doubled to give the same exposure. However, there comes a point with all real photosensitive materials when this inverse proportionality ceases to apply – this is the point of 'reciprocity failure' – and very weak illumination must be compensated by disproportionately lengthy exposure times.

[574] Koerner, Jennifer, and Potje, Karen, "Testing and Decision-Making Regarding the Exhibition of Blueprints and Diazotypes at the Canadian Centre for Architecture", *The Book and Paper Group Annual*, **21, (**2002), p15-23

[575] Except in electrochemical cells where the two processes may be separated by an electric current.

[576] 'Pigment blue 27: C.I. 77510, 77520', *The Colour Index*, (Society of Dyers and Colorists,) 2nd edn., pp2777, 3621

[577] Kirby, *loc cit*

[578] Christensen, P A, Harriman, A, Neta, P, and Richoux, M-C, 'Photo-oxidation of Water using Prussian Blue as Catalyst', *Journal of the Chemical Society, Faraday Transactions I*, **81** (1985), pp2461-66

[579] The molecule contains both primary and secondary alcohol and ether functions, which can be oxidized to give a range of substances, loosely referred to as 'oxycellulose'.

[580] Kosar, J, *Light Sensitive Systems*, (New York: John Wiley and Sons, 1965), p36

[581] An area of 1 m^2 of Prussian blue layer of optical density 1.55 contains ca 5×10^{-4} moles; this corresponds to 11.2 cc of gas at STP. (Although oxygen only constitutes one quarter of the atmosphere, one mole of oxygen can oxidise four moles of Prussian white, so the effects cancel). An A4 sheet is 1/16 m^2, hence the volume of air needed is 11/16 cc.

[582] Kirby, *loc cit*

[583] Holtzman, H, 'Alkali Resistance of the Iron Blues', *Industrial and Engineering Chemistry*, **37**, 9 (1945), pp855-861

[584] Holtzman's buffer of pH 9.4 consists of a mixture which is 0.05 molar in sodium hydrogen carbonate and 0.0165 molar in sodium carbonate.

[585] The buffer was the same as that employed by Holtzman: the solution was 0.05 molar in sodium hydrogen carbonate and 0.0165 molar in sodium carbonate.

[586] Crawford, W, *The Keepers of Light*, (New York: Morgan and Morgan, 1979)

[587] Moor I L, and Moor A H, 'The Conservation of Anna Atkins' British Algae', *Symposium on the 150th Anniversary of Photography,* Vevey,

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Switzerland, 29 June–2 July, 1989, (Vevey: European Society for the History of Photography, 1997)

[588] Wagner, S S, ‘Some Recent Photographic Preservation Activities at the Library of Congress’, *Topics in Photographic Preservation*, **4** (1991), pp136–149; American Institute for Conservation, Photographic Materials Group Meeting, 1991

[589] This was ‘purified’ water purchased from a retail pharmacist, and fulfilling the standards of purity required by the British Pharmacopoeia. It was thought most realistic to use this, rather than de-ionised or distilled water which varies in its origins, availability and quality.

[590] Reilly, *loc cit*

[591] Ware, M, *Mechanisms of Image Deterioration in Early Photographs*, (London: Science Museum and National Museum of Photography, Film & Television, 1994)

[592] The presence of the hydronium cation, H_3O^+, in the zeolytic voids will defend the Prussian blue against alkaline hydrolysis, while not presenting a direct threat to the cellulose of the paper.

[593] Keefe, L E, and Inch, D, *The Life of a Photograph,* (London and Boston: Focal Press, 1984); Reilly, J M, *Care and Identification of 19th-Century Photographic Prints*, (New York: Eastman Kodak Co., 1986); Rempel, S *The Care of Photographs*, (New York: Nick Lyons Books, 1987); Martin, E, *Collecting and Preserving Old Photographs*, (London: William Collins Sons & Co. Ltd., 1988); Hendriks, K B, *Fundamentals of Photograph Conservation: A Study Guide*, (National Archives of Canada, 1993).

[594] http://www.sp.se/en/index/services/paper/sidor/default.aspx

[595] Bilici, Sirdar, "Sulfamic acid for paper acidification": 2013 http://www.apug.org/forums/forum42/118153-sulfamic-acid-paper-acidification.html

[596] Calcium carbonate has a solubility of only *ca* 0.001 g per 100 cc water.

[597] See, for example: Brinckman, E, Delzenne, G, Poot, A, and Willems, J, *Unconventional Imaging Processes*, (London: The Focal Press, 1978), p82; Jacobson, K, and Jacobson, R E, *Imaging Systems*, (London: Focal Press, 1976) pp125-6; Kosar, J, *Light Sensitive Systems*, (New York: John Wiley and Sons, 1965), pp28–37

[598] The most recent review article on this topic at the time of writing is: Dunbar, K R, and Heintz, R A, ‘Chemistry of Transition-Metal Cyanide Compounds – Modern Perspectives’, *Progress in Inorganic Chemistry*, **45** (1997), pp283–391

[599] Sharpe, A G, *The Chemistry of Cyano Complexes of the Transition Metals*, (London: Academic Press, 1976), pp121–6

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[601] Holtzman, H, ‘Alkali Resistance of the Iron Blues’, *Industrial and Engineering Chemistry*, **37**, 9 (1945), pp855–862

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[603] Rosseinsky, D R, Tonge, J S, Berthelot, J, and Cassidy, J F, 'Site-transfer Conductivity in Solid Iron Hexacyanoferrates by Dielectric Relaxometry, Voltammetry and Spectroscopy', *Journal of the Chemical Society, Faraday Transactions I,* **83** (1987), pp231-243

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[605] Xiao-Wei Cao, Rong Wang, Gui-Hua Wang, Zong-Rang Zhang, '*In situ* Raman Spectroelectrochemical Characterization of th Prussian blyue modified Platinum Electrode',

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[609] Davidson and Welo, *Journal of Physical Chemistry*, **32** (1928), pp1191

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[628] Wilde *et al, loc cit*

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[638] Williams, *op cit*, p219

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[646] Dostal, A, Meyer, B, Scholtz, F, Schröder, U, Bond, A M, Marken, F, and Shaw, S J, ‘Electrochemical Study of Microcrystalline Solid Prussian Blue Particles Mechanically Attached to Graphite and Gold Electrodes: Electrochemically Induced Lattice Reconstruction”, *Journal of Chemical Physics*, **99** (1995), pp2096-2103

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[656] Neff, V D, *Journal of the Electrochemical Society*, **125** (1978), p884

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[658] Mortimer and Rosseinsky, *loc cit*

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[669] Properly, in a heterogeneous system, the optical density should be calculated using the Koubelka-Munk theory, which takes account of significant scattering. However the present approximation will serve for an 'order-of-magnitude' calculation.

[670] Rigorously, the yield should be calculated by integrating over the whole waveband of actinic light, to take account of the variations of I, f, and ϕ with wavelength λ. The present approximation will serve for most purposes, however.

[671] This corresponds to a pigment having an extinction coefficient in the order of $\varepsilon = 10^4$ dm^3/mol/cm

[672] The intrinsic printing exposure range of the iron-based sensitizers generally appears to be 7 or 8 stops, corresponding to arithmetic factors of $2^7 = 128$, to $2^8 = 256$.

[673] According to Kosar, *op cit* p32, commercial blueprint paper has a coating weight of 0.6 to 0.75 g/m^2 of iron salts.

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[697] The anionic formula, $Fe^{III}[Fe^{II}(CN)_6]^-$, used here to represent the Prussian blue formed in the cyanotype process, is only intended as a formalism; various cations may be present, e.g. K^+, NH_4^+, H_3O^+, or none, or even anions, with the consequence that the lattice may have defects, as explained in the previous Appendix.

[698] In this respect 'cyanotype Prussian blue' differs in its method of preparation from the 'normal' form of Turnbull's blue, which is always obtained from uncomplexed, aquated iron(II).

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[715] The identification of millilitres (ml) with cubic centimetres (cc) is not strictly exact, but serves for most practical purposes.

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[717] Since the litre is not an approved unit of the SI system, the units here should strictly be written as moles/dm^3.

[718] Though with the growth of digital imaging technology, this skill may become rare.

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[720] The Merck Index

[721] Weast, *op. cit.*, Tables F–3, F–4