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MPhys in Physics

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Universidade NOVA de Lisboa | Universidade de Lisboa

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Resumo

Esta tese explora as formas de capturar uma imagem fotográfica em vidro. Foi explorada a ideia tradicional de fotografia em vidro utilizando emulsões de gelatina de prata para a produção de impressões em vidro a partir de antigos slides de filmes familiares realizados em Portugal na década de 1960. Foi utilizada uma emulsão comercial formulada especificamente para superfícies não comuns. A preparação do vidro foi realizada de diferentes formas e foram utilizados vários tempos de exposição para criar diferentes resultados visuais.

Em combinação, a fotografia dentro do vidro é explorada na forma de vidro fotossensível. Várias composições de vidro fotossensível com prata foram sintetizadas e os efeitos da exposição a diferentes radiações e da temperatura no desenvolvimento na coloração do vidro foram exploradas utilizando diferentes técnicas, tais como espectroscopia de absorção UV-Vis e medições de colorimetria. Foram obtidos vários vidros que apresentaram um comportamento fotossensível, exibindo uma cor amarela somente após exposição e desenvolvimento de tratamento térmico. Um dos resultados mais relevantes, com maior contraste de cor foi obtido para um vidro composto por sílica, óxido de sódio, óxido de zinco e sulfato de prata. A adição de cério como sensibilizante óptico não aumenta a fotossensibilidade nas várias amostras produzidas. Numa das amostras verificou-se que a adição de 0,2% em peso de óxido de estanho, é suficiente para reduzir a prata, sem ser necessário utilizar alguma fonte de radiação, o que não permite no final obter uma imagem. Este vidro também apresenta luminescência visível que é reduzida após exposição e tratamento térmico. A luz solar é considerada uma boa fonte de exposição, pois meio-dia de exposição é suficiente para obter amostras com uma cor amarela escura após o tratamento térmico por 1 hora a 600°C. O efeito da adição de halogenetos ás composições também é explorado e pode influenciar a fotossensibilidade de alguns vidros. Descobriu-se que a adição de iões brometo ao vidro com óxido de estanho reduz o efeito de redução da prata pelo estanho e dá origem tons mais avermelhados. Foram utilizadas diferentes máscaras para criar imagens fotográficas. O protetor solar e um marcador preto permanente são particularmente eficazes e são uma opção interessante para expressão artística.

Através destas duas interpretações da fotografia em vidro, são alcançados efeitos visuais muito diferentes; embora a foto-redução da prata como mecanismo de produção de imagem seja comum a ambos, a forma que a prata assume e o ambiente circundante têm um grande impacto no resultado final. Finalmente, são exploradas formas de combinar estes dois métodos de produção artística. O uso de vidro fotossensível para adicionar cor e longevidade mais significativa a uma imagem é uma adição valiosa aos detalhes de granulação fina obtidos com emulsões de gelatina de prata em vidro. Olhamos para a ideia de 'recolorir' imagens antigas à mão com o uso de um marcador permanente para adicionar detalhes no vidro fotossensível antes de imprimir a imagem fotográfica por cima com emulsão. Dar uma forma física sólida a fotografias antigas, especialmente numa época em que as fotos muitas vezes só existem digitalmente, pode ser incrivelmente significativo e, através da combinação destes dois métodos, é possível criar peças com um sentido mais profundo de propósito e apreciação.

Abstract

This thesis explores the ways of capturing a photographic image with glass. The traditional idea of photography *on* glass using silver gelatin emulsions is explored with the production of glass prints from old family film slides taken in Portugal in the 1960s. We use a commercial emulsion specifically formulated for unusual surfaces and experiment with different ways of preparing the glass and varying exposure times to create different visual results.

In combination, the science of photography *inside* glass is explored in the form of photosensitive glass. Batches of photosensitive glass are synthesised with silver and the effects of exposure and development temperature on the colouration of the glass are explored using UV-Vis absorption spectroscopy and colorimetry measurements. Photosensitive glasses are successfully produced, exhibiting a yellow colour only after exposure and development heat treatment, and one composition is found to be particularly good. The glass is composed of silica, sodium oxide, zinc oxide, and silver sulphate. The addition of cerium as an optical sensitiser is not found to enhance the photosensitivity. A similar glass with the addition of 0.2 wt% of tin oxide is found to suffer from 'warming-in' of the colour without exposure. This glass is also found to exhibit visible luminescence which is reduced after exposure and development heat treatment. Sunlight is found to be a good exposure source, with half a day of exposure sufficient to give a dark yellow colouration upon development heat treatment for 1 hour at 600°C. The effect of adding halides to the compositions is also explored and found to impact the photosensitivity of some glasses. The addition of bromide ions to the tin-oxide-containing glass is notably found to reduce the 'warming in' effect and produce more reddish tones. Different masking materials are experimented with to create photographic imagery. Sun cream and a black permanent marker are found to be particularly effective and present interesting opportunities for artistic expression.

Through these two interpretations of glass photography, vastly different visual effects are achieved; whilst the photo-reduction of silver as the image-producing mechanism is common to both, the form the silver takes and its surrounding environment has an immense impact on the final result. Finally, ways of combining these two methods for art-making are explored. The use of photosensitive glass to add colour and more significantly longevity to an image is a valuable addition to the fine-grained detail achievable with silver gelatin emulsions on glass. We look at the idea of 'recolouring' old images by hand with the use of a permanent marker to add detail in the photosensitive glass before printing the photographic image on top with emulsion. Giving a solid physical form to old photographs, particularly in an age where photos so often only exist digitally, can be incredibly meaningful, and through the combination of these two methods it is possible to create pieces with a deeper sense of purpose and appreciation.

Contents

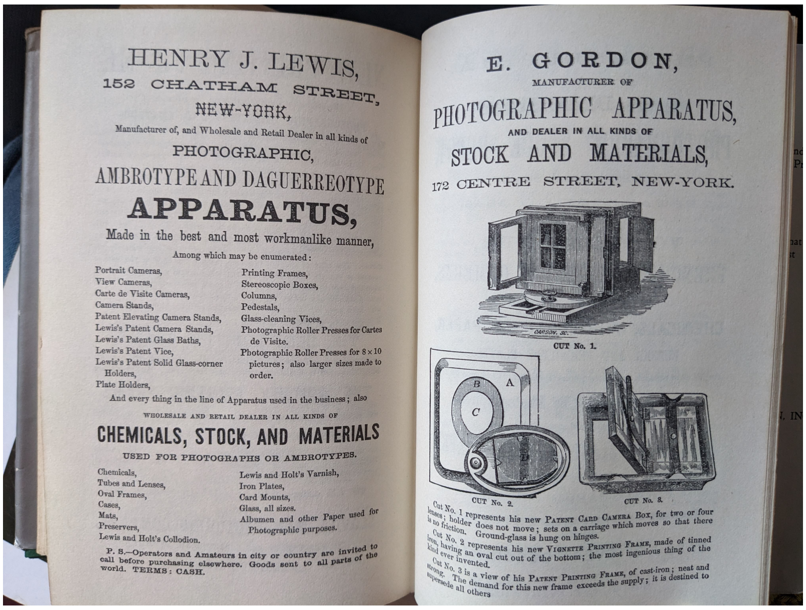
1 Introduction

Photography *From photos (φοτοσ), light, and graphos (γραοσ), writing, delineation, or painting.* "The art of producing images by application of chemical changes produced by certain substances by the action of light or other radiant energy," 1839 [1].

The earliest written reference to the camera obscura can be found in the writings of the Chinese philosopher Mozi (470 to 390 BCE) [2] however, there are theories that the principle was understood and employed for rituals and entertainment as far back as the palaeolithic period [3]. It wasn't until the 1800s that humans discovered how to fix the images they captured. Thus began our fascination with photographs, starting with the demand for portraiture from the middle classes of the industrial revolution, continuing with the arrival of the first mass-market cameras in the early 1900s and culminating with the estimated 4.7 billion digital photos taken each day in 2023 [4]. Whilst these images no longer require a substrate, most never becoming any more physical than the bits required to store them on a computer, the first photographs were commonly captured on glass. Glass presents a very intentional way of holding an image. It is an ancient and ubiquitous material but the interaction with light lends it a changing and contemporary aspect. It can be worked and transformed in a multitude of ways, and yet often the most arresting pieces are created by the light passing through rather than the form of the glass itself. From hand painted stained glass windows to silk screen printing techniques, glass as a canvas is found everywhere, from religious buildings to modern art museums. This thesis explores the methods of capturing photographic images on and in glass, comparing and contrasting their accessibility, longevity and visual impact.

1.1 The Silver Sunbeam

Following the work of Dr S. Donald Stookey at Corning in the 1940s, I set out to try to reproduce some recipes for photosensitive glass as a photographic medium for art. Having previous experience in the field and being sure to temper expectations given the small scale production methods available at VICARTE, my supervisor guided me to explore photography on glass simultaneously. With little knowledge of photography, besides snapping away on an analogue camera from time to time, the field was initially overwhelming and I fell down many rabbit holes. The first of which was Lippmann photography, as described in one of the following chapters. A gentle introduction to the history of photographic processes by Luís Pavão at Lupa and his generous showing of historic glass plates led me to focus on old photographs as art objects rather than the art of photography itself. This led me to the British artist Camilla Watson, and it was at her studio that I happened upon a copy of the book 'The Silver Sunbeam' by John Towler [5]. Written in 1864, it serves as a comprehensive guide to the art and science of sun-drawing, or photography, during the 19th century. The book covers various aspects of early photography techniques, including the chemistry of photographic processes, practical instructions for creating images using different methods, and discussions about the potential artistic and scientific applications of photography. It is a beautiful book not just for being instrumental in disseminating knowledge about photography in its early days, contributing to the development of the field, but for the old-worldly way in which it is written, describing photography as "one of the great wonders of the phenomena of created matter, so far eclipsing the seven vaunted wonders of the world, that these recede into dark nooks, like the wired dolls of an automatic puppet show". The final pages are filled with advertisements for photographic equipment and services (Figure 1) featuring beautiful typography and lithographs of old cameras and equipment. It came to be the central theme for this thesis, exploring the relationship between sunlight and silver in and on glass with an artistic application focused on images taken from the past and an appreciation for the old.



HENRY J. LEWIS,
152 CHATHAM STREET,
NEW-YORK,
Manufacturer of, and Wholesale and Retail Dealer in all kinds of
PHOTOGRAPHIC,
AMBROTYPE AND DAGUERREOTYPE
APPARATUS,
Made in the best and most workmanlike manner,
Among which may be enumerated:

Portrait Cameras,
View Cameras,
Carte de Visite Cameras,
Camera Stands,
Patent Elevating Camera Stands,
Lewis's Patent Camera Stands,
Lewis's Patent Glass Baths,
Lewis's Patent Vice,
Lewis's Patent Solid Glass-corner Holders,
Plate Holders,
Printing Frames,
Stereoscopic Boxes,
Columns,
Pedestals,
Glass-cleaning Vices,
Photographic Roller Presses for Cartes de Visite.
Photographic Roller Presses for 8 × 10 pictures; also larger sizes made to order.

And every thing in the line of Apparatus used in the business; also
WHOLESALE AND RETAIL DEALER IN ALL KINDS OF
CHEMICALS, STOCK, AND MATERIALS
USED FOR PHOTOGRAPHS OR AMBROTYPES.

Chemicals,
Tubes and Lenses,
Oval Frames,
Cases,
Mats,
Preservers,
Lewis and Holt's Collodion.
Lewis and Holt's Varnish,
Iron Plates,
Card Mounts,
Glass, all sizes.
Albumen and other Paper used for Photographic purposes.

P. S.—Operators and Amateurs in city or country are invited to call before purchasing elsewhere. Goods sent to all parts of the world. TERMS: CASH.

E. GORDON,
MANUFACTURER OF
PHOTOGRAPHIC APPARATUS,
AND DEALER IN ALL KINDS OF
STOCK AND MATERIALS,
172 CENTRE STREET, NEW-YORK.

CUT No. 1.

CUT No. 2.

CUT No. 3.

Cut No. 1 represents his new Patent Card Camera Box, for two or four lenses; holder does not move; sets on a carriage which moves so that there is no friction. Ground-glass is hung on hinges.

Cut No. 2 represents his new Vignette Printing Frame, made of tinned iron, having an oval cut out of the bottom; the most ingenious thing of the kind ever invented.

Cut No. 3 is a view of his Patent Printing Frame, of cast-iron; neat and strong. The demand for this new frame exceeds the supply; it is destined to supersede all others

Figure 1: Advertisements for photographic apparatus in the back pages of The Silver Sunbeam.

1.2 Photos on glass: Glass plate photography

1.2.1 History of photography on glass

The first crucial step in the development of the photographic process was Johann Heinrich Schulze's discovery in 1719 that silver nitrate was sensitive to light and that silver salts changed colour in sunlight [6]. It was then a matter of figuring out how to use this principle to fix an image. Photography on glass, also known as glass plate photography, played a crucial role in the early history of photography. The glass plate process allowed for the creation of high-quality images and was prevalent from the mid-19th century until the early 20th century. Over this time the field of photography advanced rapidly, a timeline of the most significant processes is outlined below [7] [8].

- Daguerreotype on Glass: The daguerreotype process, invented by Louis-Jacques-Mandé Daguerre in 1839, was the first practical form of photography. Initially, images were produced on silver-plated copper plates, but some photographers experimented with producing daguerreotypes on glass. The process involved coating a glass plate with a light-sensitive silver iodide layer and exposing it in a camera. The resulting image was a direct positive on glass, producing a sharp and detailed picture.

- Ambrotype: The ambrotype process, introduced in the 1850s, became a popular alternative to daguerreotypes. It involved creating a positive image on glass by placing a glass plate coated with a light-sensitive collodion emulsion into a camera, exposing it, and then developing the image. The final ambrotype was backed with a dark material or varnish to create a negative-positive effect, making the image appear as a positive when viewed against a dark background.

- Tintype (Ferrotypes): Tintypes, also known as ferrotypes, were a variation of the wet collodion process used for ambrotypes. Introduced in the 1850s, tintypes used a thin iron plate coated with a black lacquer or enamel, making them more affordable and durable than traditional glass plates. Tintypes became popular for portraiture, especially in travelling photo studios.

- Wet Plate Collodion: The wet plate collodion process, pioneered by Frederick Scott Archer in 1851, improved the image quality and reduced exposure times compared to earlier processes. In this method, a glass plate was coated with a collodion solution, sensitised in a silver nitrate bath, exposed while still wet, and then developed immediately. The wet plate collodion process offered greater sensitivity to light and enabled photographers to create multiple prints from a single negative.

- Dry Plate Process: In the 1870s, Richard L. Maddox introduced the dry plate process, which revolutionised glass plate photography. Dry plates were glass plates coated with a layer of gelatin containing light-sensitive silver halides. Unlike wet plate collodion, these plates could be prepared in advance and stored for later use, making the process more convenient for photographers. The dry plate process led to the widespread adoption of glass negatives, and it remained the dominant photographic method until the early 20th century.

- Autochrome: In 1907, the Lumière brothers introduced the Autochrome process, which was a pioneering colour photography technique based on glass plates. Autochromes used microscopic grains of potato starch dyed in red, green, and blue to create colour filters. These plates, when exposed and developed, produced stunning colour images, but they were complex and expensive to produce, leading to the development of other colour processes later on.

With the advent of flexible film photography, glass plate processes gradually declined, and by the early 20th century, they were mostly replaced by more convenient and accessible photographic methods. However, just as film photography has seen a renaissance today in the digital age, the interest in glass plate photography and traditional techniques seems to be on the rise. Whilst we continue to snap hundreds of identical photos on our smart phones that will never be looked at again, there is something beautiful about the creation of a physical object and the deliberate and selective act of preserving an image in such a way. It restores a value to the image that digital photos cannot possess. For photographers, the focus on composition and lighting and the long exposures necessary make the process of creating such photographs very considered and complex. For other artists, the act of transferring an existing image to a physical surface is an equally tactile and purposeful process.

1.2.2 Lippmann Process

In 1891, Gabriel Lippmann introduced a groundbreaking colour photography process based on interference phenomena, for which he won the Nobel prize in Physics [9]. Lippmann plates were created by exposing a glass plate coated with a light-sensitive silver halide emulsion through a reflecting prism [10]. The exposed plate captured both intensity and wavelength information of the light waves. During development, the silver halides were converted into tiny silver grains in proportion to the light intensity, creating a relief-like structure on the glass plate. When the developed Lippmann plate was illuminated from the front, light waves passed through the glass and were reflected back by the silver grains. As a result of the interference between the incoming and reflected waves, specific wavelengths of light were cancelled out, leading to the perception of colours. Lippmann plates were capable of producing exceptionally realistic and vivid colour images, but the process was complicated and technically demanding, making it impractical for widespread use.

Filipe Alves is one of the few people practising Lippmann photography in the world today and happens to have his studio in Lisbon. An architect by trade, he has been investigating and creating Lippmann plates since 2014. He coats the glass plates himself using an albumen emulsion. Rather than using a mercury mirror as Lippmann did it is possible to achieve the same effect safely with a thin layer of air [11]. The gelatin-air interface can act as a reflector of light.

The plate is inserted in a conventional dark slide with the emulsion side facing away from the camera lens. Inside the adapter, black velvet is attached in order to reduce scattered light. The exposure time is relatively long, making this process best suited to still life photography, and Alves often produces arrangements inspired by original Lippmann plates featuring flowers, food items and a taxidermied parrot. A curious quality of the albumen emulsion is that when you breathe on to the plate the albumen swells slightly with the heat and the colours are red-shifted because the distance between the gratings increases.

In order to best view the plates, specular surface reflection has to be separated from the image. This can be achieved by mounting a wedged glass prism (angle about 10°) onto the plate with an index-matching glue, usually Canada balsam. The images have to be observed in parallel diffuse light and shielded from all side light.

Alves has been making Lippmann plates for almost 10 years now and plans to write a book detailing his process and all he has learned. Amongst the beautiful slides he has produced (Figure 2) he also had many failures to show me, some of which had identifiable causes but many more failed for no discernible reason. Whilst it was a great pleasure to see Lippmann slides in real life it was obvious that this would not be a realistic avenue to explore further within the scope of this thesis. I do however hope to one day visit the Photo Elysée museum in Lausanne to see the collection of plates made by Lippmann himself.

Figure 2: A Lippmann plate made by Filipe Alves, mounted with a prism to aid viewing of the image [12].

1.2.3 Silver gelatin emulsions

Making emulsions from scratch is a technical process and these days there are many commercial emulsions available so for most artists making the emulsion themselves is not a worthwhile process when considering the time and costs involved and risk of failure. Whether homemade or shop-bought, the main constituents of the emulsions are the same, namely gelatin and silver halide crystals [13]. Gelatin is derived from animal collagen and acts as the binder or matrix for the silver halide crystals. It provides a stable and uniform medium to hold the light-sensitive crystals evenly distributed across the photographic surface. The gelatin also influences the emulsion's sensitivity, contrast, and tonal range and, if making the emulsion from scratch, it is important to use photography grade gelatin. Typically silver bromide is used as the photosensitive component or a combination of silver bromide and silver iodide. When exposed to light, the silver halide crystals undergo a photochemical reduction resulting in the formation of metallic silver. Finals such as stabilisers, hardeners and wetting agents may also be added to aid the stability, storage and coverage of the emulsion.

The basic process behind printmaking with silver gelatin emulsions is as follows [14]:

- Exposure: During exposure, a latent image is formed in the emulsion. The latent image consists of invisible clusters of metallic silver atoms, which are the result of the photo reduction reaction mentioned earlier. These clusters are too small to be visible at this stage.
- Development: The next step is to develop the latent image into a visible image. This is achieved through the chemical development process. The exposed photographic surface is immersed in a developing solution, typically containing a reducing agent like hydroquinone or metol. The reducing agent reacts with the exposed silver halide crystals, converting them into black metallic silver. This amplifies the density of the latent image and makes it visible.
- Fixing: After development, unexposed and undeveloped silver halide crystals remain in the emulsion. To prevent these crystals from causing further darkening of the image, the print is immersed in a fixing solution. The fixing solution dissolves and removes the unexposed silver halide, leaving behind the stable metallic silver image.
- Washing and Drying: After fixing, the print is thoroughly washed to remove any remaining traces of chemicals. Washing is essential to ensure the print's archival quality and prevent fading or deterioration over time. Once washed, the print is dried, completing the printmaking process.

1.2.4 Artists working with photographic emulsions and glass

Mary van Cline has been working with glass since 1979 and is considered a pioneer in the Studio Glass movement having invented new processes of glass working [15]. In the 80's she worked with Kodak to develop a positive photo emulsion to be coated onto glass. Her sculptures (Figure 3) often combine hot and cold working techniques, cast glass elements and photographic imagery. Time is a central theme in her pieces, which also often feature symbols and architectural elements, and possess a sense of serenity. The photographic elements, usually figures and dramatic natural landscapes, are often layered to create surreal associations whilst conveying a sense of time for healing and wholeness. Her most recent work demonstrates spaciousness by including reflecting planes and spheres that invite a participatory response from the viewer. It asks us "to be, for a little while, in another space where time does not just stand still - it does not exist at all".

Juliette Leperlier is the great granddaughter of François Décorchemont, famous for developing the pâte de verre technique. She combines her family history in glass with a formal education in sculpture and photography. In her Naiades series (Figure 4) the photograph is a woman's body that appears on a cast glass drape, playing with the optical properties of the glass so that it dresses the naked body, or deforms it, reflects it, magnifies it, in order to create a new 3-dimensional image. The glass sculpture is not just a support for the image but in dialogue with it. Time is again a central theme, the fluidity and movement of the glass drape a paradox to the stillness of the photo, the sculpture as a whole designed to mirror the amorphous nature of glass, "forces in movement frozen into time and space" [16].

Lynn Bierbaum is a photographer and glass artist who began pursuing historical photography techniques in 2016. Her ambrotypes on blown glass (Figure 5) are representational portraits of friends and family capturing memories shared with them. Whilst she began by photographing on sheet glass in the back of a medium format camera her process now takes place exclusively

Figure 3: "Cycles of the Relationship of Time", Mary Van Cline, 2000. Photosensitised glass, pate de verre, bronze patina.

Figure 4: Naiades VI, Juliette Leperlier, 2019. Silver photography on cast glass.

in the darkroom. She prints her photos digitally onto a transparent medium to create a positive and then places that on top of the light-sensitised wet-plate collodion emulsion and uses a photographic enlarger light to expose the image.

1.3 Colour in glass due to silver

Whilst silver halides in photographic gelatin emulsions produce a greyscale image through the formation of visible metallic silver, when held inside the glass matrix silver atoms can cause colouration through a different mechanism.

1.3.1 Colour producing mechanism of plasmon resonance

Noble metals have been used to colour glass for centuries [17]. The colour arises from the thermal chemical reduction of the noble metal ions and the agglomeration of these atoms to form metal nanoparticles. The nanoparticles interact with light and exhibit selective absorption, originating from surface plasma resonance oscillations of the free electrons confined in the nanoparticles [18]. The position and width of the absorption band are dependent on the size and shape of the particles formed; one peak usually signifies a distribution of spherical particles, whereas multiple peaks suggest either non-spherical particles or a multimodal distribution of spherical particles of different dimensions [19]. In the case of silver nanoparticles the band usually has a maximum

Figure 5: “Sat and Smoked a Cigarette”, Lynn Bierbaum, 2020. Ambrotype on blown glass.

at around 410 nm [20].

1.3.2 Silver stains

During the early fourteenth century, the technique of yellow silver staining was developed and initially documented by Antoine de Pise. This method involved applying a diluted silver salt to the surface of the glass, which was then subjected to firing at temperatures ranging from 500 to 650°C [21]. During the firing process, silver ions penetrated the glass through an ion exchange mechanism with potassium or sodium ions [22]. Subsequently, the silver cations underwent reduction to form metallic state nanoparticles, which aggregated and formed colloidal distributions of sub-microscopic particles ranging in size from 10 to 200 nm [23]. The colour of the glass may be from pale yellow to dark amber and is impacted by the firing time and temperature and the composition of the base glass.

1.4 Photos in glass: Photosensitive glass

The parallels between silver gelatin emulsions and photosensitive glass with silver as the photosensitive metal make them interesting areas to explore together. Photosensitive glasses are those which change colour through a process of exposure to a strong light source and subsequent heat treatment. Upon exposure, the glass develops an invisible ‘latent image’ which gradually develops a colour when heated at a suitable development temperature. The process is irreversible and the image is as permanent as the glass object itself. Photosensitive glass was first developed in 1937 by S. Donald Stookey at Corning Glass Works [24]. Following Dalton’s discovery that exposing colourless copper ruby glass to UV radiation before heat treatment caused the colour to ‘warm in’ more readily [25], Stookey experimented with different compositions to enhance the effect. After succeeding in producing a copper photosensitive glass [26] he continued his research to develop a superior gold glass with the addition of optical sensitisers [27]. It was also discovered that the metal particles can act as nuclei for forming non-metallic crystals in certain glass compositions, resulting in opal photosensitive glass [28]. Stookey’s colleague Armistead patented silver photosensitive glasses at the same time [29].

1.4.1 Composition

- Base glass: Most silicate glass compositions are suitable as long as they don't contain a large quantity of lead or other strong UV absorbing components. Borate and phosphate glasses have been found to be unsuitable as the colour developed spontaneously without exposure.
- Photosensitive metals: Gold, silver and copper are the most commonly used and can also be used in combination. Gold requires the addition of an optical sensitiser whereas silver and copper can act as their own sensitisers.
- Thermo-reducing agents: polyvalent ions, usually tin or antimony, increase the tendency of the colour to 'warm in' however in excess they cause spontaneous colouration. Thermo-reducing agents reduce the UV exposure required but also decrease the contrast of the developed image.
- Optical sensitisers: absorb the activating radiation sensitising the metal to new wavelengths. Cerium is the most important example although silver and copper compounds themselves may perform the role.

1.4.2 Theory

Unlike conventional glasses coloured with metallic nanoparticles, photosensitive glasses contain little or no thermo-reducing agents and so remain colourless on heating because the metal compounds are in a soluble oxidised state. At room temperature the metallic ions are homogeneously distributed in the rigid glass matrix and the electron mobility is limited to within a few atomic diameters. The first step in the processing of photosensitive glasses is the creation of the 'latent image'. The optical sensitisers in the glass emit photoelectrons when exposed to UV radiation. Because of the rigidity of the glass matrix at room temperature, the electrons are confined to trapping sites adjacent to the parent ion, either metal ions or imperfections in the glass network and hence the reduction of the metal ions by the photoelectrons cannot take place. The image remains invisible until the glass is subjected to a development heat treatment at a temperature between the transition and softening point of the glass. The development consists of two stages; reduction of the metal ions through capture of the photoelectrons and growth of the metallic nanoparticles through the agglomerating of metal atoms. The development time and temperature hence affects the final size of the nanoparticles and thus the colour of the image. The basic mechanism can be represented by the following steps [24]:

$$A^x + h\nu \rightleftharpoons A^{x+1} + e^* \tag{1.1}$$

where A^x is a light-absorbing ion A of valence x, $h\nu$ is a quantum of absorbed energy and e^* is an excited photoelectron.

$$M^y + ye^* \rightleftharpoons (M^0)^* \longrightarrow M^0 + * \tag{1.2}$$

where M^y is a metal ion of valence y, M^0 is the metal atom and $*$ is excess energy liberated as heat or light. In the case of silver acting as its own sensitiser the overall reaction can be written as

$$2\,\mathrm{Ag}^+ + h\nu \longrightarrow \mathrm{Ag}^{++} + \mathrm{Ag}^0 + * \tag{1.3}$$

The atoms then agglomerate to form nanoparticles as so

$$\mathrm{n}(\mathrm{Ag}^0) + \mathrm{heat} \longrightarrow \mathrm{particle} \tag{1.4}$$

1.4.3 Comparison with Silver-Halide photography

The mechanism is analogous to that of silver halide photography. The notable difference being that the glass is rigid at room temperature preventing the photosensitive components from moving whereas in silver halide emulsions the ions and electrons are free to move. Another difference is that whilst the resolution of silver halide photography is dependent upon the grain size of the emulsion (varying from 10 nm for ultra-fine-grain holographic emulsions to 2500 nm for medical X-ray emulsions [30]), the photosensitive glass image is essentially grainless which combined with the turbidity of the glass itself allows for great detail to be captured in the image.

1.4.4 Photochromic glass

Photochromic glass, another discovery of Armistead and Stookey at Corning, changes colour reversibly when exposed to light [31]. Used commercially in sunglasses lenses, the glass darkens in sunlight and almost instantaneously fades in the dark. The fundamental process closely resembles the photolytic dissociation seen in silver-halide photography, where silver halides break down into silver and halogen ions when exposed to light. The distinction lies in the irreversibility of the photographic process, resulting in the creation of enduring silver particles and a permanent photographic image. In contrast, the photochromic glass process is reversible. This reversibility signifies that no reaction products are lost from the reaction zone, and both silver and halogen can revert to their initial states upon the removal of light. This metastability is the fundamental difference between photochromic and photosensitive glass. In photosensitive glasses the silver ions are dissolved in the glass matrix rather than in silver halide crystals and the photoelectrons are held at stable trapping sites resulting in the permanent precipitate of colloidal silver when subjected to heat treatment. In photochromic glasses the species formed by irradiation are completely unstable and recombine to form silver halide particles when the light source is removed, hence there is no colloidal silver precipitate when the glass is heated.

1.4.5 Photosensitive glass use in Studio Glass

Stookey discovered photosensitive glass in 1937 however the discovery was not made public until 10 years later. This was because the military believed the glass could be used to send secret messages during WWII which could only be read by heating the glass, a kind of invisible ink [32]. Whilst photosensitive opal glass was made available commercially by Corning in the form of FotaLite it languished in obscurity until the 1990s when Newzealander John Croucher started experimenting with photosensitive recipes to make the glass compatible with that used by modern artists. His company, Gaffer Glass, produced a photosensitive ruby glass with a COE of 96 although this is no longer in production [33]. Today photosensitive glass is still not a commonly used material among glass artists, with only a few artists known to be using it in their work. Luke Jacomb, the son of the aforementioned John Croucher, is one such artist. He combines traditional Maori and Polynesisan motifs with strong colours alongside traditional venetian glassworking techniques to make his pieces (Figure 6). John Penman is another artist using photosensitive glass. He blows glass objects with photosensitive opal glass and a colour overlay and uses the shadows of natural materials such as plants and feathers from his native New Zealand to create the imagery (Figure 7) [34]. In a disparity with the work of the photographic artists previously mentioned in Section 1.2.4, the imagery used by both of these artists is much simpler and arguably decorative rather than being the central to the piece. The more primitive shadow-making techniques employed suggest a greater focus on the form of the glass piece independent of the imagery and also hint at the limitations of photosensitive glass as a photographic medium.

Figure 6: Taha Trio by Luke Jacomb, 2005.

Figure 7: Huru Platter 1 by John Penman, photosensitive glass with colour overlay. The imagery is created by the shadow of bird feathers.

1.4.6 Current state of the research and other applications

Described upon its discovery as a new photographic medium, photosensitive glass, in particular glass ceramics, has since found many more applications. By subjecting photosensitive glass to a further cycle of exposure and heat treatment it is possible to produce a glass-ceramic. The photosensitively formed metal nanoparticles can act as nuclei for the formation and growth of a variety of crystalline nanophases. Corning's FotaLite is an example in which the crystalline phase is NaF, producing an opal photosensitive glass. Stookey also discovered that with the addition of a thermally reducing step Ag nanoparticles can be made to nucleate on the tip of the NaF crystals. The length of the Ag deposit alters the spectral position of the plasmon resonance absorption peak and thus it is possible to produce fully polychromatic glass by controlling the Ag formation [35]. Fotoform is another example of a photosensitive glass-ceramic material trademarked by Corning, in this case, a Li-metasilicate phase is produced.

Despite some applications in architecture, most notably the facade of the United Nations Headquarters in New York [36], the most common use is in technology and industry. Photosensitive glass can be used to make microlens arrays [37], which have found applications in the autofocus mechanisms of cameras, scanner lens bars and optical fibre interconnects, among others [38]. In photosensitive glass ceramics the crystalline opal phase that is produced by exposure and heat treatment is more dense than the unexposed glass. When heated to above the softening point of the unexposed glass the exposed region can squeeze the unexposed region above the surface of the glass. If a circular mask is used, the soft glass will form a spherical surface because of surface tension.

Another property of these glass ceramics is that the opal crystalline region is more soluble in acid than the unexposed base glass. Placing the glass in dilute hydrofluoric acid leaches out the opal regions leaving behind a complex glass part of high precision for use as spacers in photomultiplier tubes, cell sheets in gas-discharge displays, charge plates and nozzles in ink-jet printers and more recently direct methanol fuel cells (DMFCs) [39]. Smith and Trotter were able to form electrical circuitry on glass by immersing a sample with an opal pattern in a molten silver bath containing silver ions and heating it in a hydrogen atmosphere [40]. A conducting silver film formed on the opal regions whereas the film that forms on the glassy regions remains nonconducting.

Fluorescent photosensitive glass ceramics have found potential applications as long lifetime media for holographic data storage. Pavel et al developed fluorescent glasses doped with Eu, Ce, and Sm, stable up to 400°C [41]. The recording process used microsecond exposure with lasers and subsequent heat treatment to generate a refractive index modulation, or grating, due to the difference in refractive index between the crystalline and unexposed regions, that recreates the writing interference pattern permanently in the glass.

1.5 Objectives

We will begin by exploring the traditional idea of photography on glass, focusing on the practical process of silver gelatin emulsion on glass. Through producing a series of prints from old photographic slides we investigate the effects of different preparation processes and exposures as well as common defects and their causes. From here we move to photographic images in glass, keeping the mechanism of photo-reduction of silver as a linking theme, with the production of photosensitive glasses. We explore the optical and thermal properties of the glasses produced and the effect of the exposure, development temperature and halide content on the formation of silver nanoparticles and thus the colouration of the glass. The ultimate goal is to combine these two interpretations of glass photography and explore the possibilities of using them together in art.

2 Silver Gelatin emulsion on glass - an overview of the practical process

Camilla Watson is a British artist living and working in Lisbon for the last 16 years. At her studio in Almada, she exposes photographic images onto a variety of materials. Her process is that of an artist rather than a scientist, but due to the community oriented nature of her work and the placement of pieces outside, on walls in the areas her subjects live, the longevity of the pieces cannot be ignored. She adjusts her process depending on the surface being printed onto, be it marble, plaster, wood or other materials, and experiments with suitable varnishes to protect the piece against the elements. She was generous enough to guide me through the process of printing on glass with silver gelatin emulsion.

Figure 8: An example of Camilla Watson's work, 'O tributo' 2009. A permanent street exhibit in the Beco das Farinhas, Mouraria, Lisbon.

2.1 Silver Gelatin emulsion on glass preparation

2.1.1 Producing negatives

The photos to be printed on the glass plates were from Kodachrome slides taken in Portugal in 1967 by my grandfather's sister, Sissy, holidaying with two girlfriends. Rediscovered when my parents were sorting through old boxes in preparation for a house move, the now familiar locations in the photos and the family connection gave a sense of purpose to creating the glass prints. Three of the slides can be seen in Figure 9.

Figure 9: Three of the Kodachrome slides belonging to my great aunt.

In order to print onto glass, black and white negatives were needed. The slides were scanned and black and white prints were produced digitally. Whilst I would have preferred to keep the process entirely analogue, the original negatives were likely lost long ago and so this was a compromise to use the slides. From these prints, 4 images were selected as having suitable contrast levels. A Nikon film camera mounted in a copy stand was used to photograph the prints on 100 ASA film to produce sharp, low grain negatives. The setup can be seen in Figure 10. For each print, three photos were taken at different apertures to allow a selection of the negative with the best contrast for printing onto glass.

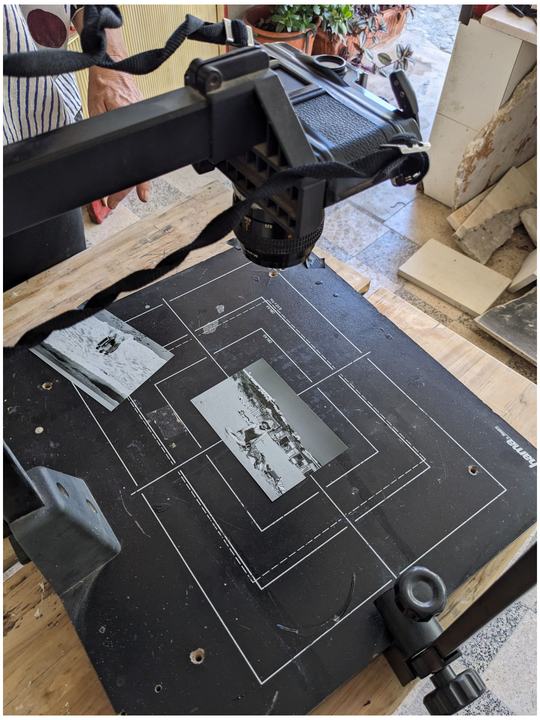


Figure 10: Copy stand used to photograph the black and white images to produce the negatives.

2.1.2 Preparing the glass

Six 20×30 cm float glass plates of 3mm thickness were used. The glass was lightly sanded by hand and then a water based varnish applied with a small hand roller. The varnish was left to dry for a week. The purpose of preparing the glass in this way is to aid adhesion of the emulsion to the glass and prevent frilling. One of the plates was left unvarnished to allow for comparison. The plates were cleaned with ethanol. A subbing layer of gelatin hardened with chrome alum was applied by pouring a small amount onto the glass plate and spreading by hand then removing the excess with a paper towel to leave a thin damp layer with as few bubbles as possible. Again this is to aid adhesion of the emulsion. The plates were left to dry overnight.

As this part of the project was focussed more towards art than science, it was decided not to delve into the world of making photographic emulsions from scratch, indeed that could be the subject of an entire thesis by itself. A commercial emulsion specifically intended for exposing unconventional materials and surfaces was used: Rollei Black Magic (RBM2). RBM2 is a fixed-grade liquid photo emulsion characterised by high edge sharpness and a cold image tone due to its silver bromide [42]. The following process took place in a dark room under a safe light. The emulsion in its solid state was cut into small pieces and put into light safe film canisters and placed in a water bath at 45°C for 45 minutes. When the emulsion was liquid a few drops of hardener was added followed by a wetting agent to aid the coverage of the plates. The emulsion was mixed and decanted into a shallow dish over a water bath. The glass plates were warmed gently with a hair dryer to avoid the emulsion dragging, with care being taken not to melt the subbing layer. A soft natural bristle brush was also heated and then used to spread a small amount of emulsion across the plate starting from the centre, working first vertically and then horizontally across and finally feathering the surface to ensure complete coverage. The plate was then placed in a light-safe cupboard and the process repeated for the other plates. Intermittently test paper sheets were also coated. The process had to be done quickly as the emulsion cools and drags more. Once prepared, the emulsion cannot be reused, so preparing an appropriate quantity and having extra surfaces prepared for coating is good practice to avoid wastage. On the day we were coating the glass plates, Camilla was able to use the remaining emulsion to coat a piece of wood to continue her community project by printing a photo of a local Ginja bar owner. The plates were left to dry overnight in the light-safe cupboard.

2.1.3 Exposure and development

The chosen negative was placed in the enlarger (Figure 11) and the image resized and focused on a piece of card the same size as the glass.

Figure 11: Enlarger for exposing the plates.

Figure 12: One of the paper exposure tests made prior to exposing the glass.

With the lamp turned off, a test piece of emulsion-coated paper was placed on the card and exposed for 5 seconds with an aperture of f/5.6. Then a section of the paper was covered with a scrap piece of card and the exposure repeated. This was further repeated once more to produce regions of 5, 10 and 15 second exposure. By selecting an area of the image with detail of interest this allows us to choose an appropriate exposure time. A resulting print demonstrating the effect, can be seen in Figure 12. The test paper was placed in the developer for 1 minute at which point the image appears. It was removed with tongs, the excess allowed to drip off, and then placed in the stop bath for 15 seconds before being moved to the fixer. The setup can be seen in Figure 13. The lights could then be turned on to inspect the result and decide on the most appropriate exposure. With the lights again turned off the glass plate was removed from the light-safe cupboard and placed on the card under the enlarger. The glass was covered with a light-safe sheet and the image refocused to account for the thickness of the glass. The glass plate was then exposed and processed in the same way as the test paper, taking care to only hold the plate by the edges so as not to damage the image. The plates were then placed vertically in a water tank to wash for at least 30 minutes (Figure 14). After washing the plates were stood vertically for a short time to allow the water to drip off and then stored horizontally on a drying rack as shown in Figure 15.

Figure 13: From right to left: developer, stop bath and fixer trays.

2.2 Results and discussion

We were able to produce six glass prints allowing for comparison between different preparation methods and exposure times and evaluation of the suitability of different image choices to the process. The exposure time and aperture for each plate along with observations are given in Table 1. Figure 16 demonstrates nicely the vast variation in results that can be achieved. A

Table 1: Details of the glass plates.

Image	Exposure/s	Aperture	Observations
Sissy	11	f/5.6	Low contrast image, good detail, unvarnished, some artefacts
Sissy	22	f/5.6	Dark, contrasty image, visible brush marks and other defects
3 in Atlantic	30	f/4	Good contrast, bubbles
Our hut	16	f/4	Low contrast image
Fisherwoman	14	f/4	Low contrast, artefacts causing a lot of distortion to the image
Fisherwoman	18	f/4	Dark, good detail, some gaps in emulsion coverage

Figure 14: Wash box with running water.

Figure 15: Once the excess water has dripped off the plates are left to dry on the drying rack below the bench.

shorter exposure time in Figure 16a gives a much lighter image, losing a lot of contrast in the foreground. This plate was left unvarnished and still the emulsion adheres well although it may be in the longevity of the image that it suffers. By comparison the plate in Figure 16a underwent double the exposure time and has much more contrast. This does come with the consequence that defects in the plate are more visible. Arguably neither is better than the other; they both show different effects which can be manipulated by the artist to achieve the desired style.

'Roughing up' the glass with sandpaper was a quick and easy way to improve the adhesion of the emulsion; however the scratch marks become more evident after development of the image. Whilst the effect is not unpleasant, giving the plates an old appearance fitting with the subject matter of the photos, it could be that sanding the glass more uniformly, for example with sandblasting, gives less visible impact on the final image.

Coating plates is without doubt a process that takes much practice to perfect, it is fair to say that glass is a very unforgiving surface. Several defects can be seen on the plates, as seen in Figure 17. The visible streaks seen in Figure 17a are likely a result of the emulsion and glass plate not being warm enough when coating, this was probably one of the last plates to be prepared. The artefacts in Figure 17b appear to be fibres from the brush used to apply the

(a) 11s exposure, unvarnished plate.

(b) 22s exposure, varnished plate.

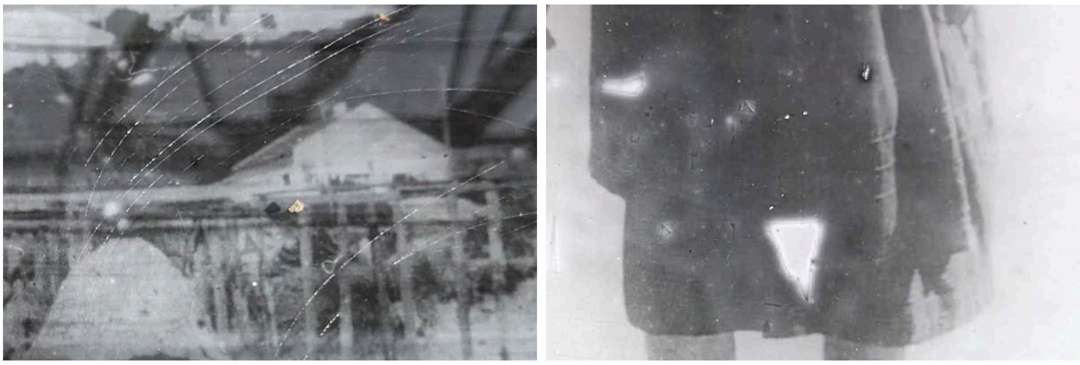
Figure 16: Comparison of different exposure times and effects produced.

emulsion. The defects in Figures 17d and 17e are the result of poor application of the emulsion which with repeated practice of the process should hopefully be avoided. Finally in Figure 17f we can see the delicate nature of the emulsion layer: in transferring the plate from the developer to the stop bath a slither of the emulsion lifted off leaving the blank squiggle seen in the image.

The results of the process could be improved by paying greater attention to the cleaning and preparation of the glass in order to reduce the presence of artefacts in the emulsion. A different application process, for example pouring the emulsion on to the glass and tipping it to coat the surface, would likely give a more uniform layer, however this has the disadvantage of requiring a larger quantity of emulsion to work with and thus more wastage. The visible brush marks also don't necessarily have a negative effect on the piece depending on the desired outcome. Thus far the process has only been performed with rectangular sheets of float glass however it is also possible to coat more irregular shapes and surfaces, and it is my intention to explore this later in the project.

The creation of these glass prints from such small slides that had lain hidden for so long brought me great joy. Whilst the colours are lost, discovering the details that were indiscernible on such a small scale was a delightful part of the process. Certainly the transformation to such a solid object imbues the images with a significance that, as slides in a box amongst many, they didn't previously have.

(a) Streaks **(b)** Artefacts



(c) Scratches **(d)** Poor coverage

(e) Bubbles **(f)** Lifting of emulsion

Figure 17: Examples of various defects seen across the plates.

3 Preliminary synthesis and characterisation of photosensitive glasses

As a jumping off point for the scientific research part of this thesis some preliminary investigations were carried out with small batches of glass produced from photosensitive glass recipes in the literature. This was an important step in directing further investigations by experimenting with light sources and establishing appropriate annealing and development temperatures.

3.1 Photosensitive glasses

Three recipes for photosensitive silver glass were chosen to reproduce. The first two recipes were taken from Armistead's patent [29], referenced in Stookey's seminal paper on photosensitive glass [24]. The third, taken from Borrelli's 2016 book [43], is referred to as a 'typical photosensitive glass composition'. From here on the samples will be referred to as A3 and A4, based on batches 3 and 4 respectively from Armistead's patent, and B taken from Borrelli's book. In all three cases carbonates were used in place of the oxides. Due to the selection of compounds available to us in the lab it was necessary to adapt the recipe for A3, replacing AgCl with $AgSO_4$ and Na_2SiF_6 with NaF. The quantity of the raw materials for each glass is given in Table 2.

Table 2: Glass composition wt%

Component	B	A3	A4
SiO_2	75.23	70.24	71.49
Na_2O	1.22	13.22	15.89
K_2O	2.37	-	-
Li_2O	9.45	-	-
Al_2O_3	9.82	-	-
ZnO	1.60	9.80	12.16
CeO_2	0.01	0.03	-
Ag_2SO_4	-	0.11	0.26
Ag	0.08	-	-
Na_2NO_3	-	5.27	-
NaF	-	1.32	-
Sb_2O_3	0.02	-	-
SnO_2	-	-	0.20

3.1.1 Synthesis and characterisation

The different raw materials were weighed out. When all the components had been added, the mixture was shaken by hand for 10 minutes to ensure a homogenous mixture. The mixture was transferred to an alumina crucible and heated in a furnace to 1300°C with a ramp of 6.5°C/min. The glass was kept at this temperature for 3 hours to allow volatilisation of the gases in the melt and to reach a good homogenisation. Finally, the temperature was increased to 1400°C to allow the glass to be poured more easily out of the crucible onto a steel plate, by decreasing the material viscosity. The samples were annealed for 1 hour at 500°C with a ramp of 240°C/min.

Samples of approximate dimensions 30×10×5mm were cut from each of the glasses using a diamond saw and polished with progressively finer grained discs on the disc sander in order to obtain two parallel faces. UV-Vis absorption spectroscopy was performed for each of the samples by using an AvaSpec-2048-SPU spectrophotometer with an AvaLight-HAL Tungsten Halogen as a light source (Avantes). The AvaSoft software controlled the acquisition of the spectra in the 200-1100 nm range.

A SPEX ®Fluorolog®-3 HORIBA spectrofluorometer (Horiba Scientific, Palaiseau, France), model FL3-22 was used to measure the emission spectra of the samples. The samples were excited at 370 nm and the emission in the range 390-800 nm was recorded with 1 nm increments with an integration time of 0.1s. A 380 nm long pass filter was used to avoid peaks from second order diffraction. The slit width was set at 4 nm to maximise the intensity of the measurements without saturating the detector.

A second set of samples of appropriate dimensions to fit in the dilatometer sample carrier were cut (length 27mm, diameter 5mm). The rods were polished to obtain parallel ends to ensure good contact with the dilatometer push rod. The dilatometry was then performed using a Netzsch DIL 402 PC dilatometer with heating at a rate of 5°C per minute until the dilatometric softening point was reached.

3.2 Photosensitive glasses - Results and discussion

Samples obtained from synthesis can be observed in Figure 26a. Sample A3 appears clear and colourless with some small bubbles visible. Sample A4 is a clear glass with a very pale yellow-green colour and some bubbles. Sample B is clear and colourless but with a large number of bubbles. In all three cases, synthesis at a higher temperature for a longer period of time would likely allow a higher amount of gas release, giving rise to glasses with fewer bubbles.

3.2.1 Thermal and optical properties

The expansion curves for each sample are shown in Figure 18.

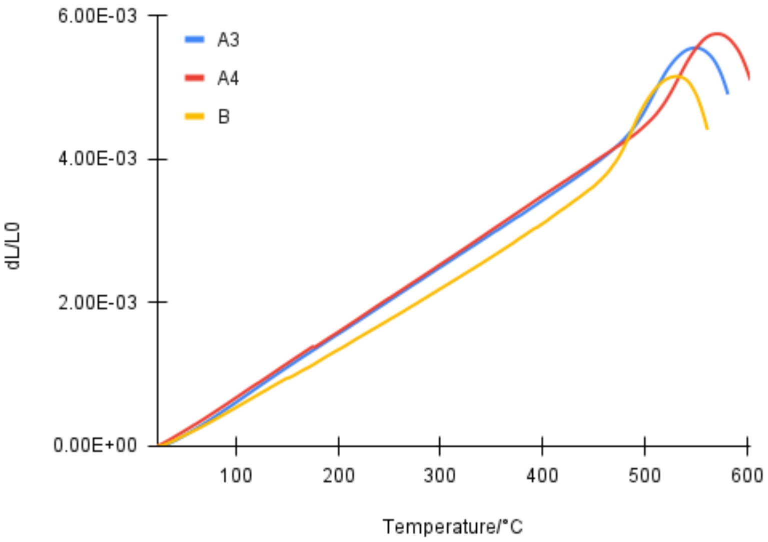


Figure 18: Thermal expansion curves for the three samples.

The dilatometric softening temperature, the temperature at which the glass visibly deforms, is easily identified as the peak of the curve. The glass transformation temperature, that is the onset of viscoelastic behaviour, can be extracted as the intercept of the extrapolated slopes in the elastic and melt regions. The measurements obtained for each sample are given in Table 3.

Table 3: The glass transition temperature, T_g, softening temperature, T_s, and coefficient of thermal expansion, CTE, obtained for each sample.

Glass	T_g (°C)	T_s (°C)	CTE (10^{-6} °C^{-1})
A3	476	543	9.4
A4	512	571	9.5
B	461	524	8.9

The glass transition temperatures for batches A3 and B are notably lower than for batch A4. Future batches of these glasses will therefore be annealed at a lower temperature after synthesis and quenching than the A4 glass. After undergoing the dilatometry heat treatment samples A3 and B obtained a pale yellow colour and sample A4 turned brown, as shown in Figure 19.

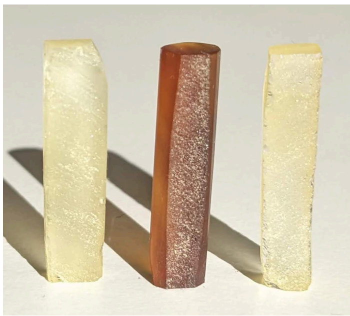


Figure 19: The unpolished samples after undergoing dilatometry. From left: A3, A4, B.

This could be explained by the slow heating rate allowing the agglomeration of silver atoms and the formation of silver nanoparticles.

Figure 20 shows the absorbance spectra of the three samples.

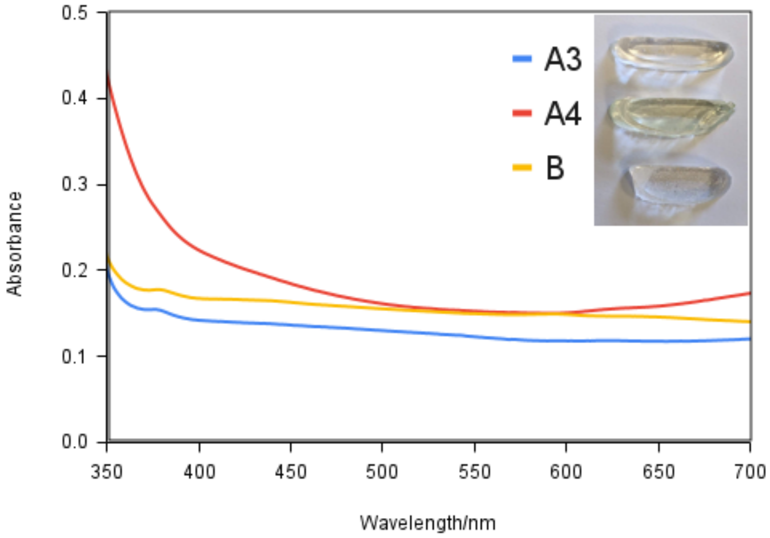


Figure 20: UV-Vis absorbance spectra of the samples prior to exposure and heat treatment.

The absorption below 350nm can be attributed to the glass itself. No clear absorption peaks are seen however A4 absorbs more strongly between 350-450nm than the other two samples hence the pale yellow-green colour.

When observed under UV light, sample A4 shows strong visible luminescence. Samples A3 and B show no visible luminescence. All three are shown in Figure 21. The emission spectra in Figure 22 support this observation; A4 has a broad emission band across the visible.

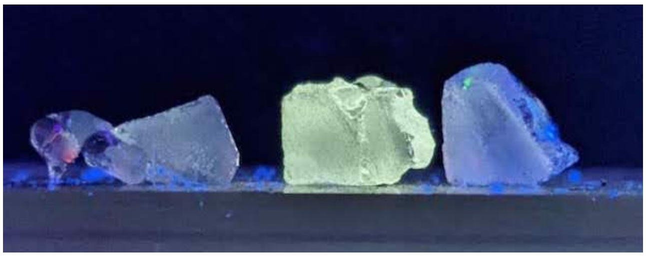


Figure 21: From left to right, samples A3, A4 and B under UV light.

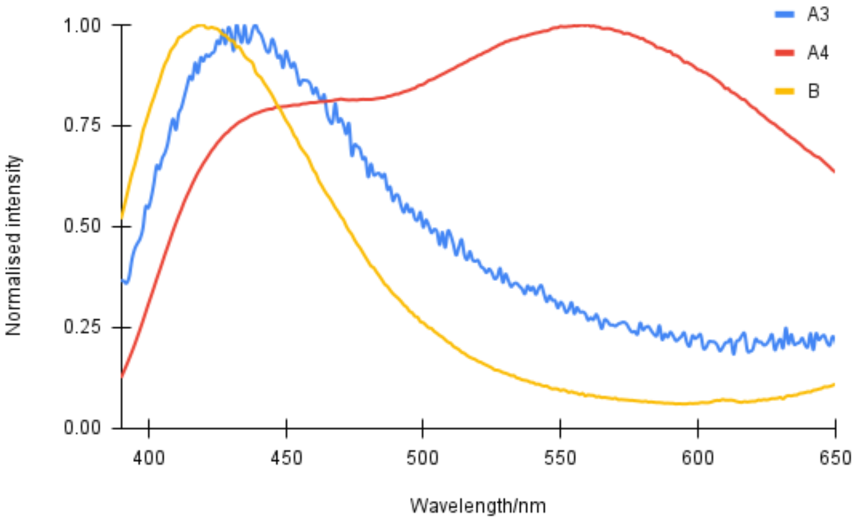


Figure 22: Emission spectra of the samples with excitation at 370nm, normalised to the maximum peak intensity.

This can be attributed to small clusters of silver ions formed during the annealing of the sample [44] [45]. The amount of silver in the raw material mixture is considerably higher in sample A4 than in the other two glasses which may explain why they show no visible luminescence as no clusters of silver ions are formed.

3.3 Exposure and development

The remainder of the glass was cut into small, irregular samples of approximately 1 cm^3. For each glass, one sample was left outside in the sun for three days (the weather being somewhat overcast, the exposure time was maximised). A second sample was partially wrapped in tin foil to act as a mask and exposed with a UV lamp of wavelength 360 nm at a distance of 15 cm for 10 minutes. A third sample was subjected to a shot from a 355 nm laser. Finally a fourth sample was half masked with black electrical tape and exposed to 330 nm wavelength radiation inside a spectrofluorometer for 75 seconds. The development heating should take place at a temperature between the glass transition temperature and the softening temperature; the colour is known to develop faster closer to the softening temperature [24]. Samples A3 and B were found to have similar glass transition temperatures so they were heated simultaneously to 500°C for 1 hour with a ramp of 360°C/h. The A4 samples were subjected to a higher dwell temperature of 535°C with the same heating profile. The A3 samples were also later subjected to a second heat treatment at the higher temperature to investigate if this would have any further effect on the colouration. Before the development heat treatment none of the samples exhibited any colour change: A3 and B remained colourless and A4 was a very pale yellow colour. All of the samples after the heat treatment can be seen in Figure 23.

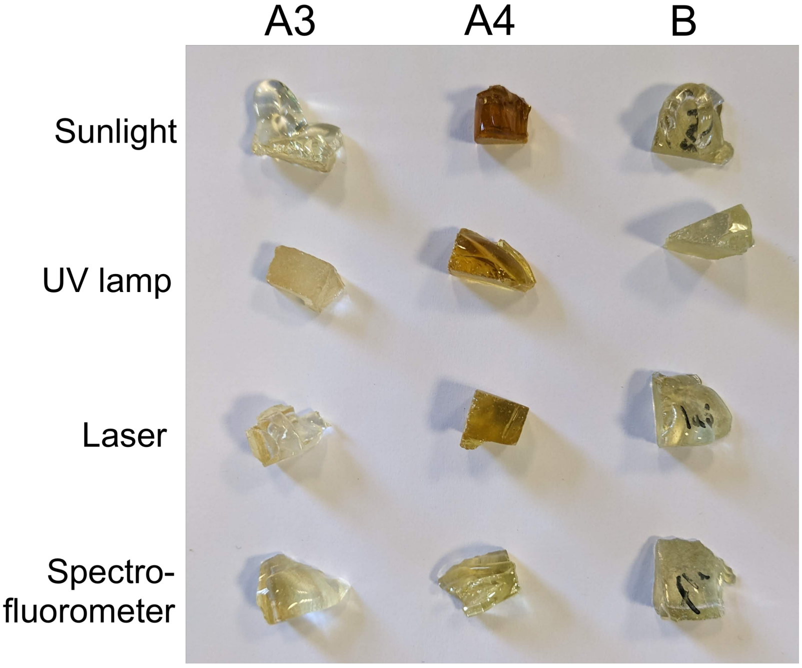


Figure 23: The samples after undergoing the development heat treatment.

The glass B samples have a very pale yellow colour which is the same for all the exposure sources. The A3 samples are also pale yellow and show some visible variation in colour intensity. Notably the sample exposed in the fluorometer at 330 nm appears colourless on one end progressing to pale yellow at the other, as seen in Figure 24.

Figure 24: The A3 sample exposed to 330nm radiation, after undergoing the first development heat treatment (500°C).

After the second heat treatment at a higher temperature of 535°C, no visible difference was seen in the A3 samples. The A4 samples show considerable variation in colour after development, varying from pale yellow to dark amber, as shown in Figure 25. We can attribute this difference in colour to the different exposure treatments [46]; it would appear that the photo-reduction of silver was highest in the sunlight-exposed sample. The irregularity of the shape and small size of

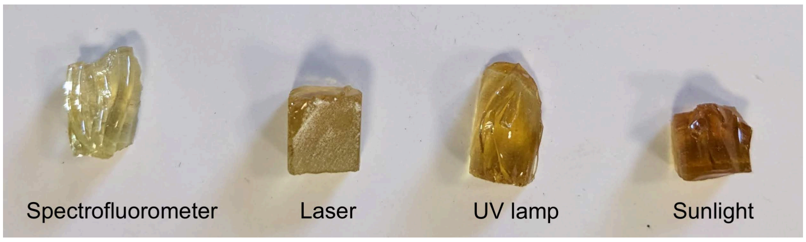
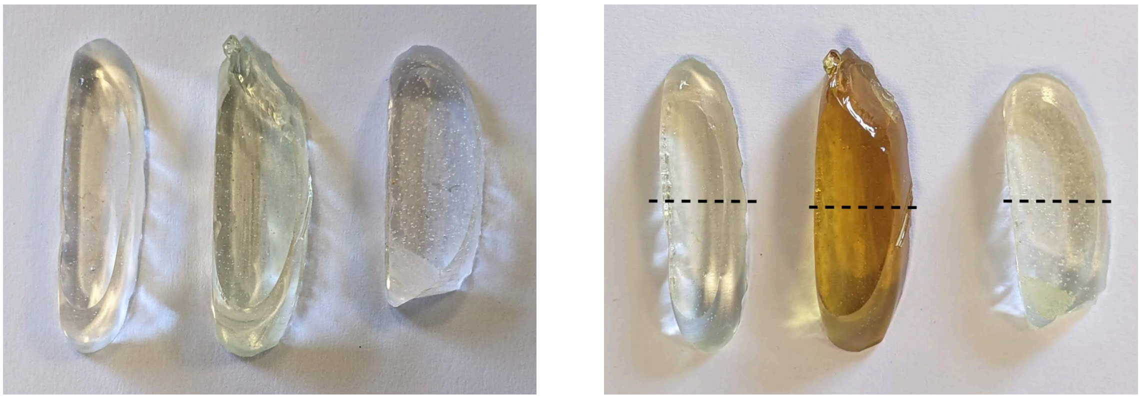


Figure 25: The A4 samples after undergoing the development heat treatment at 535°C.

the samples and the lack of polishing make it difficult to be certain of any effects of the masking. After the development heat treatment sample A4 no longer displayed visible luminescence.

The larger, polished samples produced for absorption measurements were masked with black electrical tape and foil over half of the sample length and left in the sunlight for a period of two days. Sunlight was chosen as the exposure source because the A4 sample exposed to sunlight produced the darkest yellow, and because sunlight is the most accessible source of radiation. The masks were removed and the samples subjected to a development heat treatment of 1 hour at 530°C with a 360°C/h ramp. The samples before and after the heat treatment are shown in Figure 26.



(a) From left: A3, A4, B.

(b) The dashed lines represent the approximate location of the divide between masked (below) and unmasked (above) sections of the glass.

Figure 26: The polished samples (a) before and (b) after heat treatment at 530°C.

The first clear observation is that there does not appear to be any distinction between the masked and unmasked areas. Sample A4 is dark yellow in colour, whilst samples A3 and B have only a very pale yellow colour. Thermo-reducing agents such as tin and antimony are known to reduce the exposure required to produce a latent image but excessive quantities can produce spontaneous colouration. It is therefore likely that the tin present in A4 was responsible for the reduction of the silver to its metallic state rather than the exposure process. It is also worth considering that the samples were subject to too much ambient exposure prior to the masking process. In future experiments this should be reduced by keeping the samples in a dark place whenever possible.

4 Further synthesis and characterisation of photosensitive glasses

Following the preliminary investigations, it was decided to produce larger quantities of each batch to allow for bigger samples to be cut. It was also decided to try two additional recipes. Batch 1 from Armistead's patent (A1) was chosen for being one of the simplest mentioned. It was also decided to reproduce an opaque recipe taken from Stookey's 1953 paper [47], previously explored by a student at VICARTE, referred to from here on as batch O. The annealing temperatures used from here on were based on the initial values obtained from dilatometry measurements for glasses A3, A4 and B: 470°C for all except A4 which is annealed at 515°C. It was decided to use sunlight as the exposure source as it emits strongly across a broad range of UV, so we can guarantee that the samples are receiving the correct wavelength for the photo-reduction of the silver. Sunlight also has the advantage of being an easily accessible source, particularly in Portugal in the summer, and ties in nicely with the central theme of 'The Silver Sunbeam'.

4.1 Experimental part

4.1.1 Synthesis and sample preparation

We began by synthesising the 5 different glass compositions. The quantity of the raw materials for each glass is given in Table 4.

Table 4: Glass compositions wt%

Component	A1	A3	A4	B	O
SiO_2	71.78	74.84	71.49	75.39	80.57
Na_2O	18.05	15.22	15.89	1.22	-
K_2O	-	-	-	2.37	3.60
Li_2O	-	-	-	9.43	12.80
Al_2O_3	-	-	-	9.84	2.97
ZnO	10.05	9.78	12.16	1.60	-
CeO_2	-	0.03	-	0.01	0.03
Sb_2O_3	-	-	-	0.002	-
SnO_2	-	-	0.20	-	-
Ag_2SO_4	0.12	-	0.26	-	-
$AgNO_3$	-	0.13	-	0.13	0.03

The recipes were adapted slightly from the preliminary investigations, most notably metallic Ag was substituted for $AgNO_3$ in the Borrelli recipe. NaF was also no longer included in batch A3. 100g of each composition was produced. The raw materials were weighed out and stirred thoroughly in a flask. When all the components had been added the mixture was shaken in a WAB Turbula ®T2 G 3D Shaker Mixer for 90 minutes to ensure a homogenous mixture. The mixture was transferred to an alumina crucible and heated in an electric furnace to 1300°C with a ramp of 6.5°C/min. Where the quantity of powder was too large to fit in the crucible without risking the mixture spilling over due to the volatilisation of gases, the remaining powder was added to the crucible when the temperature of the furnace had reached 1000°C. After a dwell of three hours, the temperature of the furnace was increased to 1350°C to allow the glass to be poured out of the crucible onto the steel plate. A steel plate and roller were cleaned with water and sandpaper to ensure the surface was smooth, and placed on top of the furnace to warm up. Afterwards, the glass was poured on the steel plate and was rolled out to give a larger surface area allowing the cutting of multiple samples. The glass was then transferred to a small preheated muffle furnace. The glasses were annealed for 1 hour at 470°C (515°C for the A4 batch) after which they were allowed to cool to room temperature inside the kiln. In the case of batch A3 it was not possible to pour the glass out of the crucible and a crack in the crucible prevented us from returning it to the furnace for further heating. Instead the crucible containing the glass was placed into the annealer and the glass was removed with a hammer afterwards. The glasses were cut into samples of approximately 2×2cm on a diamond saw, annealing the glasses properly ensured this was possible without the glass cracking. The samples were polished with progressively finer grained discs on the disc sander in order to obtain smooth surfaces for the optical characterisation.

4.1.2 Addition of Halides

Two further sets of glasses were synthesised in order to explore the effect of the presence of halides in the batch. Silver halides are a key component of photochromic glasses; when exposed to light they break down into silver and halogen ions but recombine when the light source is removed, resulting in reversible colouration of the glass. The composition of all samples is given in Table 5. Four recipes (A1, A3, A4 and B) were selected as the most interesting to investigate, four being the number of crucibles able to fit in the synthesising furnace at one time minimising the furnace usage required to synthesise all batches. From the original A3 recipe the combined quantity of halides contributed by the AgCl and Na_2SiF_6 was calculated and used to determine the number of moles of halide to add in the form NaH where H is Br in the first set of samples and I in the second. For each recipe the quantity of Na_2CO_3 was recalculated to maintain the same total quantity of Na in the batch. The halide batches were synthesised using the same heat program previously described (ramp of 6.5°C/min, 3hr dwell at 1300°C), again adding any excess powder when the temperature exceeded 1000°C.

4.1.3 Exposure and Development

In order to investigate the effect of UV exposure on the glass, two samples from each batch were left outside in a sunny spot for three days. One exposed sample and one unexposed control sample from each batch was then subjected to further heat treatment in an electric kiln; 1hr dwell at 550°C with a 360°C/hr ramp. The second exposed sample and a further unexposed sample were subjected to the same heat treatment but with the dwell at a higher temperature of 600°C.

4.1.4 Measurements

Absorption spectrometry was performed using an AvaSpec-2048-SPU spectrophotometer with an AvaLight-HAL Tungsten Halogen as a light source (Avantes). For some of the darker coloured samples where the spectra suffered from saturation effects repeat measurements were made with a Varian Cary-5000 UV/VIS/NIR spectrophotometer over 300-700 nm wavelength range with a 1 nm resolution for all the glass samples. Where necessary the samples were thinned on the disc sander to prevent saturation.

Colorimetry measurements were taken with a Lovibond ®TR 500 Handheld Reflectance Spectrophotometer. The samples were placed on a teflon base providing a matte white surface with high reflectivity. Three measurements were taken at different positions on each sample. The samples exhibiting no visible colour were not measured as the equipment was not precise enough to give valuable results.

Table 5: Glass compositions wt% with halides

Component	A1-Br	A1-I	A3-Br	A3-I	A4-Br	A4-I	B-Br	B-I
SiO_2	70.19	69.18	73.16	72.10	69.93	68.94	73.90	72.95
Na_2O	16.69	16.45	13.91	13.71	14.60	14.39	0.34	0.34
K_2O	-	-	-	-	-	-	2.33	2.30
Li_2O	-	-	-	-	-	-	9.24	9.13
Al_2O_3	-	-	-	-	-	-	9.65	9.52
ZnO	9.83	9.69	9.56	9.42	11.89	11.72	1.57	1.55
CeO_2	-	-	0.03	0.03	-	-	0.01	0.01
Sb_2O_3	-	-	-	-	-	-	0.002	0.002
SnO_2	-	-	-	-	0.20	0.19	-	-
Ag_2SO_4	0.12	0.12	-	-	0.25	0.25	-	-
$AgNO_3$	-	-	0.12	0.12	-	-	0.13	0.13
NaBr	3.18	-	3.21	-	3.13	-	2.83	-
NaI	-	4.57	-	4.61	-	4.50	-	4.07

The transition temperatures for glasses A3, A4 and B were assumed to be similar to those found by dilatometry for the corresponding preliminary batches. Small fragments of each batch A1 and O and all the halide-containing batches were ground to a fine powder in a Retsch™RM 200 Mortar Grinder. The glass transition temperature (T_g) was determined using a differential scanning calorimeter Pegasus®DSC 404 F (DSC) in the temperature range of 20-1000°C with a heating rating of 5 K/min, using alumina as a reference material.

4.2 Results and Discussion

In all the glasses, both with and without halides, no visible colour was seen after exposure before the samples were subjected to further heat treatment. The complete set of samples after exposure and development can be seen in Tables 9, 10 and 11 in Appendix A. In some of the samples (particularly the darker batches like A4) streaky variations in colour are visible in the glass suggesting the mixture was not homogenous when the glass was poured out. There were a lot of bubbles present in some of the batches, A3 and B being the most affected, and these glasses would have benefitted from longer heating in the synthesis process. Batches B and O, which present a much higher silica and alumina content, did not exhibit any colour change after exposure and development and all samples remained colourless, as seen in Figure 27.
Batch A3 showed a very faint yellow colour in some samples but no strong colouration was observed, as seen in Figure 28.

A1 and A4 demonstrated the largest colour changes, the samples can be seen in Figure 29. The CIE Lab colorimetry plots are given in Appendix C. Looking at the compositions in Table 4, we can see that A1 and A4 are in fact very similar, the main difference being a larger quantity of silver sulphate in A4 and the addition of tin oxide. Tin oxide is a reducing agent and thus this, combined with the higher number of silver ions, may explain the more intense colours seen in

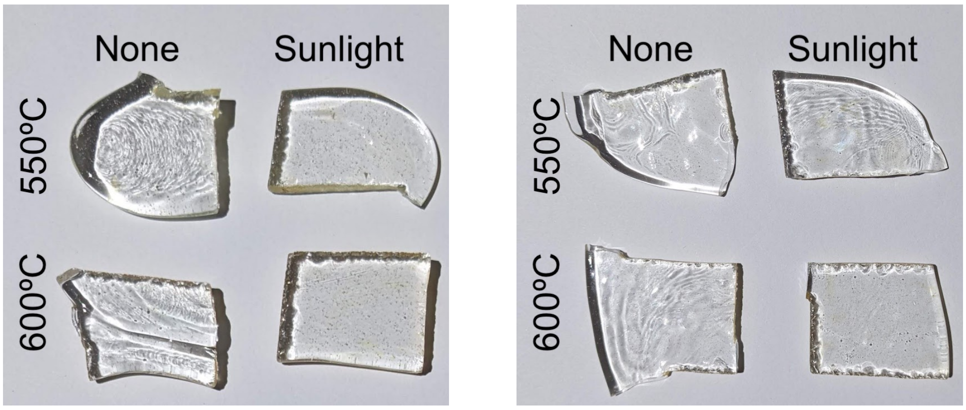


Figure 27: The B (left) and O (right) samples without halides, after exposure and development.

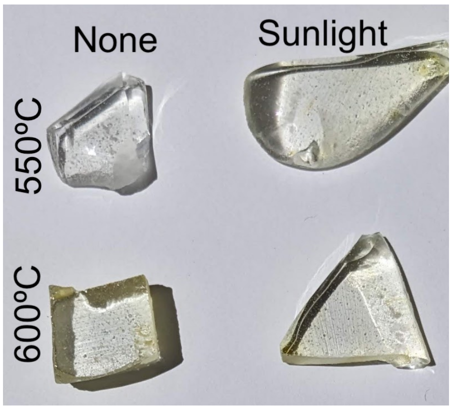


Figure 28: The A3 samples without halides, after exposure and development.

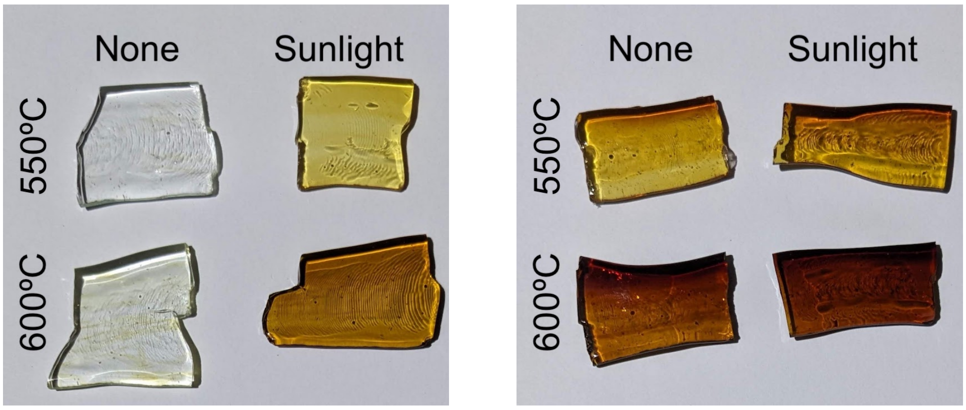


Figure 29: The A1 (left) and A4 (right) samples without halides, after exposure and development.

the A4 samples compared with A1. These were the only two recipes using silver sulphate as the source of silver ions, silver nitrate was used in batches A3, B and O. This suggests that the silver ions in the silver nitrate were not easily able to be photo-reduced to atomic silver, hence the samples remained largely colourless after exposure and development. Another notable difference between the compositions is the addition of cerium as an optical sensitiser in batches A3, B and O. Armistead described in his patent how the addition of cerium intensifies the sensitivity of the glass to the radiation and increases the colour contrast however this was not observed in our glasses.

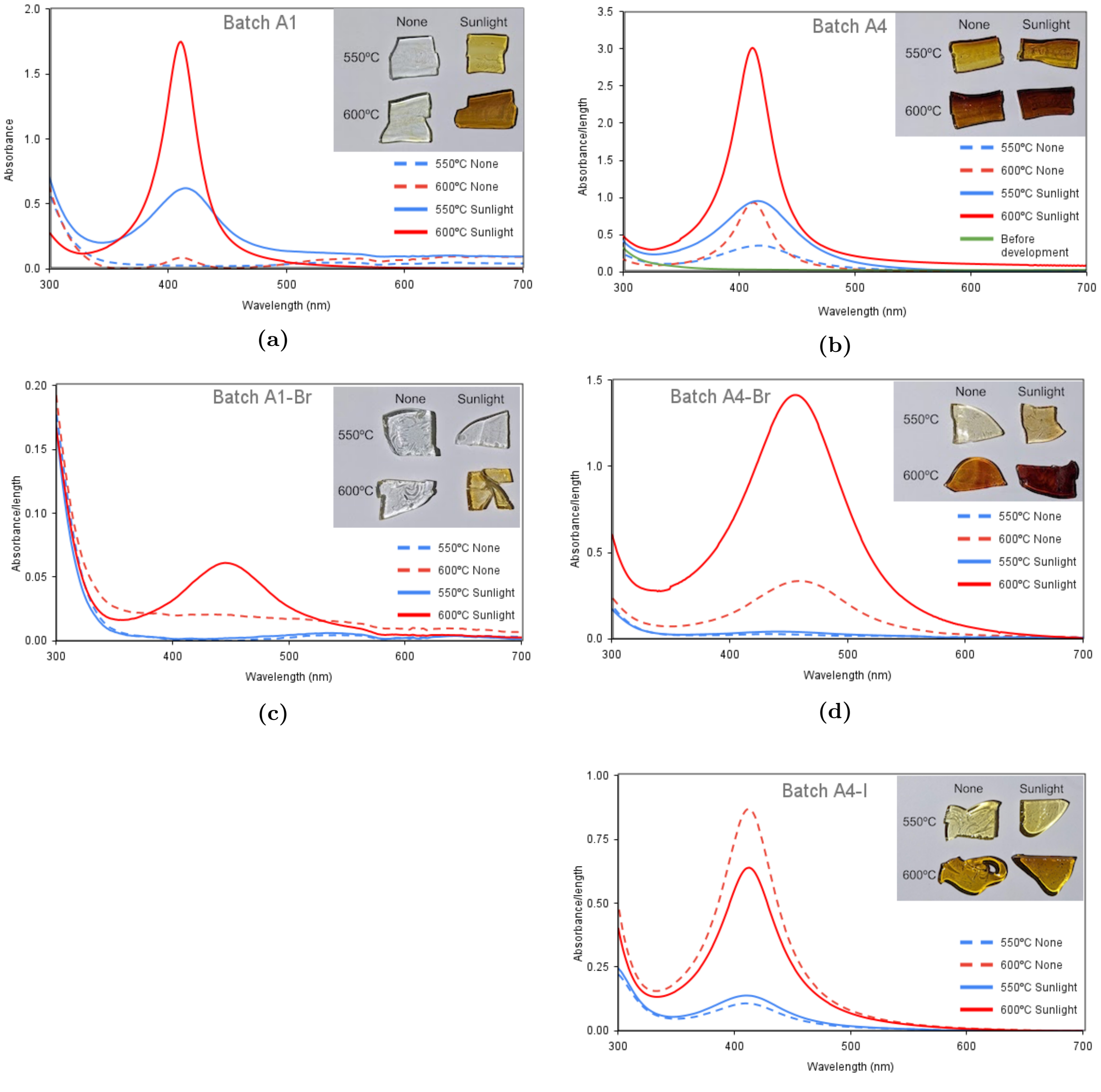
The glass transition temperature obtained by DSC for each sample is given in Table 6. A sample DSC curve is given in Appendix B. The addition of halides did not significantly alter

Table 6: The glass transition temperature, T_g, obtained by DSC.

Glass	O	A1	A1-Br	A1-I	A3-Br	A3-I	A4-Br	A4-I	B-Br	B-I
T_g(°C)	471	498	504	500	476	474	528	527	483	481

the glass transition temperature of the glasses. This was the expected result as the halides do not have an effect on the structure of the glass matrix. Batch A1 could have been annealed at a slightly higher temperature after quenching, however the glass was stable enough to cut samples on the diamond saw when annealed at 470°C so this didn't present a problem.

The UV-Vis absorption spectra for batches A1, A1-Br, A4, A4-Br and A4-I can be seen in Figure 30. The remaining spectra do not exhibit any visible peaks and are given in Appendix D. The absorbance has been divided by the sample width. The location of the absorption peaks for glasses A1 and A4 are given in Table 7 and Table 8 respectively. In all cases the peaks can be attributed to the presence of silver nanoparticles in the glass. Comparing the positions of the absorption maxima between the A1 and A4 samples (Figures 30a and 30b) they appear similar, suggesting that the silver nanoparticles are of a similar size in each glass. The more intense colouration seen in the A4 samples can thus be attributed to a greater quantity of nanoparticles forming.



(a)

(b)

(c)

(d)

(e)

Figure 30: UV-Vis absorption spectra of the A1 and A4 samples. Note that in (a) the absorbance has not been divided by the sample length as the difference in intensity between the samples was so great that the lower maxima would have become indiscernible.

Table 7: The wavelength corresponding to the maximum of the absorption band for all A1 samples, exposed and not exposed to sunlight and annealed at 550 and 600°C. 's' denotes where it was not possible to identify the position of the peak due to saturation.

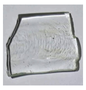
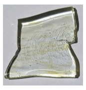
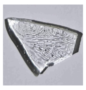
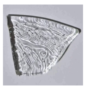
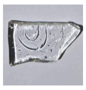
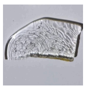
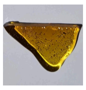
Sample	Composition	Halide ion	Exposure	Development temperature (°C)	Absorption band (nm)
	A1	-	-	550	-
	A1	-	Sunlight	550	414
	A1	-	-	600	411
	A1	-	Sunlight	600	411
	A1	Br	-	550	-
	A1	Br	Sunlight	550	-
	A1	Br	-	600	-
	A1	Br	Sunlight	600	445
	A1	I	-	550	-
	A1	I	Sunlight	550	-
	A1	I	-	600	-
	A1	I	Sunlight	600	-

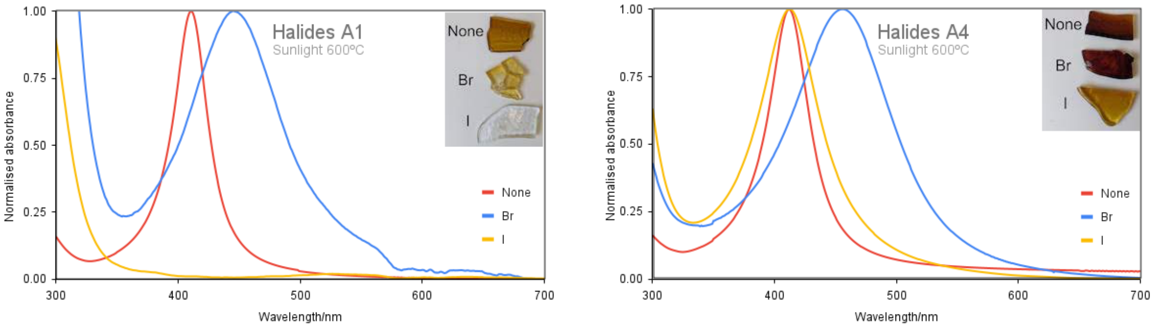
Table 8: The wavelength corresponding to the maximum of the absorption band for all A4 samples, exposed and not exposed to sunlight and annealed at 550 and 600°C. 's' denotes where it was not possible to identify the position of the peak due to saturation.

Sample	Composition	Halide ion	Exposure	Development temperature (°C)	Absorption band (nm)
	A4	-	-	550	417
	A4	-	Sunlight	550	416
	A4	-	-	600	412
	A4	-	Sunlight	600	412
	A4	Br	-	550	-
	A4	Br	Sunlight	550	442
	A4	Br	-	600	460
	A4	Br	Sunlight	600	456
	A4	I	-	550	410
	A4	I	Sunlight	550	410
	A4	I	-	600	412
	A4	I	Sunlight	600	412

The A1 samples exposed to sunlight show a more intense colour after development than the unexposed samples, as demonstrated by the broader absorption peaks in Figure 30a . This supports the theory that the photo-reduction of silver ions is occurring during exposure and thus more silver nanoparticles are able to form during the development heat treatment. The position of the peak is unaffected by exposure, indicating that the nanoparticles formed are the same size. In the A4 samples broadening of the absorption peaks with exposure is also seen however the increase in intensity is less pronounced (Figure 30b) and visually there is less of a difference in colour between the exposed and unexposed samples. Again the peak remains in the same position. Armistead notes in his patent that the presence of tin in batch 4 increases the colouration but an excessive amount destroys the photosensitivity by causing uniform 'warming in' when the glass is heated. Whilst the amount of tin used in the composition was the same as mentioned in his patent it may be that the development heat treatment we used allowed this 'warming in' to occur due to reduction of the silver by the tin. The preliminary A4 batch also exhibited colouration without exposure, as described in the previous chapter, and so the results seen here are consistent.

Again looking at the A1 samples it can be seen that development at a higher temperature gives a more intense colour. There is no significant change in the position of the absorption peak but some broadening occurs and the maximum absorption is higher. At a higher temperature the particles have more kinetic energy and coalesce to form nanoparticles more quickly, hence in the same development time more nanoparticles are able to form [48]. The same increase in intensity with development temperature was seen in batch A4.

The addition of halides to the batches had varied results. In the case of the A1 composition the photosensitive effect was reduced. With the addition of iodide no colour change was observed in any of the samples. In the bromide batch only the exposed 600°C sample exhibited a colour change. Comparing this with the corresponding A1 sample without halides the colour is visibly less intense. We also see that the absorption peak is shifted to a longer wavelength in the Br sample (Figure 31a), suggesting that the average size of the silver nanoparticles formed was larger. However it has also been suggested that this redshift could be due to the formation of a dielectric silver halide shell around a silver core [49] [50]. Transmission electron microscopy (TEM) imaging could be used to investigate this further.



(a) (b)

Figure 31: UV-Vis absorption spectra comparing halide content of the samples. The spectra have been normalised to allow better comparison of the position of the absorption maxima.

In the A3 batch the addition of halides in the exposed 600°C samples has only a very small effect on the appearance of the glass, varying from very pale yellow without halides to almost colourless with bromide and a very pale pinkish colour with iodide. However absorption peaks could not be discerned for any of these samples with the UV-Vis spectroscopy and so only visual observations can be reported.

The batch A4 halide samples all displayed a colouration. Looking at the exposed 600°C samples, all three have a strong colour: dark amber-brown without halides, reddish brown with bromide and golden yellow with iodide. The variation can be seen in the colorimetry plot given in Figure 32.

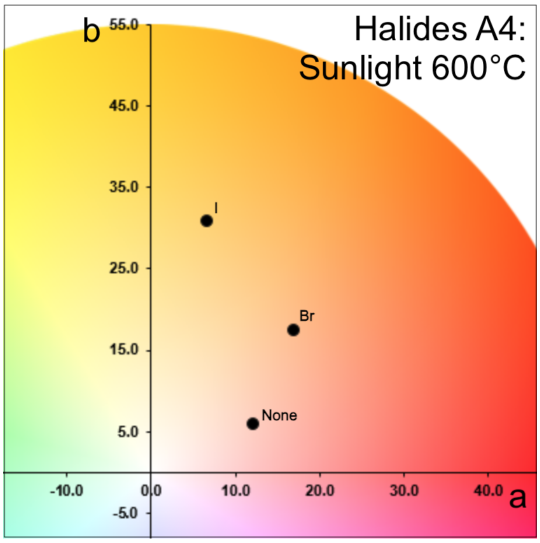


Figure 32: CIE Lab colorimetry plot for the exposed 600°C A4 samples with different halide contents.

From the spectra in Figure 31b we can see that again the absorption peak is significantly shifted to longer wavelengths with bromide, indicating that the size or shape of the silver nanoparticles present in this sample differs considerably from the other samples. The same shift is observed in the unexposed samples, however in this case the peak for sample A4-Br is much narrower. This confirms the visual observation that the exposed samples are more obviously darker in colour than the unexposed samples, a marked difference from the homogeneity seen in batch A4 and A4-I. The addition of halides appears to decrease the reduction of silver by the tin resulting in less colouration in the unexposed samples.

The difference observed between the bromide and iodide samples could be due to increased mobility of the ions in the bromide glass or a higher rate of reduction of the silver ions. It may also be that silver halides are forming rather than silver nanoparticles but more experiments are needed to understand these observations. It would also be interesting to extend the research to investigate the effect of chloride as the added halide.

However none of the samples with or without halides displayed photochromic behaviour, suggesting that the silver ions are dissolved in the glass rather than forming silver halide crystals [51]. Photochromic glasses often contain a relatively large quantity of boric oxide as boron increases the tendency of silver halides to precipitate out of solution as the glass cools [52]. None of the compositions produced here contained boron and so it could be that the phase separation necessary for photochromism did not occur.

The A4 samples before undergoing development heat treatment displayed the same luminescence seen in the samples produced in the preliminary investigations described in the previous chapter. After exposure and development the samples developed at 550°C still showed some luminescence although the intensity was reduced. The samples under UV light can be seen in Figure 33. The samples with halides showed less visible luminescence, in the iodide samples it was barely visible even before the heat treatment, as seen in Figure 34. The luminescent characteristics of the glasses are not the focus of this investigation and so were not investigated further and are presented here purely as an interesting observation. Therefore we can only theorise that it was small clusters of silver ions responsible for the emission, their formation being affected by the presence of halides in the batch. This could be a path for further extending the research in

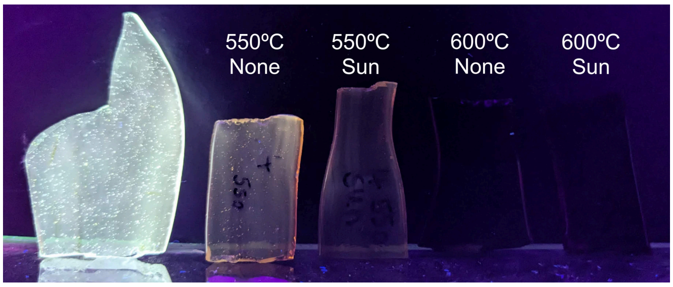
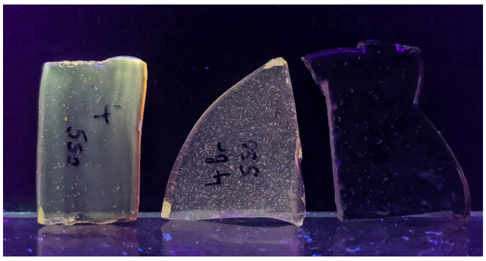


Figure 33: The A4 samples under UV light. On the left is the sample before any development heat treatment.

(a) Before undergoing exposure and development.



(b) After development at 550°C without exposure.

Figure 34: The A4 samples under UV light, from left to right: no halides, bromide, iodide.

the future. Batches A1 and O showed some faint luminescence.

An interesting observation which will be explored in the next chapter is the masking effect caused by the black permanent marker used to label the samples when being exposed. ‘4H’ (H denoting halide) can be seen on the exposed A4-Br sample developed at 600°C in a colour lighter than the surrounding glass, as seen in Figure 35.

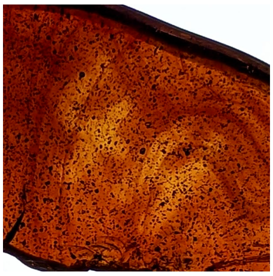


Figure 35: The A4-Br sample with ‘4H’ visible where the permanent marker unintentionally acted as an exposure mask.

4.3 Evaluation for use in art

Composition A1 was found to be a good photosensitive glass, exhibiting a yellow colour characteristic of silver nanoparticles after exposure and development. The colour was more intense when development took place at a higher temperature. Composition A4 showed colouration even without exposure making it less useful as an artistic medium as the contrast between exposed and unexposed regions is reduced, however the colours produced were much more intense than in the A1 batch. The addition of a small quantity of bromide had a significant effect on both batches, reducing the photosensitivity in A1 but producing a much greater variation in colour in the A4 samples.

Overall, the A1 composition is the most suitable for exploring as a photographic medium owing to the good contrast obtained between exposed and unexposed regions. We have also established that 600°C is an appropriate development temperature.

5 Masking materials

Based on the previous results a larger batch of A1 was synthesised to allow experimentation with different masking materials. It has already been seen that a black permanent marker blocks the UV to some extent, proposing interesting possibilities for drawing easily onto the glass. It was decided to investigate the practicality and efficacy of other materials.

The results of a preliminary experiment are shown in Figure 36. One end of the sample was wrapped in aluminium foil. Thick dots of SPF50 sun cream were applied on the remaining surface. The bottom surface of the glass was covered with black electrical tape in an attempt to limit any internal reflections. The sample was left in the sun for 5 days and then developed at 600°C for 1 hour. The absorption spectra for each region of the sample are shown in Figure 37. Whilst the aluminium foil did block the UV to some extent, it was less effective than the sun cream. The definition between the sun cream and unmasked regions also appears sharper than between the foil covered and unmasked regions. sun cream presents the possibility of different application methods which could be interesting for artistic purposes and also as an intriguing informative tool for exploring the effect of wearing sun cream against UV radiation.

(a) Application of different masking materials to a sample of batch A1 glass.

(b) The same sample after undergoing 5 days of exposure in sunlight and development heat treatment for 1 hour at 600°C.

Figure 36: Preliminary masking test.

Two further samples were cut from the same batch of A1 with dimensions of approximately 9×1.5cm. Intervals were marked on the back of the samples with a wax crayon dividing the length into 5 sections. Again the back surface was covered in black electrical tape. On one sample SPF50 sun cream was applied covering four of the sections. For the other sample a piece of lead came used for stained glass work was flattened out and taped on top of the glass sample so that it covered all but one section. Lead is known to be a strong absorber of UV. The setup can be seen in Figure 38a. Both samples were placed outside in the sunlight. Over a period of three days the sun cream was wiped off and the lead came moved down to reveal the sections, resulting in exposure times of 0, 0.5, 1, 2, and 3 days. The developed samples can be seen in Figure 38b. A better gradient was obtained with the sun cream. Although we would expect lead to block the UV completely, the development of a faint yellow colour even in the

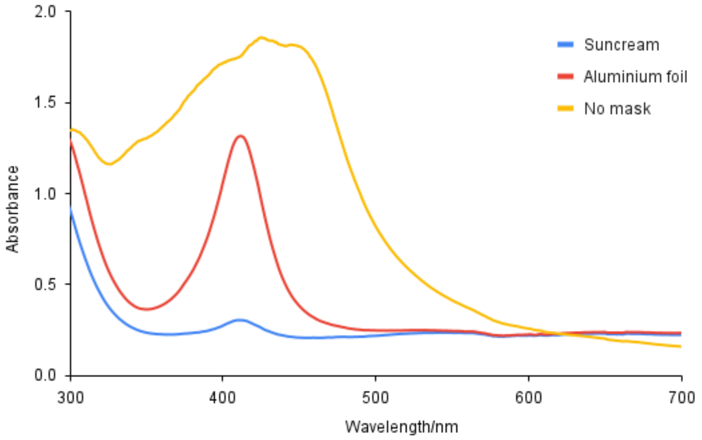


Figure 37: UV-Vis absorption spectra for the different regions of the preliminary masking sample of batch A1 glass.

section that was always masked suggests some exposure did occur, most likely the lead came was not perfectly flush with the glass and this allowed some light to penetrate. It could also be attributed to ambient exposure prior to masking but as both samples were kept together and the sun cream sample shows less colouration this is unlikely. From the sun cream sample we can see that half a day is sufficient exposure time to produce a strong yellow colour but the colour intensifies with exposure time. Polishing the side of the sample revealed the variation in colour with depth (Figure 38c), particularly in the middle section it can be seen that the colour is much more intense on the side that was facing upwards towards the sunlight. This presents interesting possibilities for working with more three dimensional pieces rather than purely flat images on a surface.

Thus far we have focused on the efficacy of different masking materials using simple shapes. In order to investigate the level of detail attainable, two more masking techniques were explored. Returning to the unintentional masking mentioned in the previous chapter, a permanent marker was used to write on another sample of the A1 glass. On the other half of the sample a black and white film negative was taped onto the glass trying to ensure as good contact with the surface as possible. The setup after a day of exposure with sunlight is shown in Figure 39a. One observation at this point is that the marker is not indeed permanent on glass and has rubbed off in some places.

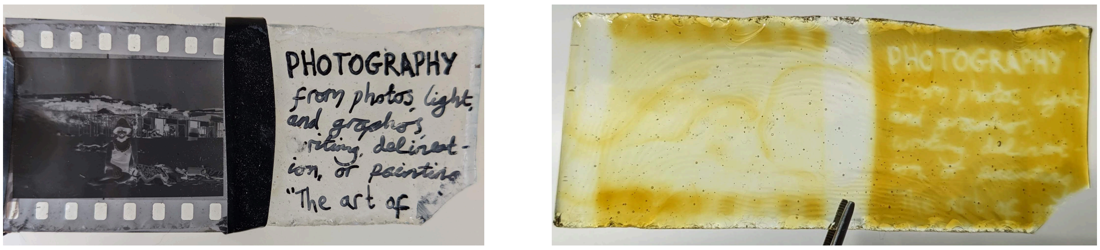
The sample after exposure can be seen in Figure 39b. The writing on the right side is very much legible, showing good contrast particularly when the handwriting size is larger. The result with the photographic negative is less successful. Whilst there is some visible colouration corresponding with the contrast seen in the negative it is generally obscured by imperfections in the glass. The lack of sharp detail seen in the masking by the film perforations also suggested that the negative was not in sufficiently good contact with the glass surface. Whilst it might be possible to achieve a better result with a larger, more contrasty negative, I don't think this is the most interesting application for this glass.

(a) Samples of glass A1 masked with lead came (left) and SPF50 sun cream (right).

(b) The same samples after exposure and development.

(c)

Figure 38: Moving masks to vary exposure time. The bottom of the samples received no exposure, gradually increasing to a maximum of 3 days at the top. A side view of the sun cream sample is shown in (c).



(a) A photographic negative and writing with a permanent marker on a sample of A1 glass after exposure but before development.

(b) The same sample after undergoing development heat treatment for 1 hour at 600°C.

Figure 39: Testing the level of detail attainable with the photosensitive glass produced.

6 Combining processes

6.1 Comparison and evaluation for use in art

Firstly it has to be said that neither of these are the simplest methods for transferring a photographic image to glass. Screen printing and laser printing with enamels give much more reproducible results and are generally more accessible to artists these days. However in both these cases it is a physical process (the addition or removal of enamel) that creates the image rather than a chemical one. Whilst this may be irrelevant for the end result, the process can be as important to the artist as the final piece, and certainly there is something to be said for watching an image appear when an exposed plate is placed in the developer solution or opening a kiln door to reveal an image that had previously been invisible.

6.1.1 Accessibility

Photographic emulsions and the necessary developing and fixing solutions are easy to obtain commercially. Access to a darkroom, be it at home or a rented space, is the other main requirement but is not usually prohibitively costly. In terms of the skills required there is certainly a correlation between the quality of the piece produced and the level of technique but like most things this is a situation where practice makes perfect (or close enough). Whilst combining photography with glass techniques such as blowing and pâte de verre opens up an exciting range of possibilities, skill with glass-working is not essential, and perhaps more important is an understanding of the basic principles of photography.

Photosensitive glass on the other hand is not easy to obtain commercially for art making purposes and synthesising the glass independently is a costly process with uncertain results, only available to those with access to a high temperature furnace. But beyond this the process of exposure and development is a simple one, so if photosensitive glass were to become more readily available, particularly in sheet form, it could be easily accessible to even beginner glass artists.

6.1.2 Longevity

There are photographic glass plates that have lasted for hundreds of years and as a substrate glass is generally much more enduring than paper. However emulsion coated plates are incredibly susceptible to degradation, be it chemical or physical, and older plates often show signs of damage [53]. Photosensitive glass images are as long-lasting as the glass piece itself, the image being completely part of the glass, and so this of course presents benefits for archival quality work.

6.1.3 Visual impact

The limitation of the silver based photosensitive glasses explored in this thesis is that only yellowish tones can be obtained and so the contrast is limited. With the production methods described here the glass is also not completely homogenous and so is not well suited to images with fine detail. However the image itself has a depth due to the distribution of silver nanoparticles within the glass that adds value to the image. Photographic emulsions can produce a range of effects depending on the application and exposure time but fine detail is highly achievable. Whilst toning is possible, the image is generally limited to black and white and must be viewed with some diffuse backlight to see the image properly.

6.2 Exhibition

Combining the two techniques offers the advantages of both, as I explored for the exhibition accompanying this thesis. The restriction of course is that the photosensitive glass piece must be exposed and developed before the silver gelatin emulsion is applied as the emulsion cannot withstand heating to the development temperature of the photosensitive glass. Retouching of photographs was once done by hand with a pencil and before colour photography became widespread it was popular to colour black and white photos by hand with coloured pencils [54]. Drawing on these two practices, I experimented with adding detail to an image by hand with suncream and a black permanent marker pen, using one of the paper exposure test images placed behind the photosensitive glass as a template. I exposed the pieces outside for three days as the weather was somewhat overcast, unfortunately there was also rain during this time and some of the pen detail was washed off. The piece before and after exposure can be seen in Figure 40. After exposing and developing the photosensitive glass I then applied the photographic emulsion to the piece and exposed the same photographic image on top, lining up with the detail created in the photosensitive glass. This proved difficult as the variation in colour in the glass couldn't be seen through the photosensitive emulsion under a red light and so a certain amount of guesswork was involved resulting in slight offsets between the images. This could be circumvented by drawing templates to position the glass before the emulsion was applied. The four pieces can be seen in Figure 41. Whilst the hand drawn marks might make no sense without the detail of the silver gelatin print, the yellow tones are reminiscent of an aged photograph, giving a suggestion of the final fate of the piece when only the permanent photosensitive image remains. The idea of retouching before the image even exists is also interesting in the context of

(a) The suncream and pen mask drawn with the photo as a guide

(b) The piece after exposure and development

Figure 40: Stages of producing a piece combining both techniques.

Figure 41: Final pieces produced for the exhibition.

modern photography. I found the success of suncream as a mask very pleasing, particularly in the context of the beach holiday imagery and the theme of sunlight throughout the thesis. There is potential for the creation of an interesting dialogue with the use of old photographs, taken at a time when sun cream use was not as ubiquitous as it is now, and modern sun protection products.

The pieces were limited in size by the quantity of photosensitive glass we were able to produce and so rather than cutting and polishing the glass to obtain regular pieces I decided to embrace the natural form of the glass, including the bubbles, cracks and squiggles. Ultimately it wasn't about achieving perfection but laying bare the whole process. In this same vein I also wanted to display the many photosensitive glass samples produced throughout this thesis considering that they constituted the bulk of the work. With silver thread I crocheted around each sample and joined them together to imitate stained glass, with crochet in place of lead came, as can be seen in Figure 42a. Hanging this with backlight illumination allowed the beautiful colours to be appreciated, rather than hidden away in a box. Camilla was also kind enough to let me use her slide projector, so that the rest of my Great Aunt's holiday photos could be projected onto the wall as part of the exhibition, again giving attention to photos that haven't been properly viewed in 50 years.

(a) All of the photosensitive glass samples produced throughout the thesis, held in a crocheted web.

(b) The final exhibition in Camilla Watson's Almada studio.

Figure 42: Details of the final exhibition.

7 Conclusion

Photography is by its most basic definition light-drawing, yet we more frequently think of it as capturing an exact snapshot of some real scene as we see it with our eyes. The two methods of photography in and on glass explored here align with these two interpretations. The traditional process of producing silver gelatin glass plates and exposing them either directly in a camera or with a negative in an enlarger matches what we think of as photography, and it was possible to achieve fine-grained detail in the pieces produced. By reproducing the steps of the entire process, from preparing the plates to exposure and development, it was possible to understand the causes of defects in the final plates and thus attain a greater appreciation of the skill required by photographers working with these historic processes, contemporarily and when they were first developed.

Returning to the simpler concept of light-drawing, photosensitive glasses, particularly when produced in small batches rather than industrially, are more suited to this interpretation. By using different masking materials, from lead to sun cream, it was possible to create images within the glass that will last as long as the glass itself. Photosensitive glasses based on silver were produced with different compositions and the effect of exposure, development temperature and halide content were explored through colorimetry measurements and UV-Vis absorption spectra. A variation of composition 1 from Armistead's 1950 patent (A1) was found to be a good photosensitive glass and it was seen that exposure to UV radiation, in this case sunlight, results in colouration due to the formation of silver nanoparticles. A higher development temperature led to a more intense colour. Whilst batch 4 suffered 'warming-in', probably due to the tin present in the composition, it was discovered that the addition of bromide ions reduced this effect and produced more reddish tones.

The science behind both processes is not dissimilar, in both cases the photo-reduction of silver ions is what produces an image, and yet an entirely different effect is created when that silver is within the glassy matrix as opposed to applied as an emulsion. Utilising this disparity presents interesting possibilities for art. Whilst the silver gelatin emulsion gives us the fine grain detail, photosensitive glass gives us a permanent image, and understanding how to apply and combine both processes is valuable knowledge for glass artists interested in photography in all its interpretations.

Whilst there are of course endless possibilities for working with these techniques and contemporary photography, I found the greatest value in rediscovering old photographs. Working with old family photographs gave meaning to the process of producing the silver gelatin plates and inspiration for working with photosensitive glass; the idea of using sun cream as a mask was unwittingly inspired by the beach imagery in the slides. In contrast to the speed and frivolity with which we take photos these days, the slowness of both these photographic methods encouraged contemplation of the process and a greater appreciation and the final results.

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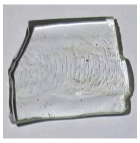
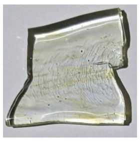
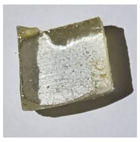
Appendices

A Photosensitive glass samples

Table 9: Samples

Sample	Batch	Exposure	Development	Observations
	A1	-	550°C	Colourless
	A1	Sunlight, 3 days	550°C	Bright yellow
	A1	-	600°C	Pale yellow streaks
	A1	Sunlight, 3 days	600°C	Amber
	A3	-	550°C	Colourless
	A3	Sunlight, 3 days	550°C	Very pale yellow
	A3	-	600°C	Very pale yellow
	A3	Sunlight, 3 days	600°C	Very pale yellow
	A4	-	550°C	Yellow to amber, streaks

Continued on next page

Table 9: Samples (Continued)

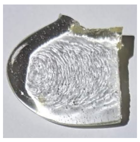
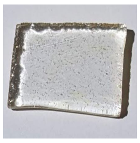
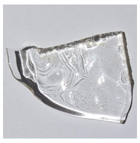
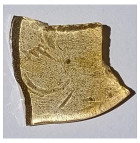
	A4	Sunlight, 3 days	550°C	Amber, streaks
	A4	-	600°C	Dark amber to brown, streaks
	A4	Sunlight, 3 days	600°C	Brown, streaks
	B	-	550°C	Colourless
	B	Sunlight, 3 days	550°C	Colourless
	B	-	600°C	Colourless
	B	Sunlight, 3 days	600°C	Colourless
	O	-	550°C	Colourless
	O	Sunlight, 3 days	550°C	Colourless
	O	-	600°C	Colourless
	O	Sunlight, 3 days	600°C	Colourless

Table 10: Bromide samples

Sample	Batch	Exposure	Development	Observations
	A1-Br	-	550°C	Colourless
	A1-Br	Sunlight, 3 days	550°C	Colourless
	A1-Br	-	600°C	Colourless
	A1-Br	Sunlight, 3 days	600°C	Bright yellow
	A3-Br	-	550°C	Colourless
	A3-Br	Sunlight, 3 days	550°C	Colourless
	A3-Br	-	600°C	Colourless
	A3-Br	Sunlight, 3 days	600°C	Colourless
	A4-Br	-	550°C	Pale yellow
	A4-Br	Sunlight, 3 days	550°C	Golden yellow
	A4-Br	-	600°C	Amber, streaks

Continued on next page

Table 10: Bromide samples (Continued)

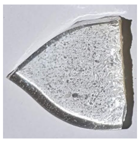
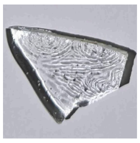
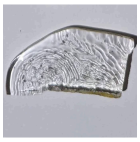
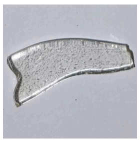
	A4-Br	Sunlight, 3 days	600°C	Dark red-brown, ‘4H’ visible
	B-Br	-	550°C	Colourless
	B-Br	Sunlight, 3 days	550°C	Colourless
	B-Br	-	600°C	Colourless
	B-Br	Sunlight, 3 days	600°C	Colourless

Table 11: Iodide samples

Sample	Batch	Exposure	Development	Observations
	A1-I	-	550°C	Colourless
	A1-I	Sunlight, 3 days	550°C	Colourless
	A1-I	-	600°C	Colourless
	A1-I	Sunlight, 3 days	600°C	Colourless
	A3-I	-	550°C	Colourless

Continued on next page

Table 11: Iodide samples (Continued)

	A3-I	Sunlight, 3 days	550°C	Very pale yellow
	A3-I	-	600°C	Colourless
	A3-I	Sunlight, 3 days	600°C	Very pale pink
	A4-I	-	550°C	Light yellow
	A4-I	Sunlight, 3 days	550°C	Light yellow
	A4-I	-	600°C	Amber
	A4-I	Sunlight, 3 days	600°C	Amber
	B-I	-	550°C	Colourless
	B-I	Sunlight, 3 days	550°C	Colourless
	B-I	-	600°C	Colourless
	B-I	Sunlight, 3 days	600°C	Colourless

B DSC

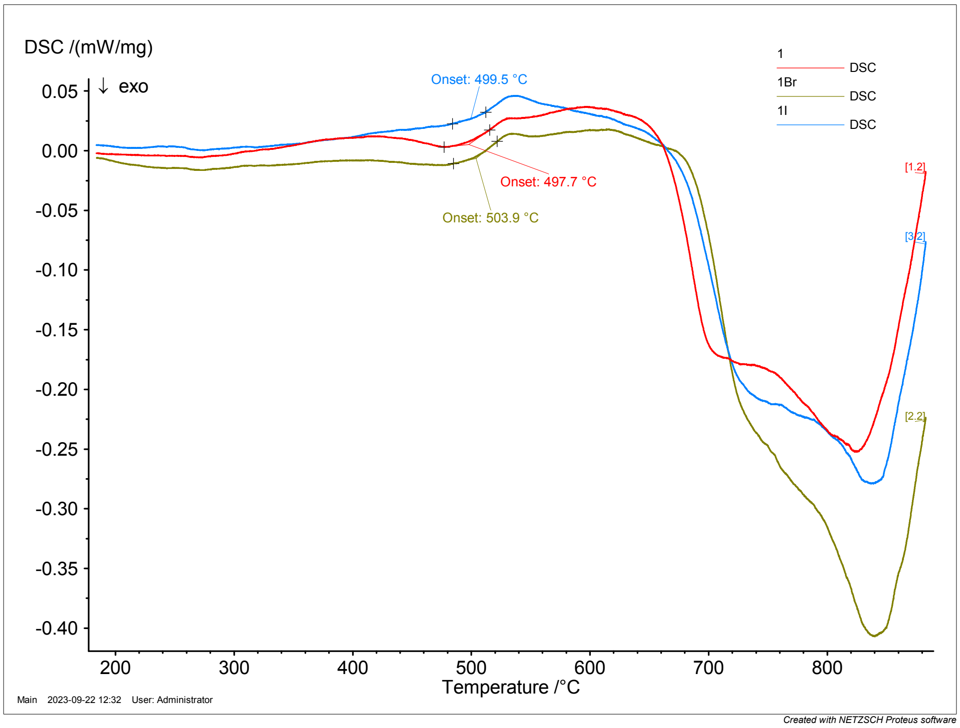
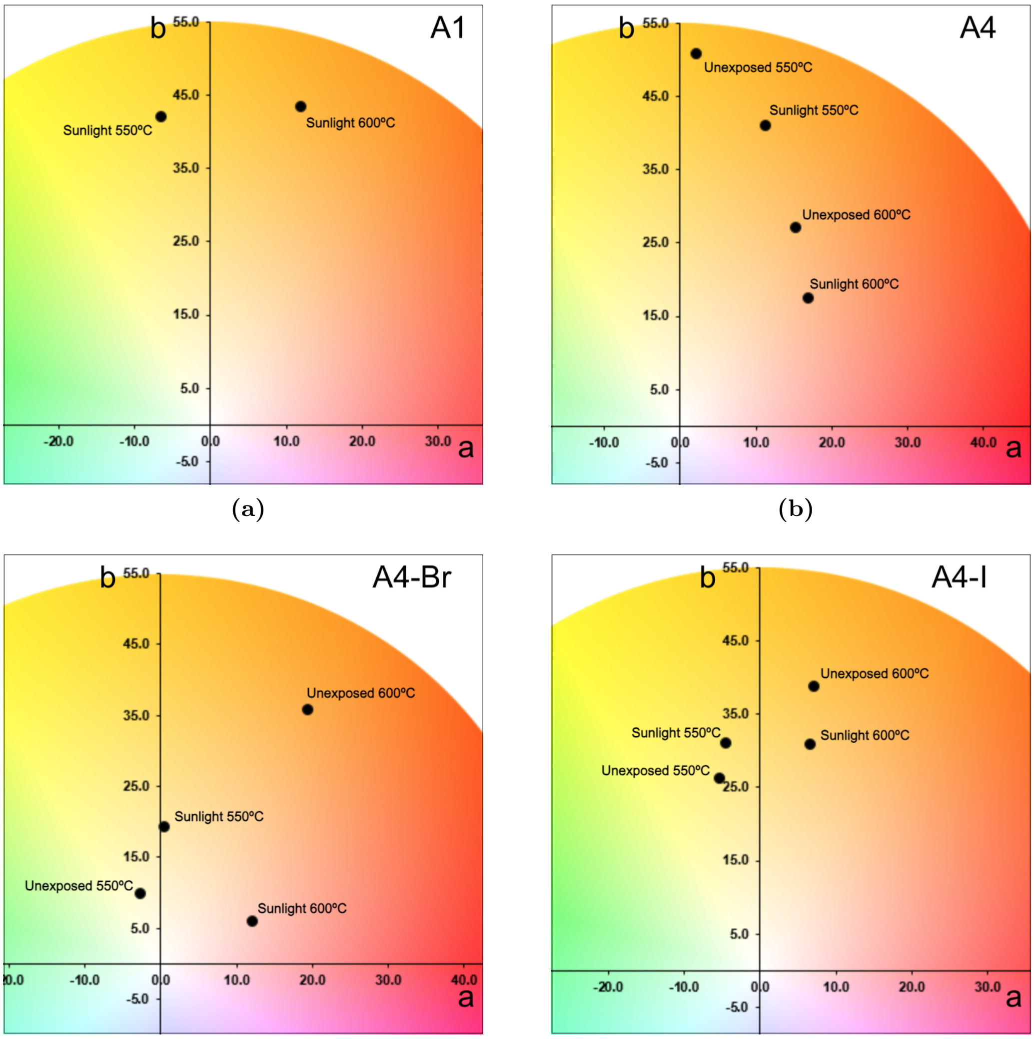


Figure 43: DSC curves for the A1 glass with different halide contents.

C Colorimetry



(a) (b)

(c) (d)

Figure 44: CIE Lab colorimetry plots. In the case of A1 only the exposed samples are plotted as the unexposed samples were essentially colourless.

D Absorption spectra

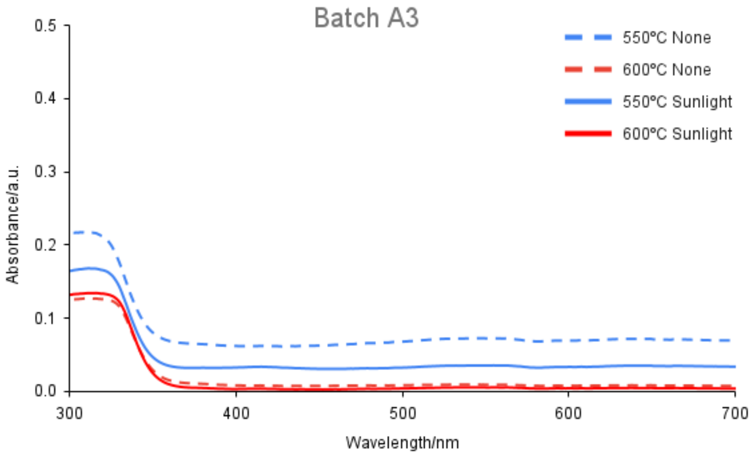


Figure 45: UV-Vis absorption spectra of the A3 samples.

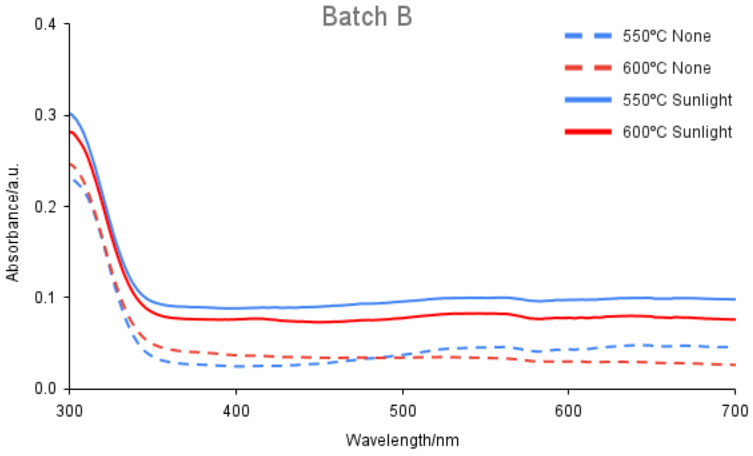


Figure 46: UV-Vis absorption spectra of the B samples.

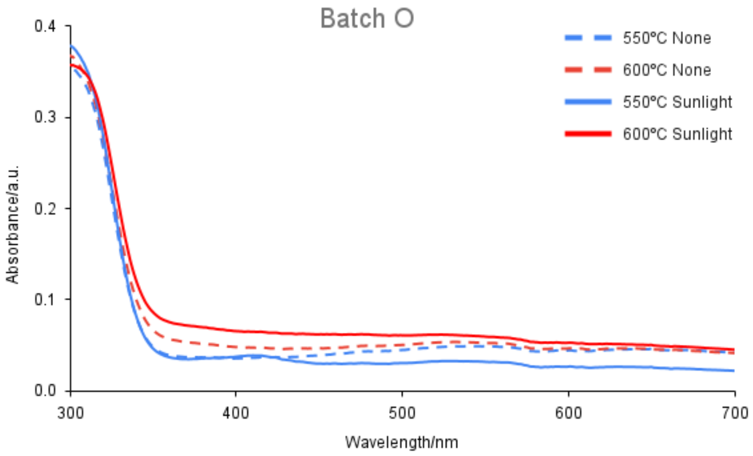


Figure 47: UV-Vis absorption spectra of the O samples.

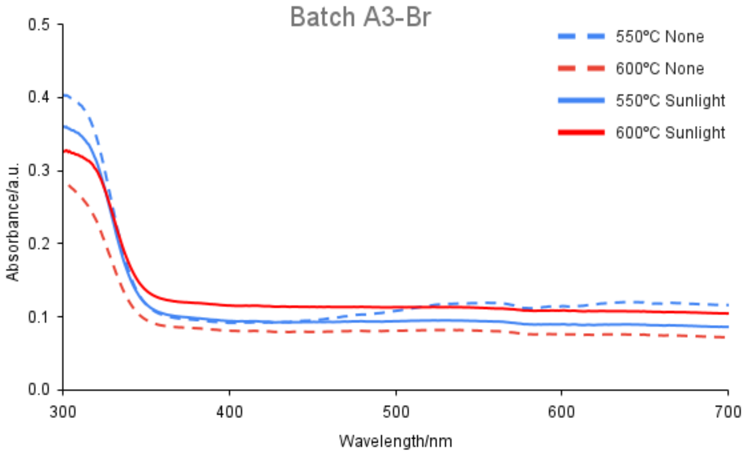


Figure 48: UV-Vis absorption spectra of the A3-Br samples.

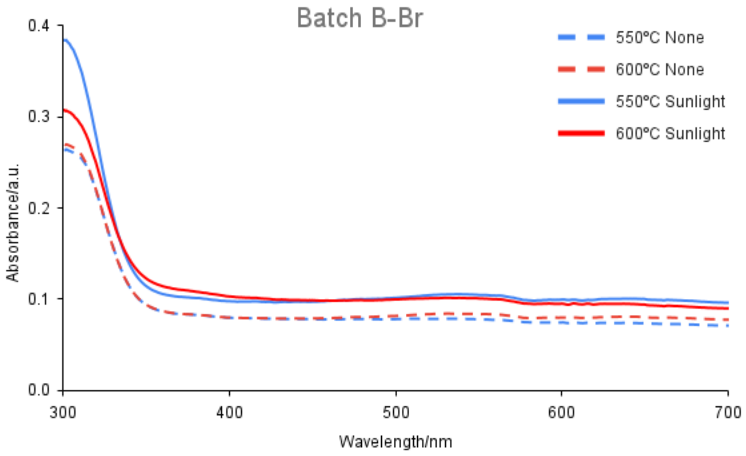


Figure 49: UV-Vis absorption spectra of the B-Br samples.

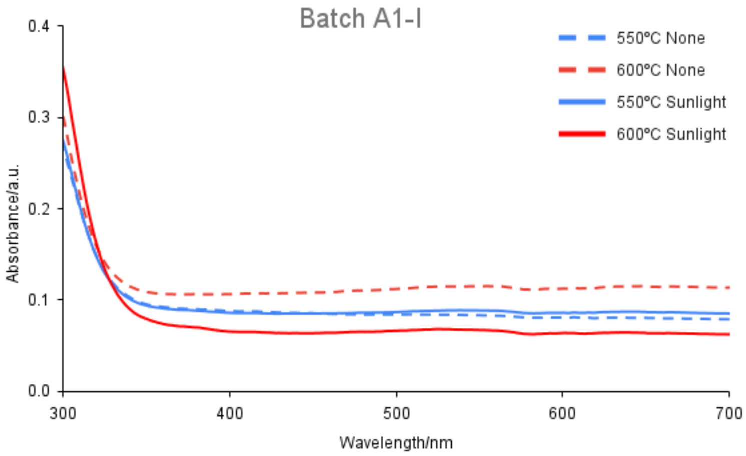


Figure 50: UV-Vis absorption spectra of the A1-I samples.

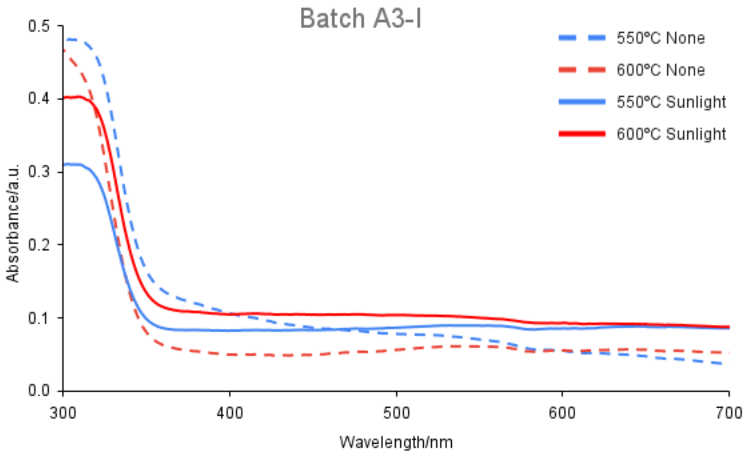


Figure 51: UV-Vis absorption spectra of the A3-I samples.

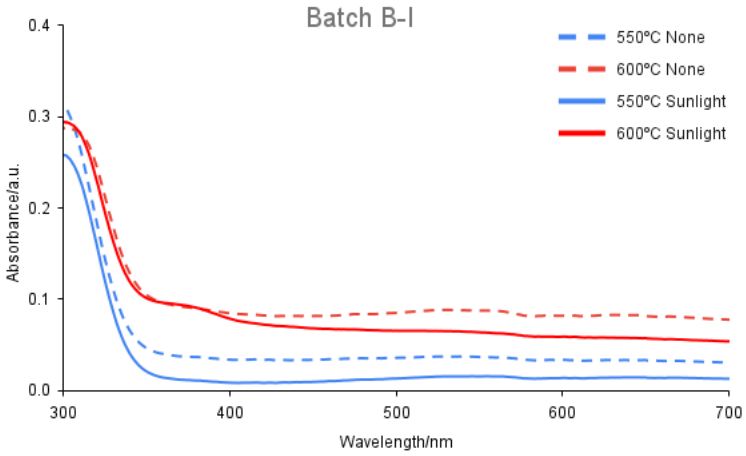


Figure 52: UV-Vis absorption spectra of the B-I samples.