

Chapter 11

Photochemical Imaging

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Abstract Photochemical imaging is dominated by silver halide technology. The early history of photography is described while introducing the essential ingredients of modern photography. The technology is described by reference to modern materials and current understanding of the photochemical processes involved. At the core is the photolysis of silver halide crystals leading to the formation of latent images. Their manufacture and chemical and spectral sensitisation are briefly described. The development of the silver images is explained. Variations on the technology of development lead to the variety of types of familiar and less familiar photographic products. Non-silver photographic systems have also provided significant commercial imaging systems, for example, Blueprints, Diazotypes and dichromated colloid/polymer systems. The last was important in the early development of photography and is still exploited today. The principles of electrophotographic systems are also briefly described.

11.1 Introduction

The topic of ‘photochemical imaging’ immediately suggests photography, ‘drawing with light’ and in particular the familiar silver halide photography. When people are asked what they would save first if fleeing from a fire in their homes

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they usually opt for their photo albums. Photographs are important, not only to the individual but to so many industrial processes and as historical records. The history of photographic science, dating as far back as the early eighteenth century, includes some of the first observations of the chemical effects of light. In other words, photochemical effects were recorded even before the emergence of the science of chemistry as we would recognise it today.

There are several other technologies which use light to make images which are not called photography. Photopolymerisation (not involving silver salts) and its application to materials used in the printing industry are covered in [Chap. 13](#). Also, photochromism is mentioned in [Chap. 4](#). These will not, therefore, be included here. A number of photochemical imaging technologies of minor commercial importance also exist and these will be mentioned but not described in detail. We will, in very brief form, include electrophotography for completion because of its importance despite the lack of chemical change in the process.

Also included are some of the chemical and physical steps which immediately follow the initial interaction of silver halide materials with light. The story of these imaging processes would not be complete without them and they serve to illustrate the diverse applications of the common photochemical process of silver halide photolysis.

11.1.1 Requirements of Imaging Systems

In this chapter and elsewhere in this book, various technologies applied to imaging systems are described. As well as printed images we are familiar with projected images in the cinema and television images at home. Before looking at the various exploitations of photochemical imaging systems including those based on silver, we should therefore first consider more generally what is required of all imaging systems, particularly colour systems. We can then see how the available processes can be tailored to suit particular applications.

We will first look briefly at black-and-white (B and W) imaging where all aspects of imaging except colour are, of course, still important. Images are composed of component areas of different apparent brightness or *luminance*. In printed images these variations are quantified as (optical) densities ranging from the darkest ‘shadow’ areas to the brightest ‘highlight’ areas. The term *tone* refers to the position of an area on a scale of luminance. The *tone-reproduction* is then the relationship between the densities of the various parts of the original and the corresponding parts of the reproduced image. This relationship is not necessarily 1:1 or even linear for a variety of physical and perceptual reasons. Elements of an imaging system must translate an input signal into a resulting output which contributes to a satisfactory final image. A display screen must convert an electronic signal into, for example, a luminous image. A photographic reflection print must convert a light exposure of an image capture device into an image density in the viewed print.

Most original scenes contain a much wider range of luminance than can be reproduced in an imaging system. Our eyes and the brain's processing of the image information have remarkable capabilities for coping with the challenge of tone reproduction and colour perception. A good example is the now obsolescent cathode ray tube (CRT) display technology. Black areas in TV images are never actually darker than the darkness of the screen when switched off, yet we take some convincing of this fact when we see the displayed image with a full range of tone reproduction including what seem to be very black shadow areas. They seem black only in relation to the bright areas in the image. For printed materials such as photographs, the perceived depth of blacks is limited, as with TV screens, by the amount of light reflected from the darkest possible areas. In the case of B and W silver halide prints these areas are where the maximum amount of silver is developed. Silver scatters light as well as absorbing it, so some of the light used to view the image is inevitably reflected from the darkest areas into the observer's eye. In practice, the maximum density of a silver reflection image is about 1.7, that is a maximum luminance range on a linear scale of only 50:1. This is well short of the range of a typical scene. A well-lit scene can often have density range of over 4.0 or 10,000:1 in luminance terms. Shadows are less interesting than bright parts of an image so we do tolerate a limited density range for most imaging purposes.

Images produced with black inks do better because inks tend to scatter light less than silver, but surface (Fresnel) reflections impose practical limits here as well. Transparent images are capable of much greater ranges, but are usually limited to a density range of around 3.5, because to provide more density would come with a cost to other factors, for example of reduced speed, sharpness and ease of chemical processing without much perceived quality benefit.

After tone-reproduction, image sharpness, *i.e.* the ability to reproduce detailed shapes, is probably the most important requirement. The issues here are largely apparent and need not be discussed in detail. The number of picture elements in a structured image such as a half-tone printed image or screen resolution in a TV monitor are obvious influences. In silver halide photography, sharpness is linked in practice to other aspects of performance such as sensitivity (speed), tolerance of films to a wide range of exposure levels and the graininess of images. Compromises are needed in the design of the materials to optimise the mix of these performance factors. For all but the highest speed films adequate sharpness is now achieved relatively easily. One limiting factor (apart from the most frequent cause of sharpness loss, namely poor focusing) is the optics of the print material. While the imaging layer of a print can be capable of being very sharp, it is exposed and viewed above a light-reflecting support. Ideally, light would bounce back from low-density areas of an image without penetrating into the support, but often in practice, cost considerations usually dictate that less light-scattering material than ideal is contained in the support. Consequently, light penetration is significant and this inevitably includes lateral penetration and loss of sharpness. An important consideration here is, however, the ability of the eye to perceive differences in sharpness beyond a limit (about 7 lines per mm), which many imaging systems can achieve without too much difficulty today.

For colour materials, the colour reproduction requirements are driven again by the nature and performance of our own imaging system of human vision. We need to take a look at how our colour vision works and then how to fool it into thinking a reproduced image using light sources or coloured dyes and pigments is a good reproduction of the experience of viewing an original image.

Figure 11.1 shows the spectral response of the three sets of cone cells [1] responsible for colour vision. The curves are normalised to show equal maximum responses, but in fact the blue-sensitive cones are much less sensitive than the 'green' and 'red'. Blue colours are therefore seen as relatively dark but the blue response is vital in determining how we see a variety of colours.

Monochromatic light will produce a response in the three sets of cones dependent on its wavelength. The total response determines the perceived brightness and the relative responses produce the experience of colour. The colour which we experience depends on this primary response, though it can be modified significantly by later processing by the brain. Surprisingly perhaps, the red and green responses overlap considerably, but this is an essential requirement if we are to experience a wide range of colours. If the responses were completely separate, then within each envelope, the colour sensation would be independent of wavelength and we would experience only three spectral colours. In practice, we are able to distinguish subtle differences in hue, particularly in the green/yellow region, an ability which was invaluable in the leafy, grassy environment our ancient ancestors evolved in.

Usually of course we do not see monochromatic light, but a continuous spectrum of wavelengths. The responses we experience are the integrals of the effects of the component monochromatic contributions to the spectral distributions of the light we sense. The results still add up to a set of three responses from the three sets of cones. The challenge for a colour imaging system is to generate, for each part of the image, at least approximately, the same three responses and therefore the same colour and lightness sensations as would have been experienced on viewing the reproduced original.

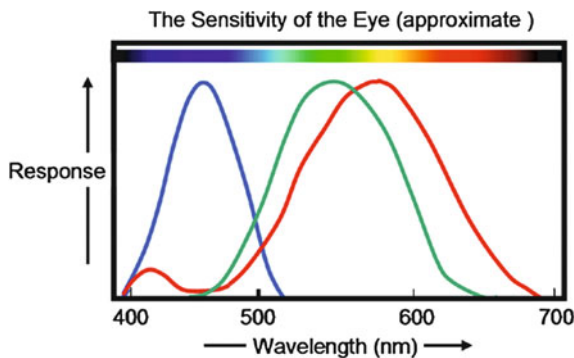


Fig. 11.1 The spectral sensitivity of the three sets of cone receptor cells

There are two broad classes of image display systems. The *additive* system uses light sources to create a pattern of light to form the image. We need a suitable set of emitters. Conveniently, if we limit the wavelength ranges of an emitter to between approximately 400 and 500 nm we see this as ‘blue’. Using the range 500–600 nm gives us a green sensation and the band from 600 to 700 nm gives us red. These correspond only approximately to the spectral responses of the three sets of cones, but systems based on red, green and blue (RGB) emitters do in practice prove an effective means of reproduction. This set of three emitted colours, are then our additive *primary colours*. The television screen is perhaps the most familiar example. Figure 11.2a shows the array of emitters of a CRT TV screen. The spectral emission of each emitter set usually spreads beyond the boundary wavelengths mentioned above with some sacrifice in colour reproduction including the gamut of colours available for the sake of improved brightness and dynamic range (contrast). Figure 11.2b showing overlapping RGB circles, demonstrates the making of three different colours from each combination of two of the RGB emitters and ‘white’ from all three. The colours are a little dull because of the black gaps between the individual emitters. By adjustment of the relative brightness of each set of emitters satisfactory reproduction of a variety of colours can be achieved. This is in part due to the contribution of the eye/brain’s ability to interpret the physical sensing of light and make adjustments for errors in colour balance. Additive colour systems are not confined to emissive systems. Film systems such as Dufay Colour and Polachrome used RGB colorants as colour filters for projected images (see Sect. 11.2.3.2).

The other class of display system is the *subtractive* system. Here, images include both reflection prints, such as conventional colour photographs or printed pages and transmission prints, such as slides and projected movie cinema images. These images provide the light sensed by the eye from a combination of a light source and colorants which modify the light source in an image-wise manner. For reflection prints the light source is the ambient light under which the print is viewed, while for transmission prints a back-light such as a light-box or a projector

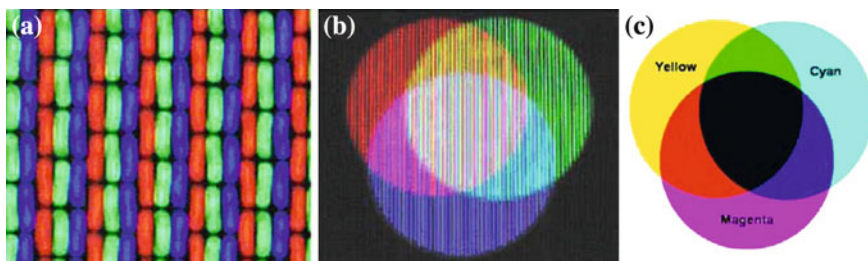


Fig. 11.2 **a** *R*, *G* and *B* emitting pixels of a CRT screen. **b** Overlapping additive colours produce the three subtractive primaries and ‘white’. **c** Two overlapping subtractive primaries remove two additive primaries leaving an additive primary. When all three overlap *black* is produced

bulb provides the light. The colorants' role is to modify the amounts of red, green and blue light seen by our eyes by absorbing ideally only one of them.

To do this, cyan, magenta and yellow colorants are used (see Fig. 11.2c). These absorb red, green and blue light respectively. This set of colorants (CMY) are therefore known as the *subtractive primaries* [2]. Where two primaries overlap, two of the RGB colours are subtracted leaving the third. The colorants are provided in the form of dyes and pigments (insoluble colorants) in media such as printing inks, ink-jet inks, electrophotographic toners and photographically produced dyes. They are often supplemented by a black colorant (K) to adjust tone-scale, improve sharpness and deepen black areas in CMYK systems [3].

In colour photography the three dyes are usually generated as part of the process of development of the silver halide emulsion. This process is described more fully later. Figure 11.3 illustrates how the negative/positive colour system reproduces an original colour pattern using the subtractive primaries. Light of various colours is provided by the original scene or object, usually by reflected or otherwise modified light. The object to be reproduced in this diagram provides red, green and blue areas as well as white (all three together), and black (none). These areas are imaged onto the first material, the negative camera-film. The film is made up of three layers [4] with other layers in between to prevent cross-talk between the colour responses. In each layer the silver halide crystals are *sensitised* to one of the RGB spectral regions. The photochemistry of the responses of the dyed crystals

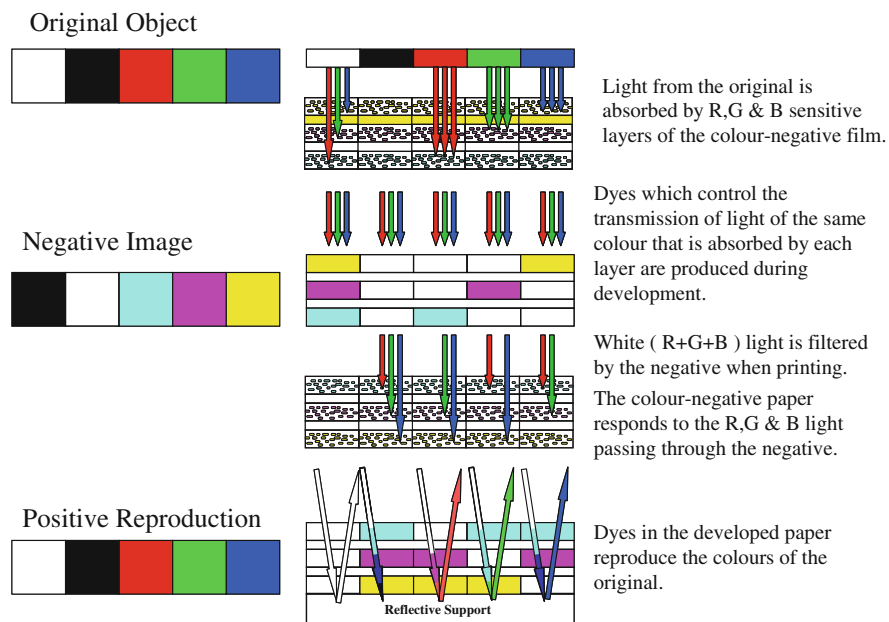


Fig. 11.3 Schematic diagram of the negative/positive colour photographic system

is described in more detail later. The blue-sensitive, yellow-forming layer is above the other imaging layers and immediately above a yellow-coloured filter layer made from silver nanoparticles [5]. This is mainly because the silver halide crystals used in films absorb and respond to blue light which needs to be filtered before the light passes to the green and red sensitive layers. The crystals in the green layer are sensitised with a green-absorbing dye which provides a degree of filtration of green light passing to the red-sensitive layer.

The exposed film is then processed and dyes are produced which absorb in the same spectral region that was used to expose the layers in which they are formed to provide the negative image. To produce the positive image, the negative is then illuminated by polychromatic light and used to expose the print material. Photographic paper has a different layer order from that of film. This is not for any good imaging reason but to overcome a problem of non-uniform response in the bottom layer caused by unevenness of the paper support. Rather than solve this problem by using smoother paper, it is mitigated by using the yellow-forming layer on the bottom. As we have observed before the eye is not very sensitive to blue light and therefore sees yellow (white minus blue) as a bright colour. Variations in its brightness are therefore of less importance. The blue-sensitive layer, though, is now no longer able to have the first bite at the blue light. To provide a response to blue light sufficiently different from the other two layers, it needs to use much faster silver halide crystals.

The colour negative-positive silver halide system has evolved over a long time during which sophisticated chemical devices have been introduced to overcome deficiencies. Section 11.2.3 describes the basic colour-forming chemicals which couple with developing agents. In modern materials some of these are themselves coloured so that when they form the required dye, the disappearance of their own colour corrects for the spectral defects of the dyes formed. Other couplers release agents which inhibit the development of the silver halide crystals. These *development-inhibitor releasing* (DIR) couplers are remarkably effective in providing mitigation of a number of deficiencies. The details of their effects are beyond the scope of this book but can be found in a number of books describing photographic technology for example “The Theory of the Photographic Process” [6]. They reduce graininess by limiting the amount of dye formed from each silver halide crystal thus allowing more crystals to participate in forming the image. The migration of inhibitor to adjacent layers provides some colour reproduction benefits and their lateral migration enhances image edges and therefore apparent sharpness.

All these sophisticated chemical functions are readily performed arithmetically in digital imaging systems but until recently the combination of image quality, robustness and permanence of silver halide prints has been difficult to match. For that reason we will look first at the earliest and most important photochemical imaging system, silver halide photography.

11.2 Silver Halide Photography

Before we look in detail at the core photochemical process of silver halide photolysis and the amplification of the photochemical response resulting from chemical development we will first explore the early history of imaging technology. By doing so will introduce the essential elements of modern photographic systems.

11.2.1 Early History

11.2.1.1 The Building Blocks

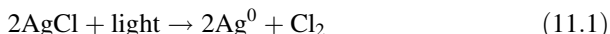
As is often the case, there are times in science and technology when a few people were doing similar things at the same time and it is sometimes uncertain as to who knew what and when. The historical accounts are often distorted by personal rivalries, races to be 'first', and the promotion of ideas, personalities and products. We can however recognise the major building blocks of the photographic system as we would recognise it today and the inventive combinations which enabled useful systems to be realised.

Firstly, we require a means of creating a pattern of light on a light-sensitive material. We need a camera. By the time useful light-sensitive materials were discovered cameras had been around a long time. The earliest reference to what we would now call a *camera obscura* dates from the fifth century BC by the Chinese philosopher Mo-Ti, who described an inverted image created by light passing through a hole in a wall of a darkened room [7] and falling on the opposite wall. A number of people described the principle and practice of imaging with this arrangement in increasing detail including the Islamic physicist Alhazen, Da Vinci and later, Johannes Kepler, who first coined the term *camera obscura*, the Latin for a dark room. Smaller, portable devices improved their versatility and their use in art enabled a breakthrough in the accuracy of perspective in paintings by, for example, Jan Vermeer. These devices, then, allowed the capture of ephemeral images and were in the wings awaiting the discovery of suitable materials before permanent images could be recorded.

The discovery of light-recording materials came along a lot later than the earliest cameras, but some considerable time before what many would recognise as the 'birth' of photography often attributed to the Frenchman Joseph Nicéphore Niepce in 1826. A hundred years earlier than Niepce's first photographs, Johann Heinrich Schultze, a German professor of anatomy, probably made the first images using light [8, 9]. In 1725 Schultze was experimenting with silver compounds and had impregnated powdered minerals such as chalk and gypsum with silver nitrate. Initially he had been using nitric acid for another purpose but this contained some silver and Schultz identified silver as the active ingredient. A jar of the material exposed to sunlight darkened on the side facing the sun and Schulze established

that light rather than heat caused the darkening. He went a crucial step further as far as photography is concerned, and partly covered the exposed surface of powder by gluing on pieces of paper not just randomly but with shapes cut out, for example, of letters. We now call these images *photograms* to distinguish them from images produced by projection. As far as the photochemistry is concerned it was probably halide impurities in the chalky substrate which enabled the formation of silver halides which we now know to be particularly effective light recorders.

Half a century later, Carl Wilhelm Scheele, more famous for his discovery of oxygen, described the reduction of silver chloride to silver metal by light in 1779:



He also noted that violet light was more effective than light of longer wavelength. This was at the time when Lavoisier was overthrowing the Phlogiston Theory and establishing chemistry as a respectable science, so photochemistry can claim to be as old as chemistry itself. Scheele also provided a potential method of fixing silver images. Knowing that silver chloride was soluble in ammonia [10], he showed that ammonia dissolved un-reacted silver chloride from the exposed, darkened powder leaving the black photolytic silver.

At the beginning of the nineteenth century, Thomas Wedgwood the scientist son of the potter Josiah Wedgwood experimented with silver nitrate. Sir Humphrey Davy presented a paper [11] based on Wedgwood's work to the Royal Institution in 1802. Again, Wedgwood's first light-sensitive materials were produced by applying silver nitrate to substrates such as paper and leather and, fortuitously present halide ions, may explain the photosensitivity. He was aware of Scheele's work on silver chloride, probably through Joseph Priestley, a fellow member of the Lunar Society, and recognised the increased sensitivity to light of paper soaked with silver nitrate by a subsequent treatment with hydrochloric acid. Despite his best efforts he failed to make the images permanent, by preventing unexposed areas eventually darkening and destroying the image. This seems somewhat surprising in view of Scheele's observation of the effect of ammonia on exposed silver chloride. Facing apparent defeat in his attempts to make his images permanent, he, as did Schultze before him, turned to other interests.

11.2.1.2 The First Permanent Images

The light sensitivity of silver-treated materials was therefore well known to those later in the nineteenth century seeking to make permanent images. These included the Frenchman, Nicéphore Niepce. He succeeded in producing images using, at first, silver nitrate-treated paper in 1816 [12] but like Wedgwood he did not discover a way to "fix" the images and make them permanent so he looked elsewhere. He was interested in lithography and familiar with the materials involved so he experimented with bitumen of Judea. In 1822 he attempted to produce photograms using bitumen on lithographic stones and copper plates. The bitumen was hardened by the

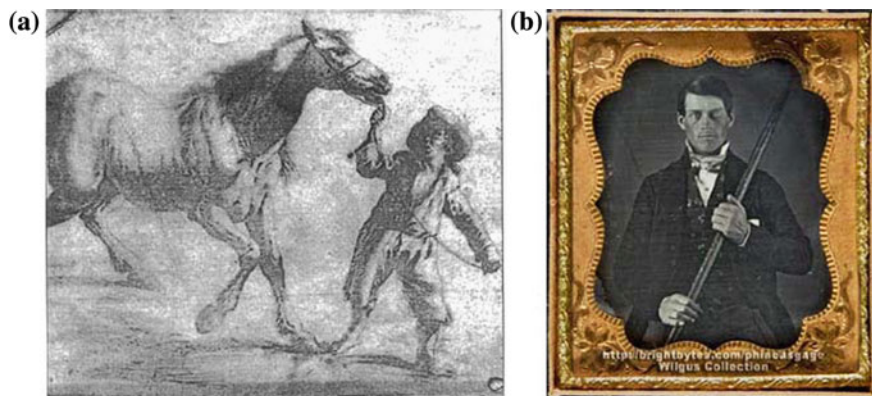


Fig. 11.4 **a** The first known permanent photographic image (reproduced with kind permission from Ref. [13], Copyright 2002, the Bibliotheque National de France). **b** A daguerreotype of Phineas Gage (reproduced with kind permission of Jack and Beverley Wilgus—Ref. [15]) (laterally reversed to show features correctly)

action of prolonged exposure to light though it is possible that it was heat, either directly or from light absorption which was responsible for the hardening due to the consequent evaporation of the lighter fractions in the bitumen. Nevertheless, he was able to produce a difference in solubility of the bitumen layer which could be revealed by treatment with primrose oil and kerosene mixtures. Etching with nitric acid provided a surface which could be inked to provide a positive image which could then be transferred to paper. The earliest surviving print, shown here in Fig. 11.4a, ‘*Cheval et son Conducteur*’ sold in Paris in March 2002 and is thought to date from 1825. It is essentially a ‘photocopy’ of a seventeenth century Dutch print made by contact printing rather than with a camera [13]. The light levels available in a camera obscura are of course much lower than can be used for photograms but Niepce persevered and eventually in 1826 produced the first permanent photographic image using a camera, a picture of the roof-tops of his home. He called the images ‘Heliograms’. He is therefore widely considered to be the inventor of photography despite the earlier technology because of the combination of a camera and a light-sensitive material.

It was a major achievement but it has to be said that the quality was not very good. The sun moves a long way in 8 hours and the etching process produced either black or white with few greys in between. In terms of photography as we understand it today it was a technological blind alley, though the use of photo-resists to produce printing plates was a direct precursor of the very important modern photolithography and photofabrication methods (see Chap. 13).

Niepce went to England to promote his invention through the Royal Society but he did not receive the publicity he sought because he was reluctant to divulge some of his techniques and on those grounds was refused endorsement. This probably persuaded him to team up with Louis Daguerre and this formal partnership seems

to have been crucial to the development of the first commercially successful photographic material, the *Daguerreotype*.

Daguerre was an imaginative and successful stage-set designer and saw his work dismantled frequently. Aware of the *camera obscura* he too sought a way to use this device to record images of his work and of course much else. Niepce and Daguerre worked on refinements to Niepce's earlier ideas but they lead nowhere. Niepce died soon after in 1833 and Daguerre using the knowledge of silver-based materials he had gained from his partner, went on to develop a process which was the first successful photographic system. Niepce had produced images in bitumen layers coated on silver plated copper and treated them with iodine vapour. This darkened unexposed areas of the metal surface thus providing an alternative method to etching for providing a positive image.

Daguerre's vital contribution was to discover that surfaces coated with silver iodide were light-sensitive and when exposed, the resulting photolytic silver could form an image. More importantly, the poor image could be revealed or "developed" by mercury vapour which was deposited in an image-wise manner forming a reflective mercury/silver amalgam. It is said, but not recorded [14], that the discovery was made when Daguerre, left an exposed iodised silver plate with no visible image on it in a drawer. A few days later when the drawer was opened the plate showed a visible image. This was subsequently proved to be due to the presence of mercury vapour in the drawer and the Daguerreotype was born (see Fig. 11.4b). The mercury treatment produced a much more visible and positive image, the lighter areas consisting of an array of reflective dots of mercury/silver amalgam.

The other vital building block used by Daguerre in 1837 (probably learned from Niepce and used 3 years previously by Fox Talbot) was a method of 'fixing' the images using 'cooking' salt solution to dissolve unexposed silver iodide thus rendering them permanent. This also improved image contrast.

Many such images from the decades following the commercial release of Daguerre's system are still in existence today due to the roaring success of this technology [15]. Again though, we must accept that the Daguerreotype's flaws, particularly the fact that only a single image could be obtained, were fatal and the system was overtaken.

11.2.1.3 The Birth of Modern Photography

William Henry "Fox" Talbot was in his teens when Niepce experimented with silver based light-sensitive materials but he must have been a fast learner. He had been a classics and mathematics scholar at Cambridge, a Fellow of the Astronomical Society at 22, a Fellow of the Royal Society at the age of 32. His interests included botany, deciphering cuneiform inscriptions and the Bible. He was also a member of the British parliament. It is for his contribution to photography, of course, that he is best remembered. Though the novelty of his work is sometimes exaggerated, he connected several known technical ingredients in a new way and developed a system which can be seen as the origin of the negative/positive

photographic systems still in use today. In 1833 he mused in his writings that it would be “charming” if the views he was experiencing could be captured as permanent images using a camera obscura. This is of course the year that Niepce, who had already successfully achieved a similar ambition, died. It was also before the introduction of the Daguerreotype in 1839 and Fox Talbot was convinced that he had made the first silver-based photographs. His earliest surviving photograph is the famous negative picture of a window taken in 1835 in his home Lacock Abbey, produced by exposing silver-sensitised paper.

To sensitise the paper it was treated successively with solutions of silver nitrate and sodium chloride which precipitated silver chloride crystals. After drying, the paper was given a final treatment with a solution of silver nitrate, gallic acid, and acetic acid. This increased the speed of the paper. We can now recognise this treatment as a form of chemical sensitisation of the silver chloride which we call ‘r-type’ or ‘reduction sensitising’, *i.e.* the production of groups of aggregated silver atoms on the surface of the silver chloride. We will deal with the details of the photochemistry of the image forming process later.

While experimenting with the sensitisation of paper, Talbot observed that high chloride levels reduced sensitivity. Daguerre had also used salt solutions to fix images. Talbot’s and Daguerre’s systems were obviously quite different and Daguerre’s considerably more advanced in 1839. Daguerreotypes were sharp while Talbot’s were not, even before they had been used to produce positives using contact exposure of a second piece of paper through the paper negative, a process which further degraded the image. Talbot’s method though had a significant advantage. It was possible to make multiple copies of a negative. When other pieces of the jigsaw fell into place this was a crucial advantage and the negative/positive system went on to dominate photography until the twenty-first century. One such piece was an improved fixing material provided by Sir John Herschel, who suggested the use of sodium thiosulfate in 1839, though this suggestion seems to have been borrowed from the reverend Reade [16, 17], who reported its use 2 or 3 years before. Herschel also coined the term “photography” in 1839 as well as advising Talbot to wax the negative image to improve its optical properties.

At this stage exposure times were extremely long. Daguerreotype portraiture involved clamping people’s heads for tens of minutes. This was despite some degree of visual amplification of the silver image by mercury. Talbot’s system involved exposure times of an hour or so despite his use of a small “mouse-trap” versions of a camera obscura having recognised that focussing the light onto a smaller area increased exposure intensity.

The formation of photolytic silver was still a very inefficient process but more significantly, all the silver in the image comes from photolytic silver and even if one silver atom resulted from one absorbed photon, exposure times would still be very long. We need another piece of the jigsaw.

Another vital breakthrough which Talbot made occurred as a result of another chance observation in 1840. His process involved a final treatment of the paper with a gallic acid solution, which the Reverend Reade [18] had combined with silver nitrate to produce light-sensitive materials. It seems that Talbot had exposed

some sensitised paper which did not work well, so he applied the gallic acid solution again. This treatment revealed the image resulting from the earlier exposure. In other words he had discovered that it was not necessary to expose the paper until the image was visible. It could be exposed briefly and the hidden or “latent” image could be revealed by the chemical treatment that developed the image. The development process amplifies the effects of light by a huge amount. We will also look at this process in more detail later.

Having reduced exposure times to minutes rather than hours Talbot had a viable system and described the ‘Calotype process’ in 1841 (from *Kalos*, meaning beautiful in Greek) by which time he had explored other halides and settled on silver iodide. Talbot’s grip on his process was maintained by patents and this unfortunately slowed technological progress, since not only potential suppliers, but even practitioners of photography had to pay royalties to make photographs. The quality of images using the Calotype process was impressive, even though it was limited by exposure and copying steps using paper. When the wet ‘*collodion*’ process was introduced by Frederick Scott Archer in 1851, it provided a way round this optical limitation. *Collodion* is cellulose nitrate made from gun cotton and as a soluble polymer could be coated onto glass plates, where it provided a host layer for the production of silver halide crystals. The exposure was made immediately after sensitisation and development was carried out with gallic acid. If dried, these layers were less responsive to light, so unlike the Calotype process, the photographic material could not be made and stored for later use.

In other words, the photographer was the photographic manufacturer and the processor and had to carry both his factory and laboratory, as well as his studio. However, the improvement in tone-scale and definition provided by collodion’s fibre-free layer compensated for this inconvenience. Furthermore, it was left unpatented and became the dominant method of negative production. For producing the positive print albumen-coated paper was normally employed. It is estimated that in 1866, at the height of its popularity, 6 million eggs were used in the UK for this purpose. Although there was no fundamental reason why albumen-based papers could not have been developed chemically, they were in practice developed by light.

Continued non-image wise exposure to light reveals a difference between exposed and unexposed crystals created during image capture. The exposed crystals or ‘grains’ darken more quickly as the production of photolytic silver accelerates, a process known as *latensification*. These so-called ‘Print-Out Papers’ or ‘POPs’ were preferred presumably because the process required less skill and no chemical processing. Exposure times were of less importance than during image capture. Prints could also be made easily by the growing army of amateur photographers. Most of the prints surviving from the nineteenth century used this photochemical method of production.

A further step forward was the separation of the production of the silver halide crystals from the coating of the substrate, such as glass or paper, with the sensitising materials. This allowed greater control over the formation and any subsequent treatment of the crystals and it also enabled crystal dispersions, which the

photographic industry now calls *emulsions* [19], to be made and coated on an industrial scale.

We now have the ingredients of modern silver halide photography, the small cameras, silver halide sensitised materials, a chemical development process allowing the copying of good quality photographs, and a method of fixing the developed image. We have not yet discovered how to extend the sensitivity of the materials to green and red light, how to get colour images or how to produce crystals which give direct positive images. It is time now to look at the chemistry of imaging in more detail with reference to modern materials. In doing so, we will fill in these gaps. A summary of the history of the development of component imaging technologies is provided in Fig 11.5.

Today, silver halide photographic materials have reached the last stages of their improvement. Digital image capture is now replacing film for a number of reasons. At the time of writing, film is still preferred for making movie films because of the infrastructure of the cinema industry and the need for large, bright projected images. Silver-based print materials for still images are steadily being displaced by temporary display and other non-photographic print technologies, particularly ink-jet, though electrophotographic printing may still eventually emerge as the dominant technology for hard copy. Many people still get their digital holiday snaps printed on silver halide paper at the supermarket. Leaving this uncertain peering into the future of imaging we should take time to celebrate the achievement of the refinement of silver-based materials resulting in the stunning images we have become used to enjoying. The level of performance of modern materials is nothing short of a miracle. Not only have several chance observations been involved in the story so far, but the sheer arithmetic of the chemistry of photography is remarkable as we shall see. Let us first look at some more details of image capture.

11.2.2 Silver Halide Photolysis

The silver halide, AgCl, AgBr, AgI and mixtures thereof, are all crystalline solids, being substantially insoluble in water, with pK_{sp} of *ca.* 10, 13 and 16 respectively. Photographic materials consist of a suitable support (polyester film, paper, glass) on which is coated one or more layers containing small crystals of silver halide (sizes varying from *ca.* 100 nm to 5 μ m, depending on the application) prepared by carefully controlled precipitation methods. By controlling such factors as temperature, rate of addition and halide concentration, dispersions (or ‘emulsions’ as the photographic industry traditionally calls them) of silver halide crystals with specific composition, size, size distribution and morphology are reproducibly prepared on large scale (up to *ca.* 1000 mol or more of silver halide per batch). Precipitations are always carried out in the presence of a colloid stabilising agent, traditionally gelatin, which binds to the surfaces of the crystals, preventing agglomeration and, to some extent, affecting the final crystal habit. Gelatin is also

Early History of Photographic Technology

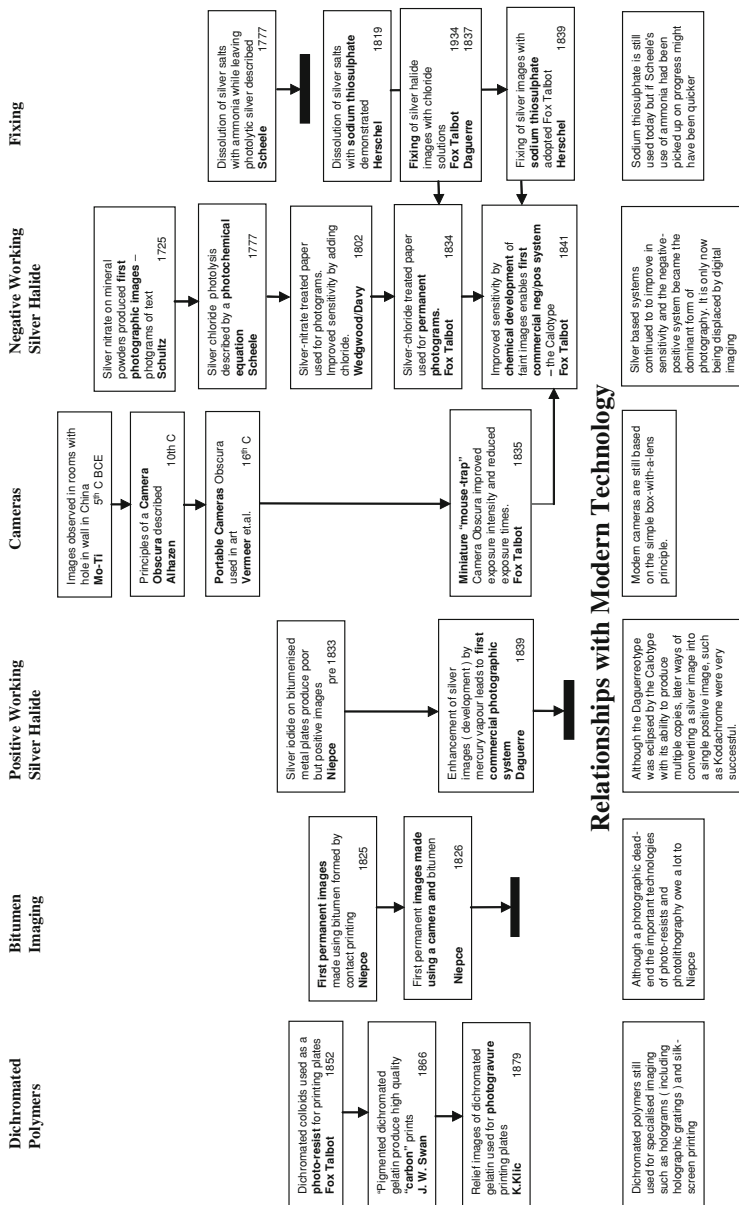


Fig. 11.5 A summary of the development of component technologies leading to modern photochemical imaging systems

the carrier medium for the coating stage, so that the various layers in a photographic material are actually layers of dried gelatin containing the various chemical components, including the emulsions, coated over the support material.

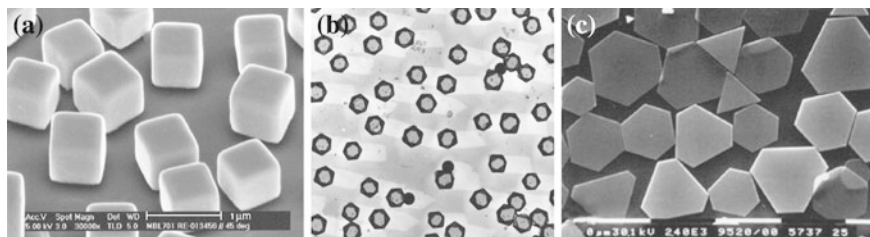


Fig. 11.6 Examples of silver halide emulsions. [Note: **a** and **c** are scanning electron micrographs of AgX crystals; **b** is a transmission electron micrograph of gold-shadowed carbon replicas of octahedral AgX crystals with the substrate fixed out]. Micrographs reproduced with courtesy of Eastman Kodak Company

AgCl and AgBr have face-centred cubic lattices (rock salt structure), while pure AgI adopts a variety of forms, including cubic sphalerite and hexagonal wurtzite, though a thermally unstable body-centred cubic form is also known to exist. In practice, most photographic products use AgCl, AgBr, or mixed phase Ag (Cl, Br) or Ag (Br, I) emulsions.

Figure 11.6 shows electron micrographs of some typical photographic emulsions, illustrating the variety of crystal shapes used. Emulsion choice depends on performance criteria dictated by the specific product application—considerations such as photographic speed (*i.e.* sensitivity to light), image contrast, processing factors (*i.e.* ease of development), image quality (graininess, contrast, tone scale, etc.) and cost all impacting on the final design.

All the emulsion types shown in Fig. 11.6 contain crystals with face-centred cubic lattice structure. The variety of shapes reflects differences in the rates of growth of [100] versus [111] faces and, in the case of the tabular grains in Fig. 11.6c the presence of crystallographic twin planes. The doubly-twinned crystals in (c) are particularly advantageous for the achievement of high sensitivity (camera speed) with minimal image graininess. These crystals, with their large surface area to volume ratio, combine a large capture cross-sectional area for light absorption with a relatively low mass per crystal. Thus, for a given coated mass of silver, there are more imaging centres per unit area, making for improved image graininess (or ‘granularity’).

In the absence of deliberately added growth modifiers, AgCl emulsions are invariably composed of cubic crystals. The natural morphology for AgBr is also cubic, but it is found that the presence of excess bromide ion during the precipitation inhibits the growth of [111] faces. Thus, a moderate bromide ion excess results in the formation of cubo-octahedral crystals with distinct [111] faces exposed at the corners. Increase the bromide ion concentration further, and regular octahedra can be produced (Fig. 11.6b). Still higher bromide levels encourage the formation of twin planes, with a progression from singly- to doubly- to multiply-twinned crystals as the Br^- concentration increases (Fig. 11.6c). The pattern for mixed halide crystals is broadly similar, with the presence of iodide in the lattice tending to push morphology somewhat further towards octahedral/twinned. Apart

from bromide ion, other substances are also known to be effective ‘growth modifiers’, influencing the final morphology of an emulsion by preferentially binding to one of other type of crystallographic face.

11.2.2.1 The Emulsion Precipitation Process

In the modern photographic industry, the precipitation process itself most often entails the continuous flow delivery of aqueous solutions of silver nitrate and alkali metal halide into a reactor containing an aqueous gelatin solution. Solution addition rate, temperature, halide excess and pH are all important variables and are generally tightly controlled to predetermined levels specific for a given emulsion formulation. It is also vital to ensure efficient high shear mixing of the incoming reactant streams as well as good bulk turnover of the reactant mixture. The silver and salt solutions are typically very concentrated (perhaps 3–4 mol dm⁻³). The precipitations follow a classic nucleation followed by growth mechanism. The mixing reagent streams constitute a zone of very high supersaturation, leading to the spontaneous formation of silver halide (AgX) nuclei. The initially formed nuclei are inherently unstable, being prone to dissolution *via* the Gibbs–Thomson effect. In a dynamic process called *Oswald Ripening*, the smaller particles redissolve and their material is deposited on other nuclei. Within fractions of a second from the start of the precipitation, the number of particles in the reactor increases, passes through a maximum and then falls to a stable number (provided reagent addition rate is properly controlled); from that point on in the precipitation, the final particle size (*i.e.* volume) is primarily a function of the number of moles of silver added to the reactor. Some emulsion preparations might involve several stages if, for example, a zoned halide distribution within crystals was desired or if the emulsion was to be of the ‘core–shell’ variety used for the direct positive (‘Reversal F’) process in which case two separate precipitation stages would be required.

All other things being equal, the final mean size of crystals in an emulsion depends on three main factors:

1. Reagent addition rate, especially in the early ‘nucleation’ stages of the reaction.
2. Net AgX solubility: influenced by temperature, halide excess (through the equilibria: $\text{AgX} + \text{X}^- \rightleftharpoons \text{AgX}_2^- + \text{X}^- \rightleftharpoons \text{AgX}_3^-$, etc.) or the presence/absence of another silver halide solvent (e.g. ammonia, thioethers etc).
3. The net number of moles precipitated (for a given nucleation regime).

By appropriate control of the precipitation variables, ‘monodisperse’ emulsions composed of crystals with near identical size (and shape) can be prepared. Such emulsions might be desirable for an application where very high contrast photographic response is required. Other product applications might call for a broader size distribution.

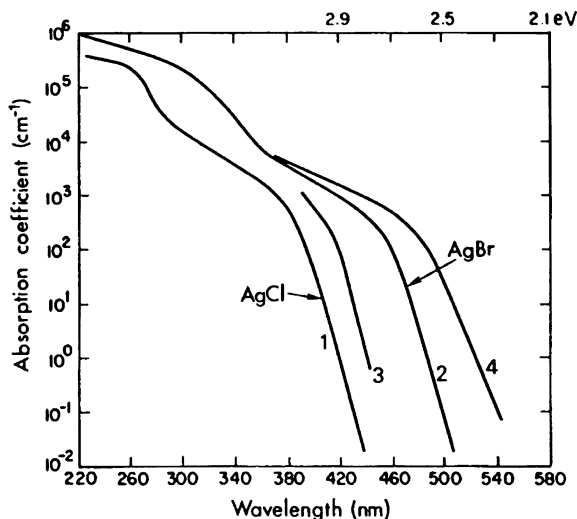


Fig. 11.7 Silver halides absorption spectra: (1) AgCl, (2) AgBr, (3) AgCl_{0.9}Br_{0.1} and (4) AgBr_{0.97}I_{0.03}. [Adapted with permission from Ref [22]. Copyright 1988, Taylor and Francis Ltd (tandfonline.com)]

11.2.2.2 Physical Properties of the Silver Halides

The silver halides are semiconductors, that is, their electronic structure is best described by the solid state model in which atomic orbitals overlap extensively to form occupied valence bands together with conduction bands that are unoccupied in the absence of external perturbation (*i.e.* in the dark at normal temperatures). All the halides absorb light in the UV region of the electromagnetic spectrum, with AgBr, AgI and mixed salts also absorbing into the visible out to *ca.* 500 nm (Fig. 11.7).

There are two main regions of absorption, corresponding to so-called ‘direct’ and ‘indirect’ transitions. The weaker absorption at longer wavelengths represents the indirect, forbidden transitions, which gain intensity *via* lattice vibrations (*phonons*). Absorption of a photon promotes an electron from the valence band to the conduction band, shown by the blue arrow in Fig. 11.8.

The silver halides exhibit photoconductive properties, since, electrons in the conduction band are mobile and free to migrate throughout the crystal structure. The positively charged hole left behind in the valence band is also mobile but with much lower mobility. The precise chemical nature of the hole species, h^+ , differs for each halide type. In the case of AgCl, the hole has been shown to be largely ‘self-trapped’, existing as a distinct Jahn–Teller distorted AgCl₆⁴⁻ species [20, 21]. In the case of AgBr, it is thought that the hole occupies a silver ion vacancy site from where it can migrate *via* an exchange mechanism to a neighbouring lattice site. The presence of silver ion vacancies is a consequence of the Frenkel defect whereby, at a given temperature, a certain number of silver ions are thermally

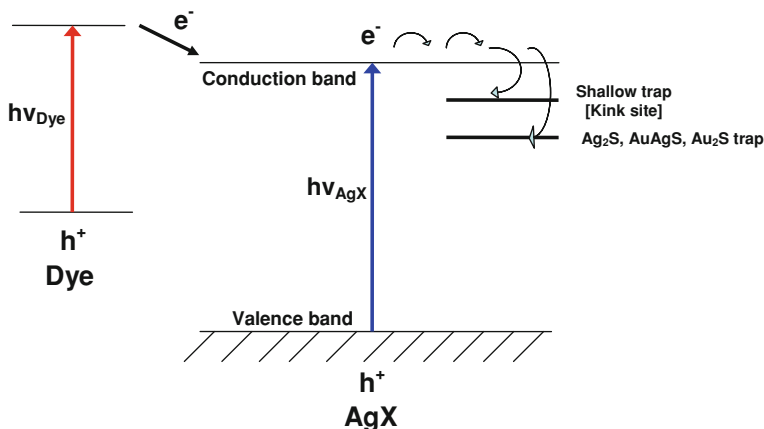


Fig. 11.8 Band model for silver halides

promoted from their normal lattice positions to occupy so-called *interstitial* sites. The defect may be considered to arise because of the significant difference in size (ionic radius) between the silver and halide ions, with Ag^+ being much the smaller. The equilibrium number of interstitial silver ions in AgBr is greater than that in AgCl , owing to the larger size of the Br^- ion versus Cl^- . The Ag^+ *vacancies* left behind experience a net negative charge, rendering them favourable for hole localisation. Interstitial silver ions are the carriers responsible for the dark electrical conductivity exhibited by the silver halides and, as we shall see, they play an important role in the photographic process.

11.2.2.3 Formation of the Latent Image

The photographic process relies on the fact that photogenerated conduction band electrons react with interstitial silver ions to produce clusters of Ag^0 atoms on the surface of an exposed crystal. With sufficient exposure to light, AgX materials will, in fact, darken, due to the formation of metallic silver. This process, called *print-out*, was actually exploited in some non-processable, low cost, recording papers to produce fairly low density black-on-white traces. The same print-out effect is used today in some silver chloride based photochromic glasses. The dark reversibility of the photochromism in this case is due to the total bleaching of the photolytic silver by the slowly diffusing positive holes such that there is no net conversion to Ag^0 . The substantially non-reversible darkening witnessed in gelatin-based coatings of AgX results from the scavenging of positive holes at the AgX surface by naturally occurring reducing moieties in the gelatin matrix.

Print-out materials are, of course, exceedingly 'slow' in a photographic sense, requiring a relatively large exposure to light in order to generate a visible effect. The miracle of modern silver-based photography is that images can be recorded

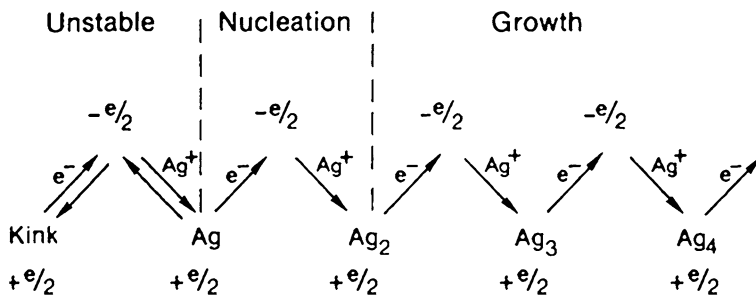


Fig. 11.9 The mechanism of latent image formation. [Adapted from Ref. [22] with kind permission from Taylor and Francis Ltd (tandfonline.com)]

with minimal exposure (and therefore very short exposure times for camera films). Such exposures generate no visible change in the recording medium until it is *developed*. It is found that clusters containing four or more Ag^0 atoms are effective catalysts for the chemical reduction of AgX particles to metallic silver by a solution of suitable reducing agent (the *developer*). The presence of one or more such developable clusters on the surface of an AgX particle constitutes a so-called *latent image*. The mechanism [22] by which latent image is believed to be formed is illustrated in Fig. 11.9.

The mobile conduction band electrons diffuse rapidly through the crystal until they find their way into shallow traps on the grain surface (Fig. 11.8). These traps are thought to be associated with crystalline imperfections that inevitably exist at the crystal surface as a result of incomplete ionic layers and partial co-ordination of lattice Ag^+ and X^- ions. These defects will carry a net electrostatic charge. Some of the kink sites on cubic [200] faces, for example, possess a net $+e/2$ charge, making them attractive trap sites for electrons. Once an electron is trapped there, the net electrostatic charge switches from $+e/2$ to $-e/2$ rendering the site attractive to mobile interstitial silver ions (Ag_i^+) and resulting in the formation of a silver atom: $Ag_i^+ + e^- \rightarrow Ag^0$ thereby resetting the trap charge to $+e/2$. A second electron may then be trapped at the same site, followed by reaction with another Ag_i^+ to give Ag_2^0 and so on.

Points to note about this mechanism are:

- Single silver atoms, Ag^0 , are unstable and require little thermal energy to re-ionise with the injection of the electron back into the conduction band.
- An Ag^0 atom at a kink site represents a slightly more favourable (*i.e.* deeper) trap for electrons than the original 'empty' trap.
- Ag_n^0 centres with $n \geq 2$ are relatively stable.
- Ag_2^0 and Ag_3^0 centres are *not* catalysts for development.

This mechanism, first proposed by Gurney and Mott in 1938 [23], helps to explain how an AgX crystal may be rendered developable by the absorption of a

very small number of photons. An important feature of the mechanism is the reversible nature of the steps leading to the formation of an initial Ag^0 atom (labelled ‘unstable’ in Fig. 11.9). In principle, a single Ag_4^0 cluster is capable of catalysing the development of the whole crystal on which it sits. Since typical emulsion crystals contain from 10^6 to 10^9 Ag^+ ions, this represents an enormous amplification factor. In practice, loss processes reduce the net quantum efficiency so that even in the most sensitive modern materials, crystals require the absorption of perhaps 10–15 photons to create at least one Ag_4^0 cluster.

11.2.2.4 Chemical Sensitisation

So far, however, we have only considered the performance of untreated AgX emulsions. Emulsions, as precipitated, are in fact not very sensitive to light—at least not by the standards of modern day photography. Untreated, or *primitive*, emulsions suffer from two major drawbacks: (a) inefficiencies in latent image formation and (b) lack of any sensitivity throughout much of the visible light region of the spectrum (see Fig. 11.7). This is why in the early days of photography those wishing to have their portraits taken would need to sit still for quite a long time! Following the explosion of interest in synthetic dyes initiated by William Perkin in the mid nineteenth century, it was soon realised that the sensitivity of photographic plates could be increased by adding certain dyes to the emulsions. This process of spectral sensitisation continued to be developed and investigated throughout the long history of silver halide photography (see Sect. 11.2.2.5).

Some of the early photographic plates probably also gained a little extra sensitivity from interaction with impurities in the raw materials (silver, halide salt, gelatin). One of those impurities was most likely sulfur since by the 1920s it was realised that by deliberately treating AgX grains with labile sulfur compounds (sodium thiosulfate being commonly used), their sensitivity to light could increase several-fold. This treatment, called *chemical sensitisation* or *chemical ripening*, is known to decorate the surfaces of AgX grains with clusters of Ag_2S . Sulfur sensitisation serves to enhance the electron-trapping capability of sites on the AgX surface, in part at least by slightly deepening the intrinsic traps provided by crystalline imperfections though the reversibility of the steps in Fig. 11.9 still applies. Some time later, in the 1940s, it was found that the inclusion of gold in the sensitisation could increase sensitivity even further.

The beneficial effects of sulfur + gold sensitisation can be best understood in the context of the loss processes which exist in unsensitised material. The two most important loss processes are (a) recombination and (b) image dispersity. The recombination of the primary photoproducts, electrons and positive holes, which competes with the formation of latent image Ag_n^0 clusters, is most likely to occur at either very high or very low light intensities. At high intensities, the high concentration of holes and electrons within a crystal enhances the probability of second order encounters. At low intensities, the electrons will spend more of their time in

the conduction band, owing to the reversible nature of the initial steps in the latent image formation process (see Fig. 11.9), thereby increasing the probability that they will encounter a trapped hole before a stable Ag_2^0 centre can be produced. Another adverse effect of high intensity exposures is the excessive number of different sub-developable Ag_2^0 and Ag_3^0 centres that form as a result of dispersity, i.e. too many different stable centres competing for photoelectrons. The loss processes occurring at low and high intensity exposures are examples of so-called *reciprocity failure*, whereby the quantum efficiency of latent image formation is reduced. Sulfur sensitisation mitigates against both these loss processes to some extent by ensuring more rapid electron trapping and increased stability of electrons in shallow trap sites. Gold is believed to make little difference to trap depths, its main role being to enhance the catalytic ability of the latent image centres at the development stage, thereby significantly reducing high-intensity reciprocity failure by rendering smaller Ag_n^0 centres developable. Certain transition metal dopants, generally introduced during the precipitation stage, can also help to offset reciprocity failure effects. For example, Ir(III) dopants act as temporary shallow electron traps. Such traps will release their electrons relatively slowly back into the conduction band, making a high intensity exposure resemble a lower intensity exposure with regards to the rate at which Ag_n^0 centres are nucleated, thereby reducing dispersity losses.

11.2.2.5 Spectral Sensitisation

The net effect of successful chemical sensitisation is to increase the sensitivity of AgX materials by >10X. This statement applies to the situation in which light is absorbed directly by AgX. Whilst sulfur sensitisation imparts a very low level of light absorption at longer wavelengths, which may have benefited the early pioneers of photography, the use of dyes is essential for achieving good spectral sensitivity throughout the visible (and into the infrared) region. Furthermore, it is necessary to be able to *selectively* sensitise emulsions to the blue, green and red regions in order to faithfully reproduce the colour information in a subject. The class of dyes found to be most effective for this purpose are the cyanines (see Chap. 4 for some examples). During the century and more that commercial photography has been in existence, literally thousands of cyanine dyes have been synthesised and screened for their possible application. Of these, only a relatively small number ever appeared in products. The great number of variables in the molecular architecture of dyes allows fine-tuning of their spectral properties. A typical vinylogous series of dyes is illustrated in Fig. 11.10a.

Many dyes have a tendency to aggregate. One class of aggregate, called *J-aggregates*, have characteristically sharp absorption spectra, making them particularly useful for sensitising in a narrow spectral region (see Fig. 11.10b). In addition to their spectral characteristics, other important dye properties include the degree of adsorption to silver halide surfaces (which depends on halide type and crystal habit) and solubility, whether organic solvent- or aqueous-based.

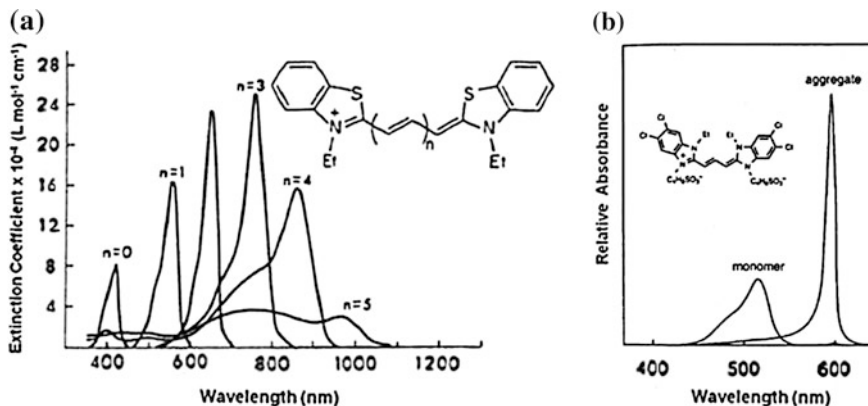


Fig. 11.10 Absorption spectra of cyanine dyes. **a** Absorption spectra of a vinylogous series of cyanine dyes in methanol solution [Adapted with permission from Ref. [62], p 197]. **b** Absorption spectra of monomeric and aggregated forms of a cyanine dye in solution. [Adapted with permission from Ref. [62], p 219]. Copyright 1977, Macmillan NY; Copyright 1989, jointly Macmillan NY and Eastman Kodak Company

The mechanism of spectral sensitisation has been shown to involve the direct transfer of an electron from the excited state of the dye into the AgX conduction band (see Fig. 11.8). In confirmation of this mechanism, excellent correlation has been demonstrated between the sensitisation capability of dyes and their electrochemical reduction potential. For the most efficient dyes, the quantum yield of the electron transfer step is close to 1.0. Using picosecond laser pulse excitation to measure the fluorescence decay rates of dyes adsorbed to AgX crystals, it has been shown that the electron transfer is very fast, with rate constants in the region of 10^{11} s^{-1} having been reported [24]. Once an electron has been transferred into the AgX conduction band, the latent image formation process ensues more or less as it does following direct absorption by AgX itself. The difference in the case of the dye-sensitised process is that the positive holes are trapped at the dye molecules.

Although chemical and spectral sensitisation markedly improve the yield of latent image silver centres for a given amount of absorbed photons, the photographic industry pays little attention to directly managing the fate of the positive holes produced on exposure. Apart from the few that are lost in recombination events, the holes either diffuse slowly to the crystal surface (following direct absorption by AgX) or are trapped temporarily at a dye molecule. Thereafter, they may be released as halogen or are consumed in chemical reaction with gelatin moieties. Hole attack on latent image centres, though possible, generally occurs with low probability in efficiently sensitised materials. At high surface coverages of certain *J*-aggregated dyes, migration of the dye-trapped hole through the dye layer is known to exacerbate latent image bleaching.

11.2.3 Photographic Development

11.2.3.1 Development of the Latent Image

The early silver halide systems for capturing images were very slow, requiring long exposure times to produce a sensible image. To make commercially successful consumer photography systems, camera shutter times needed to come down from the hours and minutes of early systems to fractions of a second. Sensitisation of the halide crystals was part of the story, but an equally important factor was the ability to take the tiny physical images formed in camera and make them useful at a later stage. This is the development process, where the latent image consisting often of clusters of only a few atoms could be converted into thousands of millions of atoms, and rendered visible to the eye. Typically the amplification factor in this process was of the order of 10^8 – 10^9 . In modern emulsions it takes only approximately four atoms of silver to make a latent image developable.

The key to this process is the catalytic effect of small clusters of metallic atoms on the surface of a silver halide crystal, which enhance the rate of reduction of the silver halide to metallic silver by a reducing agent (developer). This catalytic effect allows whole grains or crystals to be fully reduced to metal while neighbouring grains, without this catalyst, remained unreduced. This discrimination-between grains with latent image as opposed to those without-is only possible due to the differential rate of reduction caused by the catalytic effect. By tailoring the developer composition in combination with a fixed development time, temperature and pH, better and better discrimination was enabled along with shorter process times.

It should be said that development of the latent image can occur by virtue of the reduction of the original light sensitive silver halide either by virtue of the catalytically enhanced reduction rate described above (known as *chemical development* in the 'trade') or by the use of the catalytic action on a soluble silver salt introduced simultaneously with the reducing agent or by virtue of solubilising the primary halide and effecting reduction from it in its solubilised state. This is known as *physical development*. Physical development can be carried out either before fixation (see later) or post fixation; the latter is clearly not an option for chemical development. Despite the name, it is, of course, still a chemical development process.

The physical chemistries behind these processes are complex: the rate of development is dependent on many factors which include the nature [25] of the catalytic speck itself, its size, the reduction potential (See electrochemical explanations, for example [26, 27]) of the developer composition and the agitation of the process [28] to prevent undue concentration depletion. It also depends on the stage of the development process: typical negative emulsion systems are characterised by a slow initial rate (often referred to as an induction period) followed by a rapid acceleration and a final slowing as reagents are depleted. Many different compounds have been explored as developers alone and as combinations. Some combinations provided advantages in rates of development [29] compared to

expectations based on rate measurements of the components of these mixtures alone. (This is referred to as *superadditivity*). Development kinetics follow several stages depending on the process; typical chemical development of negative emulsions lead to a form of silver metal known as *filaments*. These hair-like strands of silver metal are the result of a growth pattern which typically starts as spherical, as the silver atoms are formed at a rate which is slow enough to allow them to diffuse uniformly over the surface of the expanding metal speck, but which suddenly explodes in rate and changes in configuration when the surface area becomes able to generate new silver faster than it can diffuse over it to maintain sphericity. At the very inception of development, with tiny latent images, Gibbs free energy (excess energy due to small size-Gibbs-Thomson [30] equation) plays a role in altering the effective reducing strength of the developer, allowing a relatively rapid expansion despite the small area of the developing speck. When the size is large enough to make this effect disappear, but is still small enough to continue spherical development, the development rate, although accelerating, is now at its slowest and it is thought that this phase is the cause of the observed ‘induction period’.

Successful developing agents are characterised by having oxidation potentials within a specific range. Too strongly reducing in potential would cause non-exposed grains to be reduced while too weakly reducing would cause development rates to diminish below practical use. Experiments with redox buffers of constant and defined oxidation potential showed what the useful range was—already discovered empirically [31]. An example of a common black and white developer, cheap and available in large quantity, is hydroquinone, and this combined with a relatively recent discovery as a developer [32], phenidone, is a good example of the synergistic combination of two developers to produce a development rate greater than the sum of the rates for each developer used alone (superadditivity). For more on development kinetics and a discussion of the influence of the swelling of the matrix (gelatin), diffusion, temperature, superadditivity and pre-treatments of the latent image (such as latensification) see Ref. [6].

Consumer photographers have typically used the word “development” to mean the whole process of turning exposed film into useful images—usually prints. However to the technician, the development stage is the initial part of the process to amplify the latent image. The amplified image is not useful until stabilised and this requires the process of *fixation*, mentioned earlier in discussion of physical development. Residual unreduced silver halide must be removed to prevent its gradual darkening on exposure to light (printout) and if a colour image is to be generated, the developed silver must also be removed. Residual chemicals must be washed from the gelatin layers and the film must be dried without leaving optically interfering marks. These processes have their own complexities—but these are perhaps a step too far for the purposes of this chapter.

11.2.3.2 Extensions of the Development Process

The development of silver halide can be exploited in an impressively large number of ingenious ways. For example the now obsolete Dufay Colour and Polachrome film materials used R, G and B filter arrays in combination with a panchromatic (having sensitivity covering the entire visible spectrum) silver halide layers which were developed to give positive silver images which viewed through the same filter arrays gave full colour images [33].

The majority of systems, though, make use of the oxidised developing agent resulting from silver image formation to provide a number of useful imaging effects. A complete survey of such effects and products is not possible here and since these extensions of the development process involve no photochemistry they will not be discussed in detail. Nevertheless, these chemical chains of events, are enabled by the initial photolysis of the silver halide crystal leading to useful consequences and to a variety of important photographic systems and applications, so a few of the more important examples will be described briefly below.

Chromogenic development. The most obvious extension of the development process is probably the production of dyes, and the consequent ability to form colour images. Most colour photographs have been produced in this way. The first system based on chromogenic development was Eastman Kodak's Kodachrome system introduced in 1935. After an initial black-and-white development of the negative image the remaining undeveloped silver halide provided the oxidative driving force in subsequent colour forming stages. Because the dyes were formed where silver halide remained after the initial non-chromogenic development of the negative image, the resulting colour image was positive. These stages used a processing solution containing both a developer and a compound, which on coupling with the oxidised developer formed a dye. Both coupler and developer were soluble, but the dye formed from them was insoluble and remained near the silver halide crystal, which provided oxidised developer.

Selective exposure or *fogging* of each of the three layers sensitive to blue, green and red light allowed each layer to be developed separately. The blue-sensitive layer generated the complimentary yellow (blue-absorbing) dye, the green-sensitive layer formed the magenta dye, and the red layer formed the cyan dye. Bleaching of the silver back to silver halide and its removal by a solubilising fixing agent left a high quality colour image.

The first, hugely complicated, Kodachrome process was replaced by simpler forms, which still remained very complicated and difficult to control. Despite the difficult process, Kodachrome remained available until 2009. Soon after its introduction more easily processed colour films were introduced, for example, the Kodacolor system in 1942. In this system the coupler molecules included a *ballast*, a bulky oleophilic group which allowed them to be dissolved in a substantially hydrophobic solvent. The resulting solution could be dispersed in a gelatin solution by an emulsifying process and incorporated into the layers of the photographic material. These *incorporated coupler* films soon dominated the market. Modern systems use *N-N*-disubstituted *p*-phenylenediamine developers. Cyan dyes are

formed using phenols or naphthols. Magenta dyes are derived from pyrazolones or pyrazolotriazoles and yellows are formed using couplers containing an active methylene group, which is not part of a ring such as benzoylacetanilides.

All three colour-forming layers are developed simultaneously. When the colour image is formed during the development of the latent image these systems are negative working and require a partner colour negative print material to produce a positive colour image. Alternatively, a *reversal* process using a first black and white development step, followed by fogging and chromogenic reduction of the initially undeveloped silver halide to produce a positive colour image.

Tanning development. A number of silver-based imaging systems use oxidised developer to cross-link the gelatin matrix to produce and exploit a difference in physical behaviour between exposed and unexposed regions. This can be for example, hydrophilicity. The so-called *tanning developers*, such as hydroquinone and similar di- and tri-hydroxy benzenes, are oxidised to quinones which are capable of reacting with the amino groups of gelatin resulting in cross-linking. Areas where silver development occurs become harder and more hydrophobic, and therefore more receptive to oil-based inks, while undeveloped areas repel ink. Low-cost printing plates can be produced in this way.

In 'wash-off' systems the hardened areas of gelatin layers can be made to adhere to the support while unhardened areas when washed with warm water are removed completely. The resulting images are suitable for line images since the image is either of maximum or minimum density.

Perhaps the most familiar use of differential hardening is the Technicolor process. There have been various forms of Technicolor systems over the many decades of its use in cinematography. Originally, special cameras, which split the image into three different spectral regions, were employed despite their complexity and cost. The last generation used the same colour negative film stock to generate three (red, green and blue) images on a set of black and white films. These were exposed through their supporting film bases. The films included non-photographically active dyes to control the penetration of light so that only the highest exposures reached the top-most silver halide crystals. Development in a tanning developer resulted in gelatin hardening only next to the base with low exposure building up to complete hardening as exposure levels increased. After fixing, the films were washed in hot water which removed the gelatin which was insufficiently hardened to prevent dissolution.

The films were then soaked in dye solution, cyan dye for the film with red image information, magenta for the green and yellow for the blue. The dye-soaked layers were then contacted with a receiving layer in accurate register to form the final positive image. Technicolor was, for a long time, the preferred method for generating multiple copies of films because the intermediates were relatively cheap but in recent times its complexity and the lowering costs of silver halide print films have led to its displacement.

The related large-format products exploit an important aspect of the dye-transfer technique. The dye-transfer system allows a far wider selection of dyes than chromogenic dyes which are generated *in situ* during the development process. In particular, very stable dyes of excellent hue can be used to produce

high quality archival images. The control which the complexity of the process allows is valuable to some practitioners who consider the images achieved to be of the highest possible quality.

Other Colour Systems

Silver dye bleach. Chemical processing of silver halide materials can also be used to destroy dye. The azo-dye-bleach process [34] used in Ilfachrome (formerly Cibachrome) uses the developed silver to reduce azo dyes to colourless amine compounds. Positive images of high quality and excellent stability can be produced. These materials have long been popular with photographic artists for this reason.

‘Instant’ Colour Films. The Polaroid Corporation’s instant films provided a remarkable breakthrough in photography. We have seen that early photographers carried their materials and processing equipment with them as well as their cameras. Edwin Land challenged himself with integrating a processing laboratory into a small portable camera, about the same size as Talbot’s ‘mousetrap’ camera. The developers were incorporated into the film’s layers. Each developer was chemically attached to a dye of a colour appropriate to the silver layer it developed. As with Technicolor, this enabled the use of dyes which could be selected with less restrictive criteria. Very stable metallised dyes were used in later versions.

After exposure, processing was achieved by passing the film pack through rollers. This burst a pod containing a viscous alkaline solution, which was spread uniformly between the light-sensitive layers and a dye-receiving layer. The success of the system relied on control of the diffusivity of the dye-developer. On development, the oxidised dye-developer became relatively insoluble. The diffusion rates of the dye developers through the multilayer coatings to the image receiving layers was sufficiently slow that by the time they had travelled through adjacent layers sensitive to other wavelengths than those appropriate to their hue, these layers were developed and the three separate colour images did not significantly interfere with each other. This independence of the three colour channels was helped by using auxiliary developing agents which shuttled electrons between the dye developer and the developing silver crystals and speeded up development in each layer. Since silver development prevented the diffusion of dye-developer to the image-receiving layer the system was positive-working.

Polaroid’s film product technology was initially developed and manufactured by Kodak until Kodak decided it needed a comparable product and this required the invention of a different type of development chemistry. In Kodak’s PR10 ‘Instant Colour’ films a B and W developer was used and its oxidised form, created by silver development, oxidised an immobile molecule called a *redox dye releaser*, which then released a mobile dye [35]. Where development occurred dye was released to a receiving layer and this required new positive working emulsions, described in Sect. 11.2.4. The arrival of digital photography provided an alternative to the gratification of instant photography without the limitations and expense of instant films so they have all but disappeared.

11.2.4 Direct Positive Emulsions

Another of the many chance observations made during the history of photography led to silver halide emulsions which worked in a *positive* sense, *i.e.* when imaging light exposed the crystals they do not develop whereas unexposed crystals do. E. B. Knott working at Kodak in Harrow had exposed some film and was processing it when he accidentally switched the dark-room lights on. A positive image resulted. This was later explained by a colleague, G. Stevens. The emulsion Knott was using had high internal sensitivity due mainly to a rather chaotic crystal structure, providing effective trapping sites for electrons released by exposure. At moderate exposure levels only internal latent image was formed. The crystals did not develop in developer solutions which did not dissolve or disrupt the crystals and therefore detected only the surface latent image.

In the wet conditions of the developer solution however the trap sites on the surface became more effective. This meant that when exposed during development, the unexposed crystals, instead of producing internal silver, produced surface silver at sites previously uncompetitive with the internal sites. On the other hand, crystals which already had internal silver produced from the image exposure, continued to trap photoelectrons internally because the accumulation of silver at the trap sites made them more effective traps than those on the surface despite the change in exposure conditions. They therefore did not develop. A direct-positive system was thus discovered [36].

This understanding of the observation later led to the design of relatively defect free crystals with carefully controlled internal and surface sensitivity through chemical sensitisation. Crystals of silver bromide were precipitated and treated with sensitisers. Further deposits of silver bromide then buried the sensitivity centres. Figure 11.6b shows the resulting monodispersed crystals. These direct positive emulsions designed by F. Evans [37–39] were probably the first commercially exploited examples of crystals which were so perfectly formed and uniform. Previous emulsions contained a mixture of shapes and sizes due to relatively uncontrolled precipitation processes.

The role of the non-imagewise exposure in *Reversal F* emulsions is to produce conduction band electrons. Developers are very mild reducing agents and unless silver halide solvents such as thiosulfate are present or the crystal structure is disrupted by, for example, iodide, they only reduce silver halide at a significant rate when surface silver is present. Stronger reducing agents will provide electrons less discriminately, for example, hydrazides [40]. In this context these are usually referred to as nucleating agents and they provide the same effect as a non-imagewise exposure. This is done conveniently by including them in developer solutions or even more so by incorporating them in the photographic layers. These positive emulsions found application in Kodak's PR10 Film [41] and the related Ektaflex print materials. (See 'Other Colour Systems', above.)

11.2.5 X-Ray Imaging

One might expect that materials which are sensitive to electromagnetic radiation in the UV/Vis region are also responsive to more energetic radiation and this is indeed usually the case. Ionising radiation such as X- and gamma rays produce latent image silver in silver halide crystals. The initial interaction of such rays with exposed material, results in the generation of free, energetic ‘primary’ electrons. If the photon energy of the radiation is low it is possible that the photon is absorbed but has sufficient energy to eject an energetic *photoelectron*. Higher energy photons are more likely to give up a portion of their energy and be deflected while also producing an energetic electron, a process known as the *Compton effect*. The likelihood of ionisation depends on the density of electrons in the exposed material so silver bromo-iodides are preferred to the lighter halide combinations. Subsequent ionisation events are then caused by the interaction of the primary electrons with their source crystals or other crystals within their reach. On each occasion the electrons lose energy and eventually become incapable of further damage. The main differences from light exposure is that the initial photon and the released electrons are very much more energetic than light by up to about four orders of magnitude and that the energy is deposited effectively instantaneously.

Directly exposed X-ray films are used for what are known as ‘industrial’ applications such as searching for cracks in metal objects, for example oil pipelines. The films can be made handleable in light by packaging with light-opaque materials. An improvement in efficiency can be achieved by placing the film, in particular the coated side, next to a ‘screen’ made from a heavy metal such as lead. The screen absorbs X-rays more effectively than the film providing primary electrons some of which can expose the film. This indirect exposure supplements that achieved by direct exposure.

A much greater improvement to sensitivity is obtained using a fluorescent screen to convert the X-ray energy to light, which is then used to expose silver halide film. About 5 % of X rays are typically absorbed in directly exposed films. Intensifying screens can absorb up to 60 % of the incident X-rays, two screens are often used, one on each side of the film.

The screen materials are made from a variety of heavy metals compounds such as oxides, sulfides, aluminates or silicates of metals such as zinc, cadmium and tungsten. More efficient phosphors use lanthanides. The materials are usually ‘activated’ by dopants such as silver, copper and europium. These allow fine-tuning of the emitted wavelengths and optimisation of the efficiency of the materials. Typical materials are: M_2O_2S where M is Gd or La, doped, for example, with Tb, Eu, or Pr, or $Y_3(Al,Ga)_5O_{12}$ doped with Ce or Tb (see [Chap. 4](#) for more information on solid-state lanthanide phosphors).

The screen materials respond initially to X-rays in a similar way to that of directly exposed silver halide layers except that the excited screen compounds produce emitted light rather than the chemical change resulting in latent image. Interaction with the energetic electrons produced by the X-rays promotes valence-

band electrons to the conduction band or to levels below the conduction band provided by the dopants. The return of the electrons to the ground state provides the opportunity for emission of light.

The emitted light is efficiently harvested by spectrally sensitised film. In medical applications this increased sensitivity is an important contribution to reducing the doses of radiation suffered by the patient and/or to improving image resolution.

11.3 Non-Silver Imaging Systems

Over the last few decades there has been a fascinating technical and commercial battle between technologies competing to be dominant in the digital colour print market. It is still raging. During this period the lead in terms of commercial importance and predicted eventual pre-eminence has changed many times as technological progress has been made. Silver halide paper remains a major player despite predictions of its demise over 30 years ago.

Two other major technologies, ink-jet and thermal dye transfer (sometimes erroneously referred to as *dye sublimation*) systems are widely used but no photochemistry is involved so these will not be discussed further. Also omitted for the same reason is the thermal Autochrome system developed by Fuji for small-scale digital imaging.

Photochromism is discussed in [Chap. 4](#) and photopolymerisation as applied to photo-fabrication and printing is dealt with in [Chap. 13](#). Electrophotography does involve imaging with light even though no actual photochemistry occurs so it will be discussed briefly due to its commercial importance in imaging. Before doing so, we should also look at photochemical systems which have been largely supplanted by electrophotography and digital imaging technology but which once had an important place in commercial imaging.

11.3.1 Cyanotype Printing

Whenever we talk about a technical drawing describing a plan from which an object could be made, we use the term *blue-print*. Originally called the *Cyanotype process*, this imaging method was invented by the prodigious Sir John Herschel [\[42\]](#) in 1842. It is therefore almost as old as silver halide photography. At that time, and for a long time since, it had some advantages over silver based systems. For example, it was inexpensive to produce and relatively easily processed. Herschel used Cyanotypes to make copies of his own notes. It was, in fact, the system used in the first photographically illustrated book [\[43\]](#).

The Cyanotype process is the most successful of a family of imaging methods based on the photochemistry of iron compounds. The basic system involves the photochemical formation of the pigment Prussian Blue or iron(III) hexacyanoferrate,

which explains the name of the process (see Chap. 4). Ware [44, 45] has described a number of sensitising formulations using various ferric complexes of carboxylic acids including the commonly used citrates. He illustrates the photochemical imaging step with reference to ferric oxalate. On absorption of UV or blue light an electron is transferred from the oxalate ligand to the Fe(III) and the oxidised oxalate decarboxylates. The released Fe(II) reacts with potassium ferricyanide to give the permanent blue imaging pigment.

The exact nature of the imaging pigment produced, that is, the chemical make-up, the degree of hydration and the physical form, particularly particle size, depends on the starting materials, the preparation and the post-exposure treatment of the coated materials [46]. The formation of the intermediate Fe(II) can be also used to reduce metallic compounds including those of platinum to produce metallic images. Using gold chloride, Herschel produced purple images of metallic gold in the process he called the *Chrysotype process* [47]. Cyanotypes and the variations on them are still produced today but mainly for artistic purposes.

11.3.2 *Diazotype Prints*

Cyanotype blue-prints were, for about a hundred years, the dominant method of copying engineering drawings but they were displaced by *diazotype prints*. These were sometimes referred to as *white-prints*. Originally described in a patent in 1890 the first commercially successful system did not emerge until the 1920s, when the German company Kalle began to coat and sell products, expanding to England in 1926 using the trade name Ozalid. By the late 1940s diazo copying had largely replaced blue-prints.

Diazotypes rely on the destruction of a component in a reaction to form a dye, namely a diazonium salt. This was coated on paper or film alongside a phenolic compound under acid conditions. After contact exposure to intense UV irradiation the diazonium salt remaining, by virtue of being shielded from the light by the dark areas of the original, is allowed to couple with the phenol to produce dye by raising the pH. This was originally done by exposing the diazo material to ammonia vapour. The system had a number of significant disadvantages. The dye images were not stable. The ammonia or alternative amines needed to be vented from the working environment and two-sided originals could not be copied. These problems caused the system's eventual replacement by the more convenient electrophotographic methods emerging during the 1960s. Also, before these systems completed the take-over of office copying technology, silver halide systems such as Kodak's Verifax system, based on silver halide and tanning development avoided the problems with diazotypes albeit at higher materials costs.

During irradiation of the diazonium salt, nitrogen is generated. If the salt is coated in an appropriate transparent matrix, small bubbles of nitrogen are produced and these have been used to produce opaque areas which when viewed with specular light, provide dark image areas by scattering light away from the line of sight. The process was simple, materials are cheap and quite good resolution was possible.

11.3.3 The Mead “Cycolor” System

This ingenious system may have been the first application of visible light photo-initiation of polymerisation [48, 49]. The system has the considerable merit of ease of processing, at least as simple in practice as Polaroid’s and Kodak’s instant films. These are much more complicated, chemically and physically, as described in Sect. 11.2.3. Cycolor by comparison is simplicity itself, though lacking the exceptional sensitivity of silver halide materials it is only suitable for making prints.

As with any three-colour photographic system three dyes need to be deployed in an image-wise manner. Cycolor used a single coating containing micro-capsules which were called *cyliths*. Each cylith included a chromogenic compound, in this case a leuco dye, a photopolymerisable compound, namely, a functionalised acrylic monomer and a polymerisation initiator. On absorption of light, a single electron transfer to the singlet excited state of the dye from a partner borate ion occurs. The consequent boranyl radical initiates polymerisation. The initiators, dye-borate ion salts [50], typically cyanines are selectable and/or tuneable to provide the desired spectral response by means of the number of conjugated alkene units linking the fused heterocyclic end units. Blue-, green- and red-sensitive initiators can be then selected to provide three types of cylith. Each type included an image dye in *leuco* form which could be converted to a dye of a hue corresponding to the hue of the initiating dye. On exposure to a three-colour image each cylith hardened to a degree dependent on the amount of the light absorbed.

The processing step involved simply the compression of the exposed layer to rupture the cyliths and developer capsules and squeeze out the contents. The amount of *leuco* dye released depended on the degree to which the cyliths were hardened. Image dye was then produced from the *leuco* forms by the action of developers [51]. In the most compact formats of the system, the developer were encapsulated and coated in the same layer as the cyliths. The system did not reach the necessary quality/permanence/cost criteria to make it commercially viable in the longer term and so it remains a clever curiosity and unfortunately another imaging blind alley.

11.3.4 Dichromated Gelatin/Polymer Systems

The late 1830s was the time when silver-based imaging systems were emerging from the laboratories of such as those of Fox Talbot, Herschel and Daguerre. It must have been a time of intense activity as attempts to find other better systems were made. Herschel’s Cyanotype, based on iron salts is an example. Another metal, chromium, formed the basis of a number of useful printing methods some of which are still in use today.

The early dichromate materials used gelatin or albumen. Gelatin is still used today as well as polymers such as poly(vinyl chloride) (PVC) and poly(vinyl alcohol) (PVA). The first systems stemmed from the observations by a number of

people, including the Scottish experimenter Mongo Ponton [52], of the light sensitivity of materials treated with potassium dichromate. It was the ubiquitous Fox Talbot who first combined dichromates with colloids such as gum arabic and gelatin in 1852. The exposure-dependent hardening effect was used to control the diffusion of etching solutions through gelatin layers coated on metal printing plates. The more deeply an area was etched the more printing ink it retained and transferred to the paper print.

On exposure to light, dichromated gelatin becomes hardened or *tanned*. The photochemistry of this process does not seem to have been studied extensively until relatively recently including studies by Bolte *et al.* The initial reaction involves the photo-reduction of Cr(VI) to Cr(V) by amino groups in the gelatin. Further reduction to Cr(III) follows, and then the metal ion hosts the ligands provided by gelatin resulting in cross-linking and consequent hardening [53]. A similar mechanism is proposed in systems using polymers such as PVA, which do not contain amino groups [54, 55]. In PVA Cr(V) seems to be stable enough to participate in the cross-linking effect, at least temporarily.

In 1855 Lois Poitevin added a pigment, carbon, to the gelatin or mixtures of other natural gums. It took almost a decade and several experimenters to devise a commercially practical system. In 1866, J. W. Swan supplied 'carbon tissue' which was a thin paper coated by the user with sensitised pigmented gelatin. This was exposed when dry to a negative then contacted with a second paper sheet coated with clear gelatin. The first paper tissue was then stripped off and the exposed pigmented gelatin layer developed with warm water, revealing an image directly. These were known as *carbon prints* and the materials were improved to a stage when the image quality was remarkably high. This is due to a number of factors. The imaging layer is substantially non-scattering and can retain fine image detail. The photochemically active element is molecular, rather than a dispersion of crystals as with silver halide and the hardening effect proceeds in a linear fashion over a wide range of exposures resulting in accurate tone reproduction.

A number of printing techniques were enabled by dichromated gelatin. Most, such as *intaglio*, *aquatint* and *photogravure* methods involve the use of the material to produce relief images which could be inked to provide printing plates. More recently, dichromated gelatin has been used in silk-screen printing. It is applied to the screen material and exposed and washed with water. In exposed areas the holes between the fabric's fibres are blocked while unexposed areas allow ink through to the surfaces to be printed, ranging from paper and fabrics to metals.

Today, the main interest in dichromated polymer systems lies with holographic applications including the generation of diffraction gratings. The photochemical process is molecular, not amplified by a subsequent chemical step as in silver halide processing. Only the fact that macromolecules such as gelatin or PVA are involved provides some response beyond the simple molecular scale. This characteristic becomes a strength when exposure levels are unimportant. Then, the high optical resolution of a molecular process becomes an asset. For this reason dichromated polymer systems remain in use today having started life earlier than any photochemical system other than silver halide photography.

11.4 Electrophotography

The electrophotographic process is a major imaging system which dominates office copying, and, as image quality improves, is making inroads into the mainstream photomechanical printing industry. Although no chemical changes as such are involved, in view of its current importance and its commercial potential in imaging it is briefly described here. A thorough account of the technology and photophysics is provided by Weiss *et al.* [56].

The original invention was made by Chester Carlton and a patent applied for in 1939 [57]. Carlton coined the name *Xerography (dry printing)*. Following the involvement of the Battelle Institute supported later by the Haloid corporation of Rochester, New York, the first commercial copier appeared in 1949. Twenty years later the company changed its name to the Xerox Corporation.

Modern printers have been made simpler, less expensive and more capable in terms of both versatility and speed as well providing good quality colour images but the basic principles of the system remain the same. The core of the system is a photoreceptor belt or drum. This is coated with a metallic conductive layer at earth potential. In the case of the commonly used organic photosensitive materials, a second layer, the charge-generating layer contains photoionisable molecules such as, phthalocyanines, perylenes or squarines (see Chap. 4). Above this a charge-transport layer is coated using for example poly(N-vinylcarbazole) which provides a conductive path at very high electric fields (Fig. 11.11).

Charge is applied to the belt by contact with a charged metal roller or exposure to a corona-generating charging unit. The latter includes a series of isolated wires at high voltage, typically ~ 6 kV, which generate a flow of ionised air molecules which then charge the surface of the belt to typically 600 V. During image

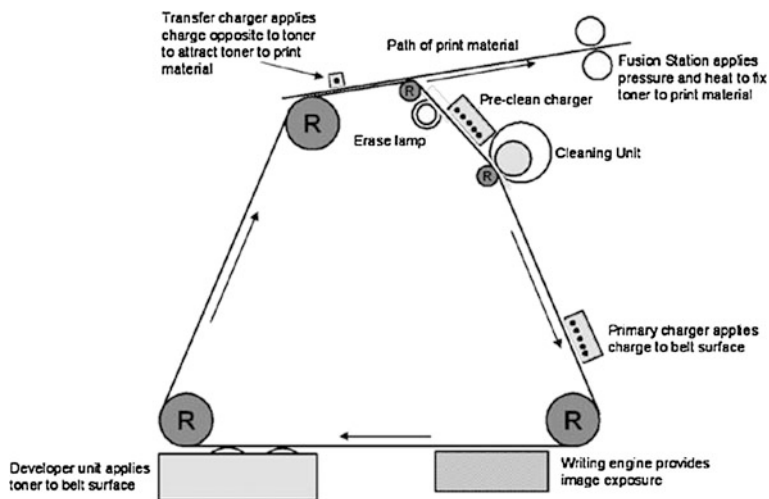


Fig. 11.11 A simplified diagram of an imaging mechanism in a typical photocopier

exposure light generates photoelectrons which are removed by the conducting sub-layer on the belt. The holes generated are transported through the upper layer and neutralise the surface charge. Today, the exposure is normally provided by digitally-controlled writing engines using lasers or LEDs.

Once the imagewise surface charge is produced it can be decorated by pigmented ‘toner’ particles. This is done by charging the particles using a *tribocharging* process. Often the toner particles are transported to the belt surface by using larger magnetic ‘carrier’ particles. These are mixed with the toner particles and the mixing process produces a transfer of charge from the toner particles to the carriers. The toner particles achieve a voltage opposite to the charge of the areas of the belt they are to be attracted to while the carrier particles have the same charge but at a lower voltage. The magnetic carriers form the bulk of the mixture which is picked up by a magnetic roller forming a ‘magnetic brush’ which can be used to apply the toner particles to the belt.

This process of converting an image in surface charge to a pattern of pigment particles is a development process which has an element of amplification by virtue of the mass of light-absorbing pigment compared with the amount of light used to discharge the belt to produce the image.

The pigmented image is then transferred with electrostatic assistance to the printed substrate. In the case of colour images an intermediate surface is usually used for indirect transfer of the four pigments which due to their light-scattering properties, as with photomechanical printing, include a final black pigment. Various other components of a printer are required to prevent image defects but are not included in this brief summary.

11.5 Conclusions and Further Reading

We have seen that the earliest descriptions of chemical processes include an equation involving light as a vital component. This reaction also involved silver halide, the predominantly important photochemical imaging material.

It is interesting to note that the two earliest imaging materials involved in the initial photolytic step of their imaging systems, namely silver halides and dichromated polymers are the only ones remaining in commercial use in any real sense. All the others have come and gone including the once important, iron-based blueprints. It is therefore curious that neither silver, chromium or iron had a high profile in the academic discipline of photochemistry. ‘Calvert and Pitts’ [58], one of the most widely used textbooks on photochemistry in the late twentieth century, barely mentions them at all.

The various forms of photochemical imaging including artistic, scientific and personal photography, X-ray imaging, photographic methods in the printing industry and photofabrication touch almost every aspect of our lives. Most of the decoration we see, the recorded memories we have, the manufactured goods we

use have at some point used photographic materials. The importance of photochemical imaging is difficult to exaggerate.

No single previous publication seems to cover the full scope of this chapter but there are several which provide wide scope and extensive detail. Although some are included in the references cited, the following books are recommended for further exploration:

The Origins of Photography (1982) by Helmut Gernsheim (Thames and Hudson, London) is an up-date of *The History of Photography* (1955) (Oxford University Press) by Helmut and his wife, who are major photographic collectors.

Out of the Shadows, Herschel, Talbot and the Invention of Photography (1992, Yale University Press, New Haven and London) recognises John Herschel's largely undervalued contributions including his support for Talbot.

The Keepers of Light (1979) by William Crawford (Morgan and Morgan, New York) covers important and obscure silver and non silver systems. Historical accounts are thorough and unusually accompanied by practical recipes for the reader to follow to reproduce the techniques described.

The Theory of the Photographic Process, (Ed. James T H [6]) in its various editions is the pre-eminent reference work for silver halide technology and science. It is however somewhat biased towards Kodak products since its authors are drawn from Kodak employees.

The following topics may be pursued using the references provided:

- Computer modelling of latent image formation [59, 60],
- Theory and practice of precipitation [61],
- Spectral sensitisation [62–65].

Another valuable source is *Photographic Sensitivity* (1995) by T. Tani (Oxford University Press, USA [66]) as is *The Handbook of Photographic Science and Engineering* [67]. A particularly useful source of mechanistic information for a range of systems is *Electron Transfer in Chemistry* (Ed. Balzani V, Volume 5, Wiley–VCH Germany), which includes sections on: photographic development, bleaching, spectral sensitisation; electrophotography; and photoinduced electron-transfer polymerisation initiating systems relevant to the Cyclic system and other photopolymer technologies.

References and notes

1. The rods in the retina respond to much lower light levels. They are saturated at normal light levels but at low levels they produce an achromatic response to the wavelength range below about 600 nm. Moonlit scenes are therefore lacking in colour. To become active the rods need to recover from the saturation caused by high light levels and this process of dark adaptation takes up to 30 min or so. Their activity can be preserved by using red illumination. For example, in a submarine if the red lights used were to fail suddenly the rods would still be responsive whereas white light failure would leave the crew essentially blind for several minutes

2. Artists may disagree. Artists' primaries are blue, red and yellow. Many do recognise that the best blue for mixing with yellow to get the best greens is 'Phthalo' blue, a phthalocyanine pigment which is in fact the best cyan available in the paint box. Also, Permanent Rose which is a decent magenta is often recommended for a mixing red. Since it is possible to get a blue from a cyan and magenta and a red from a magenta and yellow, while it is impossible to achieve a magenta or a cyan from a mixture of blue red and yellow, the traditional artists' case is weak if not simply wrong.
3. The letter K is used to avoid confusion with Blue.
4. In practice, two or even three layers make up each blue-, green- and red-sensitive sets of layers to improve the sensitivity/image structure (grain and sharpness) response.
5. Dispersion of very small silver particles can be highly coloured and of various hues depending on particle size. Carey-Lee silver is a suspension of very small silver particles of narrow size distribution. It provides a strong yellow colour and is removed conveniently during processing when the developed image silver is removed by bleaching and fixing.
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13. Reproduced by kind permission from Bibliotheque National de France, the image appeared in "The Independent" Newspaper in the UK, Jan. 17, 2002 prior to its auction in Paris.
14. Crawford W (1979) The keepers of light. Morgan and Morgan, New York p24
15. The example of a Daguerreotype shown here, is reproduced with kind permission from the collection of Jack and Beverley Wilgus. It is of Phineas Gage who became famous after an accidental explosion drove the metal spike he is holding through his cheek and out through his forehead. The fact that he made a good physical recovery but suffered major personality changes made him one of the most famous medical cases of all time.
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