Natasha Shannon Hogan
8 August 2010

Student papers from the *Preservation and Conservation of Photographic Materials* course at The Centre for Photographic Conservation. *- 21 June - 30 July 2010*

ph.1447 Platinotype. *From the collection of The CPC.*

Causes of Degradation of Photographic Materials

Photographs come in many shapes and forms, as does their deterioration. Due to the complex chemical and physical nature of photographs, great care must be taken in the storage, display and handling of photographic materials. Common forms of deterioration found in photographic processes include: fading, discolouration, silver mirroring, physical damage and loss.

Environment

Photographs are sensitive to their environment including air quality and material surroundings. Photographs require a stable environment with low temperature and relative humidity of between 30-50% RH (Adelstein, 2009 p. 2). A fluctuating RH can cause distortions in the primary substrate and fissures in materials that behave elastically including colloid layers of albumen, collodion and gelatine. A high RH attracts pests and moulds to the gelatine, albumen, or starch found in many paper supports, colloid layers and matting agents. A high RH and EMC (elevated moisture content) in the object can turn gelatines to a gel state and lead to the degradation of the silver present in many silver-based photographs (CPC, 2010). A low RH can cause embrittlement and stress to photographic materials (CPC, 2010).

Light

Fading of photographs can occur due to a variety of causes including exposure to light, airborne pollutants and oxidation. Exposure to light can cause acid hydrolysis of material supports such as a ligneous mountboard. This acid hydrolysis can cause discolouration of the photographic image (Moor, 2010). Ian and Angela Moor in their 1992 article, *Exhibiting Photographs: The Effect of the Exhibition Environment on Photographs*, describe the process as follows:

> "...silver itself is not light sensitive in that it can not be oxidized by light alone. However, silver can be oxidized by aggressive oxidizing agents liberated by the photochemical affect of light acting upon other materials in the photograph, its support and containment materials, and in the immediate environment."

When light causes the oxidation of materials, these oxidized materials may oxidate the silver found in many photographic images. Many forms of photographic deterioration are due to a high temperature and elevated moisture content. This causes the common form of hydrolytic deterioration known as silver mirroring (Moor, 2010). Hydrolytic deterioration is commonly found along the edges of paper in the grain direction because moisture absorbs faster in the direction of the grain of the paper.

The majority of photographic materials are highly sensitive to light. Silver-based photographs vary in their stability depending on the type of silver in the photograph. Photolytic silver is very light sensitive, colloidal silver is less sensitive and filamentary silver is stable to light (CPC, 2010). Light damage and fading is cumulative. Photographs should be exhibited for short periods of time with limited light levels or whenever possible, a facsimile should be made for exhibition. Certain photographic processes such as photogenic drawings are highly sensitive to light and must never go on display. If a photograph has not been fixed or was poorly fixed or poorly washed, it may be more sensitive than other photographs of the same process. For this reason, it is paramount that great care be taken when exposing photographs to light.

In the 2003 book, *A Guide to the Preventive Conservation of Photograph Collections*, Dr. Bertrand Lavédrine categorizes photographs into three categories in regard to light levels suitable for display. He recommends the following light levels in an environment that has UV and IR filtered out. The most sensitive category termed, *objects particularly sensitive to light* include: chromogenic development, color photographs, instant photographs and 19th century photographs. For photographs in this category he suggests a maximum illumination of 50 lux and they should not exceed 12,000 lux-hours annually. In practice this means that an exhibition that is open to the public 8-hours a day can only be on display for 30 eight-hour days. The next category, *objects very sensitive to light*, includes dye transfer photographs, dye bleach colour photographs and resin-coated black and white photographs on resin-coated paper. He suggests that the very sensitive photographs be on display with a maximum illumination of 75 lux for no more than 42,000 lux-hours annually, which amounts to 70 eight-hour days if displayed at 75 lux. The next category, *objects sensitive to light*, includes black and white photographs on baryta paper, and monochrome or pigment photographs. For this category he suggests a maximum illumination of 150 lux with an annual maximum of 84,000 lux hours. This amounts to 70 eight hour days displayed at 150 lux. (Lavédrine, 2003, p. 161-163).

Extended term storage is recommended for original photographs and negatives. Extended storage conditions have a temperature in the range of -18°C to 13°C with a relative humidity range of 30%-50% depending on the material type. Medium-term storage is appropriate for surrogate or copy photographic material and has a temperature range of 13°C to 24°C with an RH of between 30-50% depending upon the material type (CPC, 2010). In order to prevent off-gassing, nitrate and acetate negatives should be stored in frozen storage.

Common forms of silver degradation

Silver-based photographic processes are prone to a number of unique forms of deterioration. Silver mirroring is commonly found on glass negatives, sheet film negatives, roll film and conventional silver-based black and white prints. It is caused when silver in the colloid or emulsion layer is oxidized and migrates to the surface and reduces back to metal. This form of degradation is commonly the result of being subjected to a humid environment and high EMC (CPC, 2010). Additionally, silver mirroring occurs at the edges of the print or negative as this area has often been exposed to water absorption. Silver mirroring, the result of a reductive-oxidative reaction, occurs in the demax areas of photographs as that is where the highest concentration of silver is. Silver reduces environmental sulphur from the air or adjacent materials and the sulphur is oxidized and reduced to silver sulphide (CPC, 2010). When a silver image presents image density loss this suggests that a photograph has reacted with sulphur (CPC, 2010).

Residual Processing Chemistry

Many prints contain residual chemicals that are inherent to the processing. These chemicals may react with light and cause discolouration, damage and loss of image. Images often fade or present forms of deterioration along the edges as these areas have the most contact with air and oxidising agents.

Materials, Housing and Handling

Caring properly for photographs can prevent a variety of common forms of degradation. A stable environment, good handling practices and safe housing will reduce the risk of physical damage and damage from pests and unexpected disasters. When photographic materials are handled, gloves should be worn as fingerprints leave residues that can damage colloid layers and be permanently visible in the image surface. Materials for housing of photographs should only be used if they have been tested and PAT (photographic activity test) approved for use with photographic materials.

Inherent Deterioration by Process

Some photographic processes are inherently less stable than others due to their chemical composition. Photographs that were stabilized rather than fixed are inherently unstable. Stabilization is common to early photogenic drawings, salted paper prints prior to 1843 and some gelatine prints (CPC, 2010). Photographs that are fixed in hyposulphate of soda are inherently more stable as hypo solubilises the insoluble silver halide (CPC, 2010).

Non-paper-based photographs

There are a number of photographic processes on non-paper supports. Processes that involve metals are prone to forms of metal degradation. Silver is prone to the development of tarnishing from either silver oxide and/or silver sulphide. Copper may tarnish from either copper sulphate or copper oxide. Iron may develop rust due to the oxidation of the iron. As with paper processes, it is common for the tarnishing and deterioration to start from the edges of the metal plate and work inwards. Many metal objects are housed in cases which can provide an excellent protective barrier from airborne pollutants and oxidatants. They should be stored in a cool, dry environment with a stable RH.

Processes that involve glass may be susceptible to glass deterioration. Deterioration of glass in a collodion positive can result in delamination of the colloid layer. Deterioration of the cover glass of a cased object may result in the formation of silicates and salts within the case. When glass disease occurs, the work must be stored at a lower RH to slow down the glass deterioration (CPC, 2010).

Tintypes and collodion positives may be varnished. When there is loss to the varnish area, the metal plate may be exposed. This makes the photographs prone to oxidation and sulphidation (CPC, 2010).

Daguerreotype images are composed of a silver-mercury amalgam and wet collodion positives, including ambrotypes contain mercuric chloride that is reduced to mercuric dioxide (CPC, 2010). Mercury is a health risk and objects containing mercury should be stored at a temperature below 25°C as mercury above this temperature begins to vaporize and pose a serious health hazard and a hazard for the object and surrounding materials (CCI, 2002).

Paper-based photographs

The composition, size, weight, material and chemical makeup of photographic paper substrates greatly impact the stability of the image. Paper objects by nature are prone to physical damage including: folds, tears, abrasion and surface loss and must be handled and stored carefully. Paper substrates vary greatly in their makeup and this effects the stability of the image. Photographic papers may contain impurities, sizing agents, optical brightening agents or lignins. Lignins are a source of gelatine staining and can be a source of silver image degradation (Burge, D.M., Nishimura, D.W., & Reilly, J.M., 2002).

Certain photographic processes are prone to different forms of deterioration in addition to deterioration of the primary substrate. Some of the **early photographic processes** are so light sensitive that they cannot be displayed. Early processes such as **photogenic drawings**, **calotypes** and **salted paper prints** that have been stabilized, must not be displayed under any circumstances (CPC, 2010). They must be stored in a well sealed environment, free from airborne pollutants and oxidising agents. Salted paper prints and calotypes that have been fixed in hyposulphate of soda are more stable than those that have not been fixed. These one layer processes are extremely fragile as they readily absorb oxidizing agents and pollutants from the atmosphere. Types of deterioration commonly found in fixed salted paper prints are loss of image density and warm rusty ochre colour discolouration due to atmospheric sulphides or residual sulphur from the hypo fixer (CPC, 2010). Discolouration and image loss that is green-black comes from residual silver thiosuphate due to inadequate fixing (CPC, 2010). There is no silver mirroring with salted paper prints as there is no colloid. When silver iodized it will immediately reduce sulphur from the air to silver sulphide (CPC, 2010).

Cyanotypes and blueprints are inherently very stable and are safe for display if they have been adequately fixed (CPC, 2010). These prints may be damaged by alkaline environments so they must not be stored with any buffered paper enclosures. **Diazotypes**, like cyanotypes will be harmed if exposed to alkaline environments and the same precautions must be taken in the storage and care of these photographs (Ferreira, L.M., Vieira, J., & Vilela, M., 2006).

Platinotypes and **Palladiotypes** are very stable photographs and they are not prone to fading. As they are not silver based images, they do not present any of the common signs of silver deterioration including fading and silver mirroring. Residual iron salts in the paper can cause discolouration of the demin areas of the image, but these photographs are stable and safe for display (CPC, 2010).

There are a number of photographic processes that use **pigments** to form the image including: **collotypes** (a photolithographic process), **photogravures** (a photoengraving process), **carbon prints** (a pigmented photographic process), **Woodburytype prints** (photomechanical process), **bromoil prints** (a pigmented photographic process), **bromoil transfer prints** (photolithographic process). If stable pigments and good quality paper substrates are used, these processes are inherently very stable (CPC, 2010). However, pigments vary, so it should not be assumed that all pigmented prints are stable to light. **Gum bichromate prints**, are pigmented photographic prints, but unlike those mentioned above, they involve a layer of gum arabic to which pigment is added upon. This layer of gum may develop fissures due to fluctuations in relative humidity (CPC, 2010).

There are a variety of chemical processes that fall under the category of **gelatine silver-based photographic images**. The processes vary in their stability and are prone to different forms of deterioration. Gelatine prints are prone to mould as gelatine is an organic material that readily absorbs moisture from the atmosphere and provides a food source for pests and moulds. Silver mirroring, image density loss, fading, staining and discolouration are all forms of deterioration found on gelatine prints.

Albumen prints are reactive to changes in the environment and the albumen layer is inherently prone to fissuring. Fissuring occurs in alignment with the grain direction of the print or the grain direction of the support that it is on (CPC, 2010). Albumen prints are often mounted, and if unmounted they tend to roll inwardly as the albumen shrinks. Albumen photographs are less prone to silver mirroring than many silver-based photographic processes because the sulphur from the air or environment interacts with the albumen of the photograph and creates silver sulphate which causes yellow discolouration (CPC, 2010). The fermentation of the sugars in albumen, known as the Maillard reaction, is a common form of deterioration that results in yellow discolouration (CPC, 2010).

Collodio-Chloride prints are inherently more stable than gelatine prints although they are very prone to surface abrasion. Collodion deterioration forms iridescent colours on the surface of the print. Collodion prints are prone to fissuring and will fissure in all directions (CPC, 2010).

There are a variety of **colour photographic processes** and depending on the process, they vary in their stability. Some dyes used in colour processes can fade quickly at room temperature and must be stored in frozen storage (Adelstein, 2009 p. 2).

Glass Negatives

Photographic negatives on glass are inherently fragile as they are glass objects. **Albumen negatives on glass** are prone to silver mirroring as they are not varnished. They are prone to yellow discolouration of the demin areas (CPC, 2010). **Wet plate collodion negatives** on glass are prone to physical damage including losses, pinholes and scratches. The negatives tend to be varnished and this protects the surface. Unvarnished negatives are prone to silver mirroring (CPC, 2010). **Gelatine dry plate negatives** on glass may present silver mirroring (CPC, 2010).

Plastic Negatives

Plastic as a support for negatives provides a flexible support, but is inherently delicate to abrasion and physical damage. **Cellulose nitrate negatives** are soft, easily abraded and creased and are prone to planar distortion. Gases released from cellulose nitrate negatives form nitric oxide, nitrous oxide, and nitrous dioxide that degrade the negative and can damage materials adjacent to the negative (CPC, 2010). Cellulose nitrate negatives are highly flammable and must be stored in an appropriate environment or they may spontaneously combust. The deterioration involves yellow to orange to white discolouration, silver mirroring, a greasy surface texture and the smell of nitric acid (CPC, 2010).

Acetate negatives are not easily creased or marked, but do present planar distortions. Deterioration of acetate negatives may involve the smell of acetic acid and red or blue discolouration from residual ferric irons (CPC, 2010). With advanced deterioration, the photographic base shrinks and the gelatine emulsion does not. This results in brittleness and the formation of bubbles and blisters.

Hydrolytic environments allow deterioration of acetate and nitrate negatives to increase (CPC, 2010). Environmental monitoring and cold suppressed storage environments are important measures that should be taken in order to slow down the deterioration process of these negatives. Housing these negatives in a manner that allows them to breathe reduces their volatility (CPC, 2010). The volatile acids can cause acid hydrolysis of other materials including any adjacent photographs.

Polyester negatives do not present planar distortions and are very stable. When handling all plastic negatives, care must taken to properly handle, store and protect them from surface abrasion and dust.

Bibliography

Adelstein, P. (2009) IPI Media Storage quick reference: Negatives, Prints, Tapes, CDs, DVDs. 2nd edition. Image Permanence Institute.

Baglioni, P., Cattaneo, B., Chelazzi, D., Giorgi, R., Merlo, C., & Serena, T. (2008) Physico-chemical characterization and conservation issues of photographs dated between 1890 and 1910. *Journal of Cultural Heritage.* vol. 9, 2008, pp. 277-284.

Burge, D.M., Nishimura, D.W., & Reilly, J.M. (2002) Effects of enclosure papers and paperboards containing lignins on photographic image stability. *Journal of the American Institute for Conservation.* Autumn-Winter 2002, vol. 41, no. 3, pp. 279-290.

Canadian Conservation Institute (2002) CCI Notes 1/7: Mercury in Museum Collections. Canadian Conservation Institute [accessed on 25/7/10]. Online at: http://www.cci-icc.gc.ca/publications/ccinotes/enotes-pdf/1-7_e.pdf

Ferreira, L.M., Vieira, J., & Vilela, M. (2006) Discolouration of architectural photoreproductions: Causes and Prevention. *Restaurator*. 2006, pp. 1-8. -- About Diazotpyes

Lavédrine, B. (2003) A Guide to the Preventive Conservation of Photograph Collections. Getty Publications, Los Angeles

Moor, A., Moor, I. (2010). *The Preservation and Conservation of Photographic Material Parts I and II course.* [Lectures, discussion and workshop notes] The Centre for Photographic Conservation, London, 233 Stanstead Road, Forest Hill, London, SE23 1HU, June and July, 2010.

Moor A., & Moor, I. (1992) *Exhibiting Photographs: The Effect of the Exhibition Environment on Photographs.* In: Conference Papers: The Imperfect Image: Photographs: their Past, Present and Future, Windermere, Cumbria. The Centre for Photographic Conservation, London. pp. 193-201.

Swain, L. (1998) *Collections Management: Storage.* In: New Museum Registration Methods. (eds. Buck, A. & Gilmore, J.A.) 4th ed. pp.105-116. American Association of Museums.Washington, D.C.

Watkins, S., McElhone, J., & Freeman, S (2004) Chapter 1 - Exhibition Guidelines for Photographic Materials. In: Photographic Materials Group Conservation Catalog. American Institute for Conservation. Online at: http://www.conservation-wiki.com/index.php?title=PMG_Chapter_1_-_Exhibition_Guidelines_for_Photographic_Materials_(published_2004)

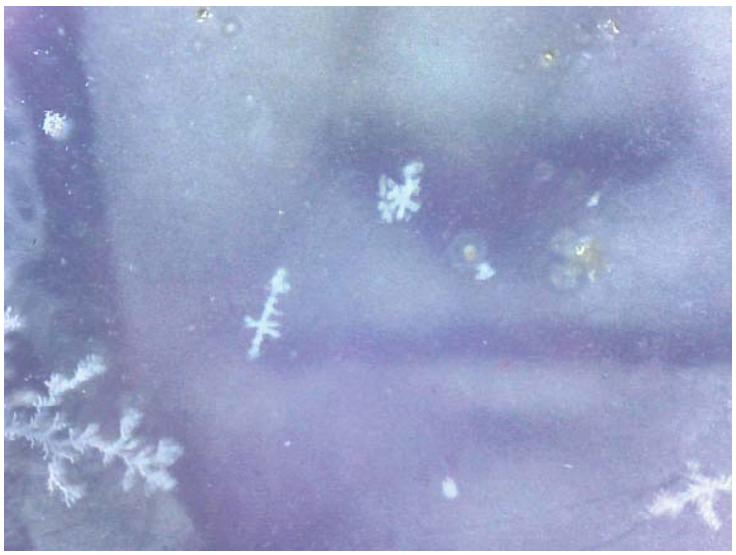
Photographs of Common Forms of Deterioration

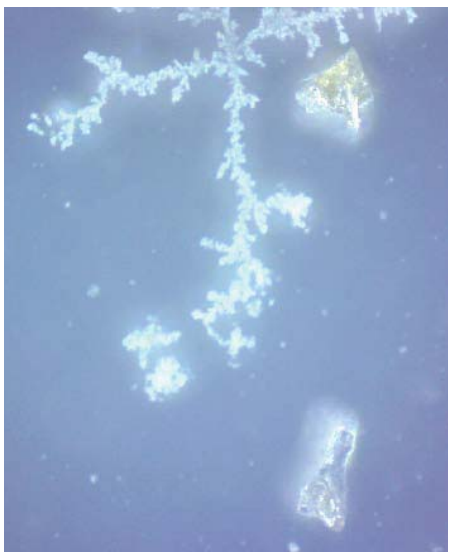
SILVER SULPHIDE DEGRADATION

ph.1439 Gelatine Chloride P.O.P.
The orange/pink spots in the image are silver sulphide spots and are a form of reductive oxidative deterioration and there is density loss in the trees. *From the collection of The CPC.*

GLASS DETERIORATION

ph.1435 Daguerreotype
above: Hand-coloured daguerreotype; *below:* detailed photographs of salts and silicates formed inside the glass cover. *From the collection of The CPC.*



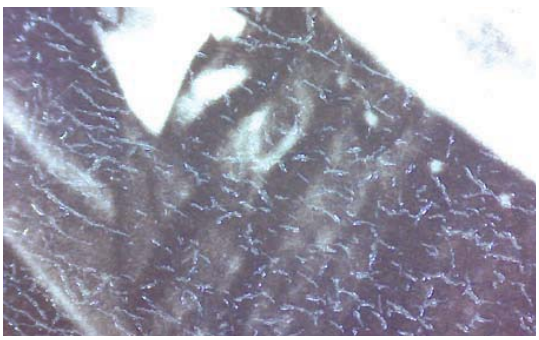


FINGERPRINT

ph.1630 Gelatine Chloride P.O.P.
left: Detail of fingerprint in the surface of a photograph.
From the collection of The CPC.

ALBUMEN

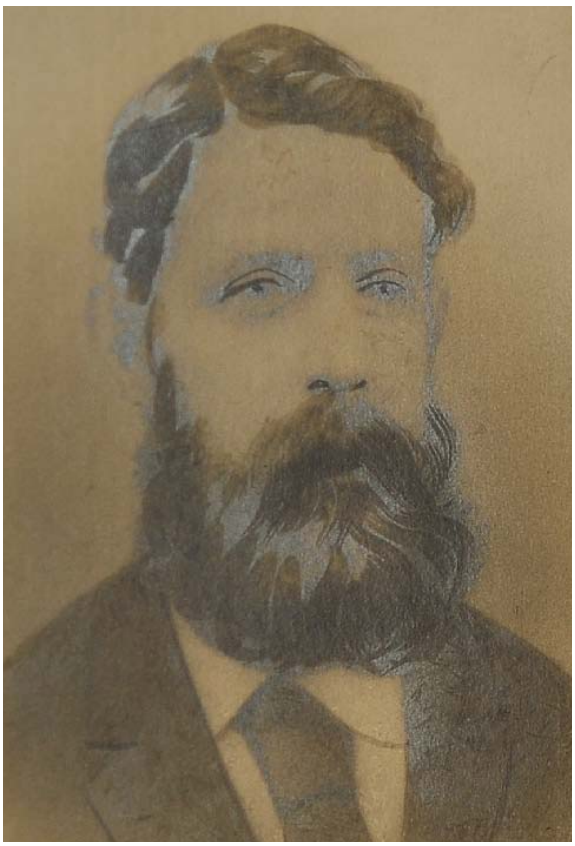
ph.1457 / ph.1458 Albumen Photographs
above and left: Yellow discolouration at the edges is a form of sulphuric degradation.
below: Detail of fissuring in the colloid layer.
From the collection of The CPC.



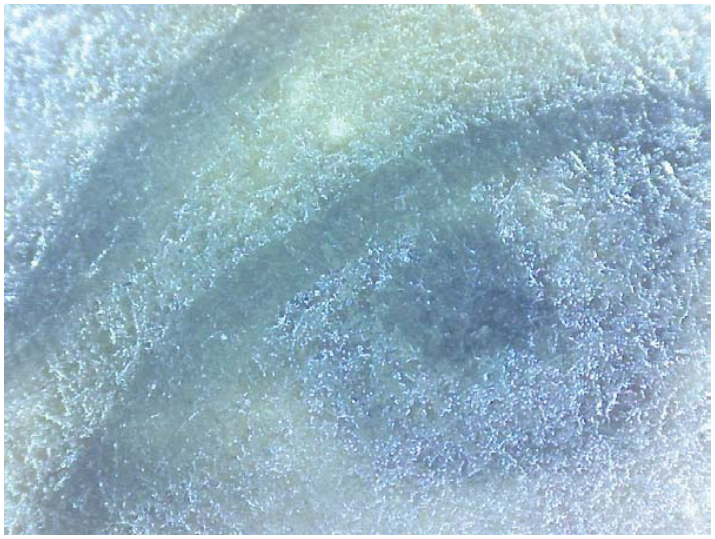
COLLODIO-CHLORIDE FISSURING

ph.1460 Collodio-Chloride P.O.P.
left: The jagged fissures in the colloid layer are unique to collodion photographs and is a common form of deterioration.
From the collection of The CPC.

SILVER MIRRORING



ph.1449 Gelatine Bromide D.O.P. (hand-coloured)
This image has silver mirroring in the darkest areas of the image. *From the collection of The CPC.*



ph.1449 Gelatine Bromide D.O.P. (hand-coloured)
Detail of areas that had been hand-coloured. The hand coloring has prevented these areas from developing silver mirroring. *From the collection of The CPC.*

CELLULOSE NITRATE NEGATIVE

ph.1466 *above:* Degraded cellulose nitrate negative. Negative has a greasy texture, yellow-orange discolouration, and silver mirroring. *From the collection of The CPC.*

ACETATE NEGATIVE

Api42 (neg. no. Y1367113) *above:* Degraded acetate negative. Negative has the characteristic bubbles and blisters found in degraded acetate negatives.
From the collection of The CPC.