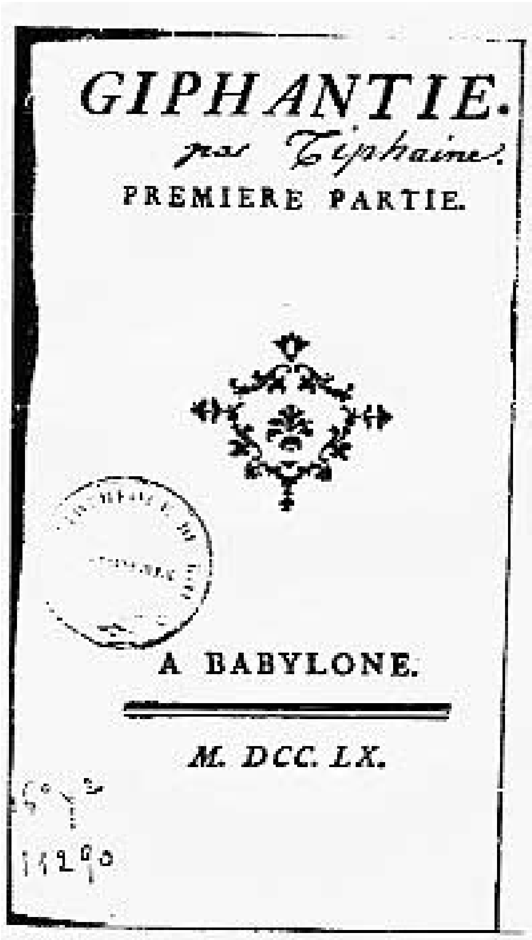
P02: A Subtle Matter Viscous and Quick

The search for image permanence

WC 3935

Charles-François Tiphaigne de la Roche was an early example of a science fiction writer who, like Jules Verne and Isaac Asimov much later in the genre, made uncannily accurate predictions of future developments in technology. In 1760 he published *Giphantie*[1]*, a view of what has passed, what is now passing, and in the present century what will pass in the world.* We would probably classify the author's fantasies about the future more as science fantasy than science fiction, but whatever we call them, one at least was remarkably prophetic.



In *Giphantie*, a traveller arrives at a strange land hidden in the quicksands of the African desert which, like Prospero's island, is inhabited by "elementary" spirits. The Governor shows him into a room where the traveller is astounded to see, through an open window, a raging storm at sea. He rushes across the room and goes to look out the window but bangs his head instead on a solid wall. Stunned, he turns to the Governor who explains:

The window, that vast horizon, those black clouds, that raging sea, are all but a picture…..You know that the rays of light, reflected from different bodies, form a picture, and paint the image reflected on all polished surfaces, for instance, on the retina of the eye, on water, and on glass. The elementary spirits have sought to fix these fleeting images: they have composed a subtle matter, very viscous and quick to harden and dry, by means of which a picture is formed in the twinkling of an eye. They coat a piece of canvas with this matter, and hold it in front of the objects they wish to paint. The first effect of this canvas is similar to that of a mirror; one sees there all objects, near and far, the image of which light can transmit. But what a glass cannot do, the canvas by means of its viscous matter, retains the images…. This impression of the image is instantaneous, and the canvas is immediately carried away into some dark place. An hour later, the impression is dry, and you have a picture the more valuable in

[1] This is an anagram of his first name.

that it cannot be imitated by art or destroyed by time…. The correctness of the drawing, the truth of the expression, the stronger or weaker strokes, the gradation of the shades, the rules of perspective, all these we leave to nature, who with a sure and never-erring hand, draws upon our canvasses images which deceive the eye.[2]

It would be another 70 years before de la Roche's prediction would come true, and even then, the "correctness of the drawing" left much to be desired. Nonetheless, the search had been on for a long time before this remarkable prediction was made for some kind of chemical or substance which would "fix" the images projected in *camera obscurae* so that their remarkable verisimilitude could be preserved for ever. Whereas in Ancient times and during the Renaissance, any notion of rendering images permanent other than by tracing or painting over them were necessarily as fanciful as de la Roche's "elementary spirits", by the 18th Century, the knowledge of chemistry had advanced far enough for the thinkers of the day to suggest some more realistic possibilities. From this time on, experimenters including academic pundits, scene painters and even village parsons, began tinkering with various chemicals and materials, in the search for some "subtle matter" which would preserve the images which inspired them in their *camera obscurae.*

The Halides of Silver

From very early on, the search for a chemical effective in fixing an image focussed on the salts of silver which, until very recently, have actually been the backbone of photography. Photographers often refer to a group of these as the *silver halides*[3], a collective label which includes the chloride, bromide and iodide. However, it was another salt, silver nitrate, which first attracted attention. Even as early as the Middle Ages, various alchemists knew that silver nitrate turns black: for example, Albertus Magnus (1193–1280) reported that it "*colours the human skin with a black colour very difficult to remove*"[4]. However, there is no evidence he knew this was due to the action of light upon the salt, breaking it down into its components, silver, nitrogen and oxygen, of which the silver, in this very finely divided state, appears black.

Albertus Magnus, issued Germany 1961

[2]Quoted in Gernsheim, H: *The Origins of Photography*, Thames and Hudson, 1982, pp. 22-23
[3] The word is unusual in that it derives from the Celtic word, hal = salt.
[4] For this and most of the following, see Quoted in Gernsheim, H: *The Origins of Photography*, Thames and Hudson, 1982, p.19ff.

As late as 1658, Johann Rudolph Glauber advocated the use of silver nitrate to darken wood, making it look like ebony. However, he too seems to have been unaware of the role of light in the process although there is a suggestion that an earlier experimenter with the substance, Angelo Sala, might have seen some connection when he wrote in 1614 that *"When you expose powdered silver nitrate (lapis lunearis) to the sun, it turns black as ink"*. Later, Wilhelm Homberg made a small box out of bone which he "marbled" by coating the bone in silver nitrate solution, exposing it to the sun and then removing some of the surface black to expose the white bone beneath. This he presented to the Académie Royale des Sciences in Paris on 4 September 1694. Most historians however, seem to agree that these two men believed it was the action of the sun's *heat,* not light, which caused the transformation while Homberg's contemporary, the great Anglo-Irish chemist Robert Boyle, attributed it to the action of *air*.

Sir Robert Boyle, (25 January 1627 – 30 December 1691)

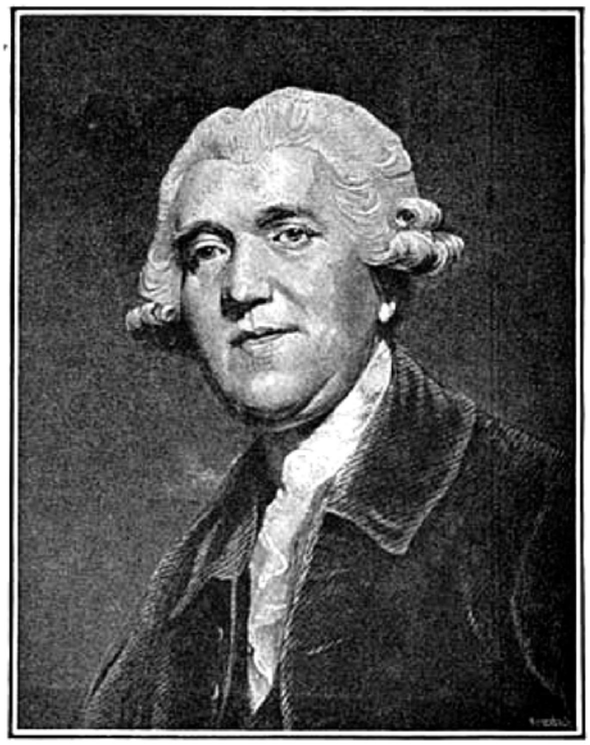
That it was light, not heat or air, which causes silver nitrate to darken was first clearly demonstrated by Johann Heinrich Schultz, professor of anatomy at the University of Altdorf. Like many discoveries, this was more by good luck and close observation than the outcome of a planned experiment. In 1725 while attempting to make phosphorus according to alchemical principles, he saturated chalk with nitric acid. At the time, unbeknownst to him, the chalk contained a little silver so that, when he placed it near a window in the sun, the side of the deposit facing the sun turned dark while the opposite side remained white. Struck by this, Schulz tried repeating the process with heat, but nothing happened. He then tried variations, in one cutting out letters from paper and placing these over the bottle containing the chalk and nitric acid and placing these again in the light of the sun. To his great pleasure, the words on the side facing the light were legible even though, when he showed others, they accused him of some kind of trickery.

Schulz then made up a new mixture of chalk and nitric acid but this time, because the chalk was free of silver, the experiment failed. When he remembered that the original mixture had contained silver, he made up a new lot, this time with even more silver in it, and he found the mixture darkened more rapidly… The rest, as they say, was history because he reported his discovery to the Imperial Academy at Nuremburg. However, maybe because he was more interested in the alchemical transformation of chalk into phosphorus, he missed the significance of his discovery by seeming to consider it was the darkening of silver carbonate, not the nitrate, which was the essential feature of the experiment. Had he realised it was the nitrate — which, like all nitrates, is soluble in water — and saturated paper with the salt, he would have been recorded by history as the inventor of photography.

It was Jean Hellot who first coated paper with silver nitrate but, according to his communication to the Académie Royal des Sciences in Paris in 1737, he was more interested in secret writing — a weak solution of silver nitrate in water works as an invisible ink which shows up only after a longish exposure to light.

Silver chloride

Silver nitrate is not the only silver halide which is light sensitive. Another in the family, silver chloride, was first tested by Giacomo Battista Beccaria who, at the time was professor of physics at Turin University. He more or less replicated Schulz' experiments with silver and chalk, presumably in this case using Hydrochloric acid. However, it was Dr William Lewis, FRS, who repeated and confirmed Schulz' experiments and published his results in *Philosophical Commerce of Arts* in 1763. Lewis died in 1781 and his notebooks were bought from his estate by Joshiah Wedgewood, the famous potter. These notebooks contained not only details of Lewis' own experiments but also notes from other experimenters. Wedgewood also took Lewis' laboratory assistant, Alexander Chisholm, into his own employment. Chisholm had not only been Lewis' assistant for over 30 years, he was also a highly educated, classical scholar so that Wedgewood made him tutor in chemistry and classics to his own son, Tom, who was then only 11 years old. This boy, although sickly and destined to die young, would eventually grow into a young man who was to play an



JOSIAH WEDGWOOD, F.R.S., & S.A.

important part in the development of photography. We will return to him later…

Several important features of silver chloride were to be exposed in this latter half of the 18th Century which, had their full significance been realised, could have meant that a practicable form of photography might have been invented fifty years earlier that it was. For example, the well-known Swedish chemist Carl Wilhelm Scheele showed that the "black" which remained when silver chloride was "darkened" by exposure to light was actually metallic silver. He demonstrated this by darkening some silver chloride powder on a sheet of paper and then attempting to dissolve it in ammonia. As he expected, Scheele found some of the black powder remained after the unexposed chemical had been dissolved, thus proving that light reduces the salt of silver to its elemental form. It had been known earlier that silver chloride is soluble in ammonia but ammonia will not dissolve metallic silver. Now it was demonstrated that the darkened part of an image was metallic silver, the corollary was clear: ammonia could be used to wash away the unexposed silver salt, which otherwise would darken on continued exposure to light, so rendering the image permanent. However, as we will see, this practical application of Scheele's experiment was overlooked so that attempts to "fix" images obtained on paper in a *camera obscura* were frustrated until well into the next century.

CARL WILHELM SCHEELE.

Scheele also made another important discovery which had practical application in photography in years to come. He sprinkled some silver chloride powder onto paper and exposed it to light of different wave lengths. He found that the chemical exposed to red light took much longer to darken than that exposed to light at the other end of the spectrum, showing that violet light was much more *actinic* or "chemically active" than other wavelengths. Again, Scheele was not seeking to find solutions to problems in photography: in this case, he was attempting to show that light was not a single, homogeneous substance and so it was left to a Swiss experimenter, Jean Senebier to examine in greater detail how different wavelengths of light affect the salts of silver.

Senebier was the Chief Librarian in Geneva, but he was also a man of independent means and spent much of his time on scientific experiments. It is not surprising that he was interested in the properties of light: he is best known for demonstrating *photosynthesis* — plants take in carbon dioxide and give off oxygen. In 1782 he published the following table of the times it took for light of different parts of the spectrum to darken silver chloride:

Colour	**Time to darken Silver chloride**
violet	>15 seconds
Purple	25 "
Blue	29 "
Green	37 "
Yellow	5½ minutes
Orange	12 "
Red	20 "

Relative chemical activity of different colours of light - Senebier, 1782

Senebier also carried out other experiments which would have practical application later in photography. These included studies of the effects of light on resins, some of which hardened and became insoluble in turpentine.

Sir William Hershel FRS

The sensitivity of silver chloride to the various colours of light was taken a big step forward when, in 1800, Sir William Herschel FRS, the famous astronomer, discovered that there were rays of light beyond the red end of the spectrum. These we know now as *infra-red*. Inspired by this, Johann Wilhelm Ritter in Jena, investigated the spectrum of light even further and found what is now called *ultra-violet* at the opposite end to the infra-red. Ritter, perhaps because he was a chemist, soaked a strip of paper in fresh silver chloride solution in a dark room and then exposed it to the spectrum of sunlight. He noted that the darkening action began much more rapidly beyond the violet end of the spectrum and then proceeded increasingly slowly as it progressed towards the red end. Hence, Ritter showed not only that ultra-violet exists but that it is much more actinic than any of the visible wavelengths of light. This invisible end of the spectrum came to be commonly known as the *chemical rays* as distinct from the visible rays of light.

That was in 1801. In the previous year, Ritter had invented electroplating and in the following year (1802) he invented the dry cell battery we all know so well. In 1804 he started work at the Bavarian Academy of Science in Munich and remained there until his early death in 1810 when aged only 33.

Johann Wilhelm Ritter

Like Ritter, Thomas Wedgewood, the fourth son of the famous potter, Joshiah Wedgewood, also made a very significant contribution to photography but died young. Born in 1771, Tom Wedgewood died in 1805 at the age of 34. Three years before his death, in 1802, he published a method for making what today we would probably call "photograms". He soaked a piece of paper in a solution of silver nitrate and then placed on top of it whatever objects interested him. After exposure to light, the silhouette of the object remained on the paper. While this is essentially a photographic process, Wedgewood had no way of preserving the image and so it would fade when returned to the light.

Tom Wedgewood, 1771-1805

Wedgewood was interested in the education of young children and his experiments were directed towards discovering ways in which pictures could be made which would assist children to learn. In the search for such a method he used a variety of media, including coating some of his father's pots with silver nitrate, and even impregnating leather with the chemical as well as paper stock.

It was left to a friend, Humphry Davy, whom we probably know best for his invention of the Miner's Safety Lamp, to establish Wedgewood's reputation which he did by publishing in the Journal of the Royal Institution an article entitled *“An Account of a Method of Copying Paintings upon Glass, and of Making Profiles, by the Agency of Light upon Nitrate of Silver. Invented by T. Wedgwood, Esq.”* This gave details not only of Wedgewood's accomplishments but also of his unsuccessful attempts to obtain a permanent image and, backed by this powerful man, inspired further experimentation for the next 40 years until successful methods were found.

Sir Humphry Davy FRS

Davy, of course, was a Fellow and eventually President of the Royal Society, the discoverer among other things, of iodine and given credit for many years for discovering chlorine (actually Carl Scheele had discovered chlorine 36 years earlier but had been unable to publish his results). With Michael Faraday as his assistant, Davy proved that diamonds are pure carbon by actually igniting one using the sun's rays while on a visit to Florence. Among his many other accomplishments, in 1807 he isolated potassium and sodium and a year later, calcium, strontium, barium, and magnesium. In that same year he discovered aluminium. And for these and his many other accomplishments, many in the fields of electricity and electrostatics, he became the first subject of a form of verse known as a *Clerihew:*

> *Sir Humphry Davy*
> *Detested gravy.*
> *He lived in the odium*
> *Of having discovered sodium.*

Davy was also awarded a medal by Napoleon and has a crater on the moon named in his honour….

But Davy's manifold achievements should not be allowed to blind us to those of the young man whose reputation he established with his article. Wedgewood first began to work with a *camera obscura*, an instrument which had come into the family's circle because his father, Joshiah, obtained one in 1773 and used it to make sketches of the stately homes of England which were then transferred to a 1,200 piece dinner service commissioned by Catherine the Great.

At the time his father bought the *camera obscura*, Tom Wedgewood was only 2, so he grew up with a knowledge of the instrument. He also grew up in the society of some of the great scientific minds of his day. His father belonged to a club which met once a month between the years 1770 and 1790. The members met only on the night of the full moon, so not surprisingly, this club which its members called the *Lunar Society* was christened the *Lunatic Society* by outsiders at the time! Even so, members included *inter alia*, Dr Joseph Priestley (the discoverer of oxygen); James Watt (of steam engine fame) and his partner, Matthew Bolton; William Murdoch (who invented gas lighting); Dr Erasmus Darwin (a famous botanist and physician, the grandfather of Charles Darwin); Sir William Hershel (astronomer); Sir Joseph Banks (well-known to us in Australia because he accompanied James Cook on his voyage to Australia in 1760 but who was then President of the Royal Society); Dr Joseph Black (a famous chemist)…

The younger Wedgewood attended Edinburgh University after which he spent some time studying the relationship between heat and light. One of his father's associates and fellow "Lunatic", Dr Joseph Priestley, one of the most learned men of his time, was himself interested in optics and chemistry and was fully conversant with the research results published by both Schultz and Scheele — indeed, he had contributed a chapter to the English translation of Scheele's book when it finally appeared.

There was a further connection between Wedgewood and the discoveries of Scheele: it was during the winter 1797-98 that he met the young Humphry Davy (then an apprentice apothecary) in Penzance, Cornwall. The two young men saw a lot of each other throughout 1798 during which time Davy become the superintendent of Dr Beddoes' Pneumatic Institution near Bristol. This was significant because Dr Beddoes, a former professor of chemistry at Oxford[5], had translated Scheele's work. In all probability, Wedgewood and Davy together conducted at least some of the experiments Davy later credited entirely to his pal.

We don't know exactly when Tom Wedgewood began his experiments with paper impregnated with silver nitrate, but the timing of his friendship with Davey suggests it was probably in those closing years of the 18th Century when he had the both access to scientific information not otherwise readily available in Britain and — almost certainly — the inspirational support of one of the great genius of the age. If he did begin his experiments then, he had only 5 or 6 years left in which to search for a way to create images from light and to make them chemically permanent.

However, it is important to note that Wedgewood — at least according to Davy — gave up experimenting with the *camera obscura* because the images formed thus were "*too faint to produce in any moderate time, an effect upon nitrate of silver*." Many years later, such images were obtained in a *camera obscura* but using exposures of several hours which — in Wedgewood's terms — was probably not a "moderate time"!

[5] He had been forced to resign because he expressed approval for the French Revolution.

Instead, Wedgewood turned to making contact images — as I said earlier, what we call *photograms* — by placing various objects on a sheet of paper or white leather impregnated with the silver salt, pressing them into contact with a sheet of glass, and exposing the sandwich to sunlight whereby an image was obtained in two or three minutes. Of the two, paper or leather, it was the leather which produced the image faster because as a residue of the tanning process, traces of gallic acid remained in the leather. Many years later, researchers found that gallic acid "developed" the "latent image" much faster than allowing light to produce a visible image unaided.

Wedgewood suggested that this method would prove useful in copying "all such objects as are possessed of a texture partly opaque and partly transparent". Such objects included the "woody fibres of leaves, and the wings of insects" as well as paintings on glass, then a fashionable form of art. While copying such paintings, Wedgewood found, as had Scheele and Senebier before him, that the different colours in the original affected the intensity of the image formed on the white leather beneath. Davy, in his paper detailing his friend's experiments, added a lengthy footnote referring to the experiments by Hershel, Ritter and another researcher, Wollaston, showing that this information was known at the time, at least to him and probably to Wedgewood.

Late Eighteenth Century "shades" or silhouettes

Another popular art form of the time — from about 1760 onwards — was making silhouettes of people. Commonly called *shades*, they were much cheaper and faster to produce than painted likenesses (It was because they were cheap that they came to be called silhouettes after the infamously penny-pinching French finance minister Etienne de Silhouette). Wedgewood also seems to have considered his methods would have been suitable for copying, maybe even creating, silhouettes.

A photogram of lace made by Fox Talbot in the 1840s by a process similar to that used by Tom Wedgewood at the beginning of the century.

Whatever silhouettes or other images Wedgewood was able to produce, unfortunately none have survived. Although he found that the image was permanent in the sense that it could not be scrubbed off the paper or leather with soap and water, eventually the entire piece blackened because of the continuing reduction caused by light of the silver nitrate to its metallic state.

It is tragic that neither Wedgewood nor Davy realised from their reading of Scheele that ammonia could be used to wash away the unexposed silver nitrate and so render their images no longer susceptible to light. Wedgewood tried varnishing his images but warned this did not work, and that copies of paintings on glass or of silhouettes made by this method could only be examined by the dim light of a candle for a few minutes and then put away in a dark place.

However, it was Davy, reporting not only Wedgewood's experiments but also his own using the faster silver chloride as the light-sensitive agent, who summed up the rather abortive progress of photography to this point when he wrote:

> *Nothing but a method of preventing of the unshaded parts of the delineation from being coloured* [ie, darkened] *by exposure to the day is wanting, to render the process as useful as it is elegant.*

Wedgewood died three years after his findings were published by Davy. Had Davy not done his friend such good service, it is possible that Wedgewood's contribution to photography would have been forgotten. As it was, later publishers took up the article and re-published its information in prestigious journals so that, although Wedgewood had failed to preserve his images, his concept of what photography could be entered the consciousness of the next generation of experimenters who, thirty years after Tom Wedgewood's death, succeeded in producing the first permanent photograph.