

## A local microscopic model for the formation of silver mirroring on black and white photographs

G. Di Pietro <sup>a,1</sup>

<sup>a</sup> Division of Health, Science and Design, University of Canberra, Canberra ACT 2601 Australia

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### Abstract (English)

Black and white photographs are made of a gelatine emulsion containing silver grains laid on a support material that can be glass, plastic or paper. Due to the small size of the silver grains, the corrosion of the silver grains is the starting point for a variety of degradation forms appearing visually different like yellowing, silver mirroring and red spots. In this paper we focus our attention on the formation of silver mirroring, a bluish metallic sheen commonly seen on silver gelatine glass negatives. As a result of the analysis of the composition of the silver mirroring particles and of the structure of the silver mirroring layer we suggest a modification of the current model for the formation of silver mirroring. This model enables us to understand what are the characteristics that differentiate the formation of silver mirroring from the formation of other corrosion based photographic degradation forms.

### Résumé

Les photographies en noir et blanc sont constituées d'une émulsion de gélatine contenant des grains d'argent, étalée sur un support matériel constitué de verre, ou bien de plastique ou encore de papier. Les grains d'argent connaissent un processus de corrosion qui, à cause de la petite taille des grains, aboutit à différentes formes de dégradation se manifestant visuellement de plusieurs façons, comme le jaunissement, le miroir d'argent (*silver mirroring*), et les taches rouges. Cet article porte sur la formation du miroir d'argent, un reflet métallique bleuté communément observé sur les négatifs en verre. Nous proposons une modification du modèle courant de formation du miroir d'argent, basée sur l'analyse de la composition des particules et de la structure de la couche du miroir d'argent. Ce nouveau modèle nous permet d'identifier les caractéristiques qui différencient la formation du miroir d'argent de la formation des autres formes de dégradation des photographies basées sur la corrosion.

*Keywords:* black and white photographs, degradation of photographs, silver mirroring.

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### 1. Introduction

Black and white (B&W) photographs are made of a gelatine emulsion containing silver halide crystals that are turned to silver grains during processing. The emulsion resides on a support material that can be paper, plastic or glass. The silver grains have dimensions of the order of microns and, in photographs chemically developed, a complex dendritic form. Their small dimension and the presence of kinks result in them having a very large surface area. This explains their susceptibility to undergo reactions and corrosion processes. Indeed, the oxidation of the silver grains and the subsequent reduction of their dimension and formation of silver ions in the emulsion are of the basis for at least three visually different degradation forms of B&W photographs: the shift towards a yellow tone in the image areas, the formation of red spots and the formation of silver mirroring, a bluish metallic sheen mostly present at the edges of the photograph (Figure 1).

In this paper we shall focus our attention on the formation of silver mirroring with the aim of understanding the detailed mechanism leading to its formation, and be able to identify which compounds and reaction conditions are likely to result in silver mirroring or in other corrosion based degradation phenomena.

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<sup>1</sup> Corresponding author: TEL: +61 2 62012121: FAX: +61 2 6201 2048: email: [Giovanna.Di.Pietro@canberra.edu.au](mailto:Giovanna.Di.Pietro@canberra.edu.au)



Figure 1 Silver gelatine glass negative with wide silver mirroring stain, partially obscuring the image. Cueni study collection (~1910).

### 1.1 Historical review of the models on silver mirroring formation

The first account of silver mirroring dates back to the 1882 (British Journal of Photography 1982), just two years after the invention of modern B&W photography. Even in these early stages silver mirroring was attributed to the action of hydrogen sulphide (“sulphuretted hydrogen”) (British Journal of Photography 1901), and the formation of silver mirroring was defined as a “slow sulphiding” (British Journal of Photography 1918). A key date in the understanding of the silver mirroring process is 1963. In this year Henn and Wiest (1963) proposed a model, called here the Oxidation-Migration-Re-aggregation model (OMR). According to the OMR model the silver image particles are first oxidized, silver ions are formed, and then migrate in the gelatine. When the silver ions are reduced to silver they either re-aggregate within the emulsion forming small particles appearing as red spots, or they re-aggregate at the emulsion top surface forming silver mirroring. The analysis of the composition of mirrored areas with an electron microprobe concluded that they contain “appreciable but highly variable amounts of silver sulphide”.

Feldman (1981) published the first transmission electron micrographs of mirrored photographs. Later Hendriks of the Public Archives of Canada (Hendriks 1984, Hendriks 1991a), showed, by using TEM images, that silver mirroring not only consists of a layer of colloidal particles clustered at the emulsion top surface but also that mirrored emulsions have a number of signs of corrosion: the image silver grains are smaller, they have a more rounded shape, and they are surrounded by very small particles. The compounds responsible for such degradation were thought to be a large category of oxidizing and reducing compounds present either in the photograph itself as a result of improper processing, or in the surrounding air, or in the filing enclosure. Although he did not publish results on the chemical composition of the mirroring particles, he believed them to be made of a very thin layer of elementary silver centred on a silver sulphide nucleus. The mechanism leading to the formation of a surface layer of particles, the peculiarity of silver mirroring, was not explained in detail. An attempt to solve this matter was done by Nielsen and Lavedrine (Nielsen and Lavedrine 1993) who showed by analysing TEM images that underneath the mirroring layer a distribution of smaller particles existed. Such particles are considered to be proof for a migration of the silver salts towards the surface although no driving force for this movement was suggested.

### 1.2 Open questions

In conclusion: the OMR model and its subsequent refinements still leave two main questions unanswered regarding the formation of silver mirroring. These are: the chemical composition of the silver mirroring particles and the driving force for the formation and /or aggregation of particles at the emulsion top surface.

Answering the first question is crucial in understanding which compounds are actually responsible for the formation of silver mirroring. If the silver mirroring particles are made of elementary silver (Ag) then the compounds responsible for silver mirroring, apart from oxidant compounds, have to be searched for among silver reducing substances (e.g. aldehydes) while if they are made of silver sulphide (Ag<sub>2</sub>S) they have to be searched for among sulphur containing substances (e.g. hydrogen sulphide H<sub>2</sub>S).

Answering the second question is crucial to distinguishing the formation of silver mirroring, which microscopically has been shown to be layer of colloidal particles clustered at the emulsion top surface, from the other corrosion based degradation forms of black and white photographs, which microscopically consist of small particles aggregated within the emulsion bulk.

The first question will be answered by analysing the chemical composition of the silver mirroring layer.

The second question will be answered by analysing the particle shape and the density of the particle distribution underneath the mirroring layer. The particle shape and the density of particles are properties inherited by the mechanism of formation of silver mirroring. A surface layer of particles, like silver mirroring, can result either from particles formed within the emulsion bulk and then migrating towards the emulsion surface or from particles formed directly at the emulsion surface. These two mechanisms lead to two different trends for the particle shape. In the first case, the particle shape is predicted to be spherical at great distances from the surface and ellipsoidal close to the surface as colloidal particles cannot escape from the emulsion and cluster once their spatial density is sufficiently high. In the second case, particles would be formed by the reaction between silver ions, results of the oxidation of the image grains, and an external compound and, as the reaction has not a preferred direction, their shape is predicted to be spherical at any distance from the surface.

## 2. Experimental Procedure

The following experiments were performed on silver gelatine glass negatives. These formed the most common class of negative photographic processes between the 1880s and the 1920s. Silver gelatine glass negatives are particularly prone to silver mirroring because they have a relatively thick, non-hardened emulsion, and because they were mostly not lacquered. The negatives examined belong to the Cueni study collection, a collection of about 150 glass plate negatives of the Swiss painter and amateur photographer Adolf Cueni active in the Basel region in the years 1910s -1920s. The Laboratory of Image and Media Technology of the University of Basel presently owns the plates.

### 2.1 Chemical composition of silver mirroring

The spectroscopic methods suited to determine the chemical composition of silver mirroring have to fulfil two requisites. The first requisite is that they have to distinguish between compounds present in the mirroring layer, with thicknesses of the order of hundred nanometres, and compounds present in the emulsion bulk, of thickness of the order of fifty microns. The second requirement is that they have to be able to detect silver sulphide, which means either determination of the amount of sulphur and silver in the mirroring layer or detection of the presence of silver sulphide directly. The simple detection of sulphur is not sufficient to draw definitive conclusions because sulphur compounds can arise from the protein cystine, one of the constituent proteins of the gelatine, and from the incomplete removal of sodium thiosulphate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>), the usual fixing agent.

These criteria suggested that successful analysing techniques might be X-Ray Diffractometry (XRD) on powder samples and X-Ray Photoelectron Spectroscopy (XPS). Both techniques satisfy the second criteria because XRD detects the crystalline structure of silver sulphide and XPS provides quantitative results of the sample atomic composition. Moreover, XPS is a truly surface analysis because the electrons used in the apparatus have energy of only few hundreds of electron volts. This energy is so small that uniquely the electrons emitted from atoms distant at maximum 10 nanometres from the sample surface can escape and be detected. X-Ray Diffraction on the surface of mirrored emulsions and Scanning Electron Microscopy with Energy Dispersive X-ray analysis (SEM-EDX) were also tested but did not give reliable results. Indeed the penetration depth of X-rays with energies of the order of 8 KeV (typical of the XRD apparatus) and the penetration depth of electrons with energy of 20 KeV (typical of the SEM apparatus) largely exceed the thickness of silver mirroring layer. Table 1 summarizes the spectroscopic analyses performed.

### XRD analysis

The XRD analysis on powder samples was performed at the XRD facilities of the Netherlands Institute for Cultural Heritage (ICN), Amsterdam, under the supervision of Mr. P. Hallebeek. The XRD instrument is composed of an X-ray generator (Philips PW 1010) using a CuK $\alpha$  X-Ray source at wavelength  $\lambda=1.5406 \text{ \AA}$  and energy  $E=8.041 \text{ keV}$  and of a Debye-Scherrer powder camera with a double coated CEA Reflex 25 film. The sample, consisting of few powder grains, is fixed on the tip of a glass fibre with cedar oil and it is continuously rotated during the measuring time (order of a few hours) to cover all the possible mutual positions between the incoming beam and the crystal planes within the sample. This instrument is able to detect the crystal composition of extremely minute amount of sample, of dimension of the order of  $0.5 \text{ mm}^2$ . The silver mirroring was scratched off the plates with a scalpel under a loupe, with careful attention in removing only the mirroring layer and not the underlying emulsion. The total amount of material was of the order of few powder grains.

### XPS analysis

The measurements were performed at the XPS laboratory, Institute of Physics, University of Basel, under the direction of Prof. P. Oelhafen with an in-house built XPS apparatus. The samples, of dimensions approximately of  $1\text{cm} \times 2 \text{ cm}$ , are fixed with metal screws on a metal holder and inserted in the spectrometer where an air pressure of  $10^{-9}$  millibar is reached in 10 hours. In spite of the high vacuum attained during the measurement, no damage was visible on the samples. The samples are then bombarded with X-ray and the spectra recorded in a few minutes. Due to high surface charging effects it was possible to record spectra only from the silver mirroring areas close to the metal screws. In these areas the surface charging was minimised because the electrons could diffuse to the metal holder and dissipate. The percentage atomic composition  $M_i$  of the sample can be calculated from the XPS spectrum (a graph of the number of the emitted electrons against the detected energies) because the area  $A_i$  of the peaks is proportional to the amount of atoms ejecting the electrons. It is given by the following formula:

$$M_i = \frac{A_i}{C_i} \times \frac{1}{\sum \frac{A_i}{C_i}} \quad [1]$$

where  $C_i$  is the photoionization cross-section for the atomic core electron  $i$

**Table 1 Spectroscopic analyses**

Samples	Analysis
<b>Plate 1</b>	
1a	XRD powder
<b>Plate 2</b>	
2a	XRD powder
2b	XRD flat
2c	XPS flat
2d	SEM-EDX
<b>Plate 3</b>	
3a	XRD flat
3b	XPS flat
<b>Plate 4</b>	
4a	SEM-EDX

## **2.2 Size and shape distributions of the silver mirroring particles**

The size and shape distributions of the silver mirroring particles were analysed by using Transmission Electron Micrographs (TEM) with a LEO EM 912 microscope available at the Interdivisional Electron Microscopy Laboratory of the University of Basel. Small portions (dimension  $1 \times 2 \text{ mm}^2$ ) of mirrored emulsion of a historical non-processed glass negative were removed by immersing the plate in a solution of water and alcohol and using a knife blade and tweezers under the loupe. The samples were then embedded in a resin, a standard mixture of epoxy embedding medium,

hardener (DDSA and MNA) and accelerator (BDMA) all produced by Fluka. They were laid flat on a resin drop and, after removing the water in excess on the emulsion, they were covered with a second drop of resin and inserted in an oven at 60 degrees for about 8 hours. Afterwards, slices of 70 nm thickness were cut in the cross-section direction with an ultra microtome. The slices were transferred on a grid and they were inserted in the microscope where images with magnification of the order of 10000 times were taken. As the negative was a non-processed plate, long electron exposures had to be avoided in order not to develop the silver bromide grains physically. The TEM micrographs were digitised and the digital images analysed with the software NIH Image®. The software Mathematica® was used in the statistics analysis of the data.

### 3 Results

#### 3.1 Results on the chemical composition of silver mirroring

The XRD analysis on powder samples has shown that the silver mirroring scratched off from plates 1 and 2 is composed at 100% of silver sulphide  $\text{Ag}_2\text{S}$ . No other crystalline compounds were detected. In the case of the detection of a single compound the error in the mass composition of the sample attained by the instrument used in this measurement is of the order of 5-10%.

The XPS analysis revealed in sample 2c (Figure 2) the presence of the following elements: carbon C (40%), oxygen O (11%), silver Ag (29%), sulphur S (14%), iodine I (4%) and mercury Hg (2%). The percentages refer to the relative atomic composition and are calculated from the spectra using formula [1]. In sample 3b carbon C (49%), oxygen O (10.5%), silver Ag (25%), sulphur S (11%), bromine Br (3%), iodine (1%) and mercury Hg (0.5%) were detected. As the spectral resolution of the spectrometer, measured as the full width at half maximum (FWHM) of the Ag 3d5/2 core-level signal is 0.93 eV, the error in the atomic composition is of the order of 10%.

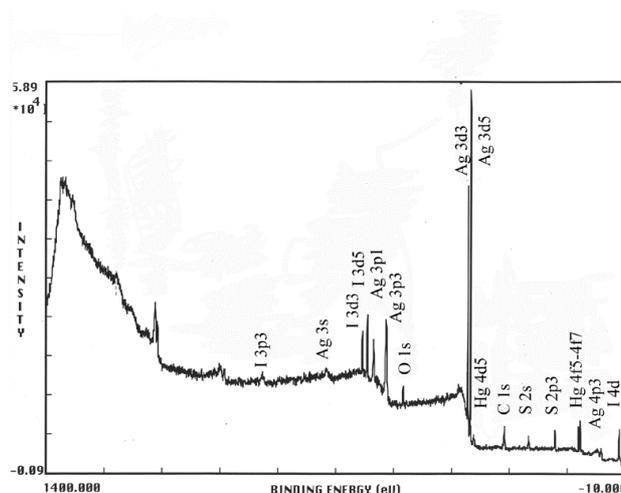


Figure 2. XPS spectrum of sample 2c.

In both samples the main component is carbon, arising from the collagen contained in the gelatine emulsion. Other major constituents are silver and sulphur. The ratio between the amount of silver and the amount of sulphur in the mirrored areas ranges between 2.07 and 2.27: almost the stoichiometric ratio for silver sulphide  $\text{Ag}_2\text{S}$ . Moreover the S(2p) peak has in both cases a negative shift (ranging from -4.5 to -6.3 eV) suggesting that sulphur is in the  $\text{S}^{2-}$  state (Hammond et al. 1975). This indicates that silver sulphide is present in the mirroring areas. The detected amount of oxygen arises probably from the collagen present in the emulsion; indeed, the absence of the O(1s) peak at 529 eV excludes the presence of silver oxide  $\text{AgO}$  or silver dioxide  $\text{Ag}_2\text{O}$ . The presence of bromine in sample 3b is consistent with the fact that plate 3 is a non-processed negative.

The results are summarized in Table 2.

**Table 2 Results of the analysis of the chemical composition of silver mirroring**

Sample	XRD Powder	XPS
1a	Ag <sub>2</sub> S	
2a	Ag <sub>2</sub> S	
2c		Ag <sub>2</sub> S O,C,I,Hg
3b		Ag <sub>2</sub> S O,C,Br,I,Hg

### 3.2. Results on the size and shape distribution of the silver mirroring particles

The samples were difficult to cut because of the softness of the specimen core. Although the slices often broke apart after cutting, it was possible to obtain some sections suitable for the analysis of the particle distribution (Figure 3).

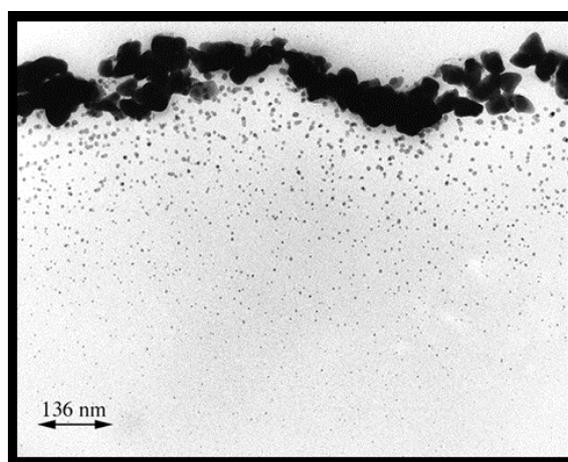


Figure 3. TEM micrograph of the cross-section of a mirrored area on a non-processed glass negative

The micrograph shown in Figure 3 was digitised and used to analyse the variation of area, density and sphericity of the small silver mirroring particles residing underneath the main layer. With the help of the software Adobe® Photoshop® the upper silver mirroring particles were removed and the image was divided in five stripes. With the help of the software NIH Image® each stripe was converted in a binary (black-white) image (Figure 4).

In each stripe the particles were counted and the particle mean area  $a$  (cm<sup>2</sup>) and the length of the axes of the ellipse best fitting each particle were calculated. Figure 5 show the resulting depth profile of the silver mirroring spatial particle density while Figure 6 show the resulting depth profile of spherical and ellipsoidal particles. The percentage of spherical particles (star symbols) is almost constant in the emulsion and equal to the 60%. The particles with axes ratio bigger than two (triangle symbols) are always less than the 20% and show a slight increase in the uppermost 200 nm.

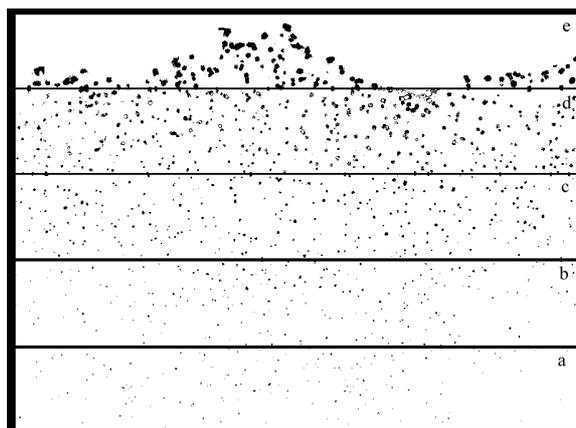


Figure 4. Result of the division in five stripes and of the binary conversion of Figure 3.

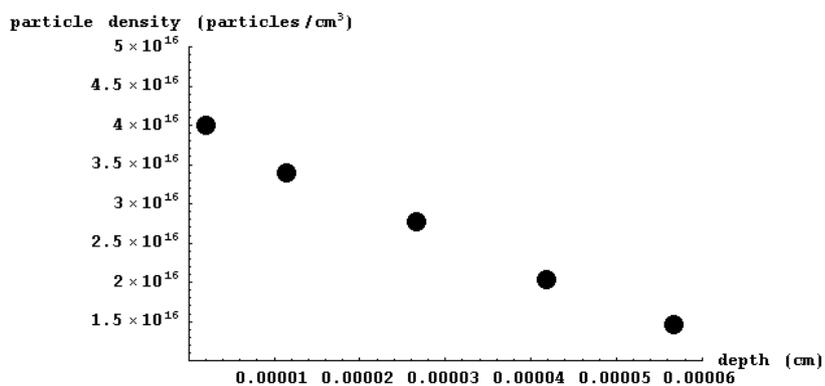


Figure 5. Depth profile of silver mirroring particle density.

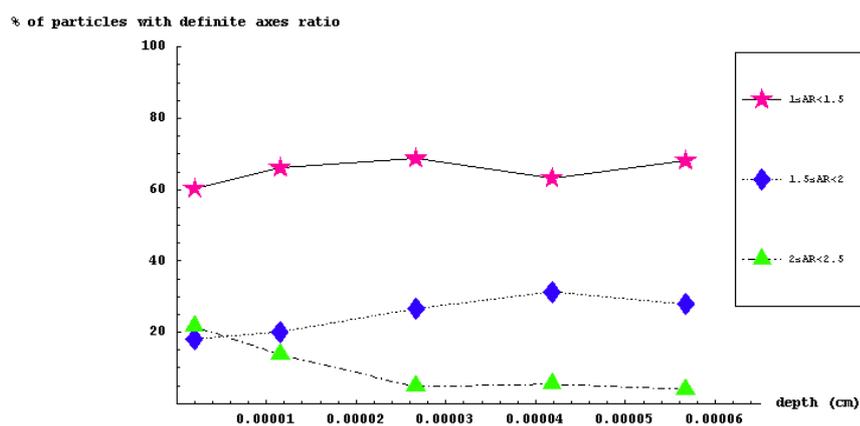


Figure 6. Depth profile of the percentage of spherical (with ratio between the lengths of the ellipse axes between 1 and 1.5) and ellipsoidal particles.

#### 4. Discussion

The experiments have shown that the material contributing to silver mirroring is silver sulphide and that the majority of the particles beneath the main silver mirroring layer have a spherical shape up to the area closest to the emulsion surface. This allows us concluding that silver mirroring is due to the reaction between silver ions, product of the oxidation of the image grains, with environmental sulphur containing compound, possibly hydrogen sulphide, and that this reaction takes place at the emulsion top surface. On the contrary yellow discoloration takes place if the reactants are present within the emulsion. This happens either if they are the result of processing steps, so they are somehow born with the photograph, or if they can penetrate into the emulsion due to their high solubility and to their low reaction rates.

The OMR model for the formation of silver mirroring can be modified in a model consisting of the following steps: Oxidation, Diffusion of silver ions, Reaction with external sulphur compounds and Growth of silver sulphide particles (ODRG).

##### Oxidation

As in the classic OMR model the first step in the formation of silver mirroring is the oxidation of the image silver grains. This step has already been described in detail by other authors (Henn and Wiest 1963, Brandt 1987, Hendriks 1991b). Here I add only two comments relative to the case in which the oxidant compound is hydrogen peroxide.

For hydrogen peroxide partial pressures typically found in museums (of the order of ppbs), the amount of hydrogen peroxide dissolved in an emulsion is of the order of  $10^{-6}$  mol cm<sup>-3</sup>, which is calculated assuming that the hydrogen peroxide is dissolved in the water contained in the emulsion and applying the Henry's law [2]:

$$c_0 = p \times H^* \times mc \times W_{H_2O_2} \quad [2]$$

where p is the partial pressure of hydrogen peroxide, H\* is the Henry's coefficient ( $H^* = 1.8 \times 10^2$  mol cm<sup>-3</sup> atm<sup>-1</sup>), mc (-) is the moisture content of the gelatine and  $W_{H_2O_2}$  (g mol<sup>-1</sup>) is the molecular weight of hydrogen peroxide ( $W_{H_2O_2} = 34$  g mol<sup>-1</sup>). The amount of hydrogen peroxide dissolved in the emulsion is two orders of magnitude lower than the amount of silver on average found in an emulsion, of the order of  $10^{-2}$  g cm<sup>-3</sup>, which corresponds to  $2 \times 10^{-4}$  mol cm<sup>-3</sup>. This means that the oxidation step is always under the control of the amount of hydrogen peroxide

The second comment is concerned with the trend of the amount of hydrogen peroxide dissolved in the emulsion with changing relative humidity and changing degree of gelatine cross-linking. This follows the trend of the moisture content of gelatine (McCormick-Goodhart 1995, Yapel et al. 1994) and it is plotted in Figure 7.

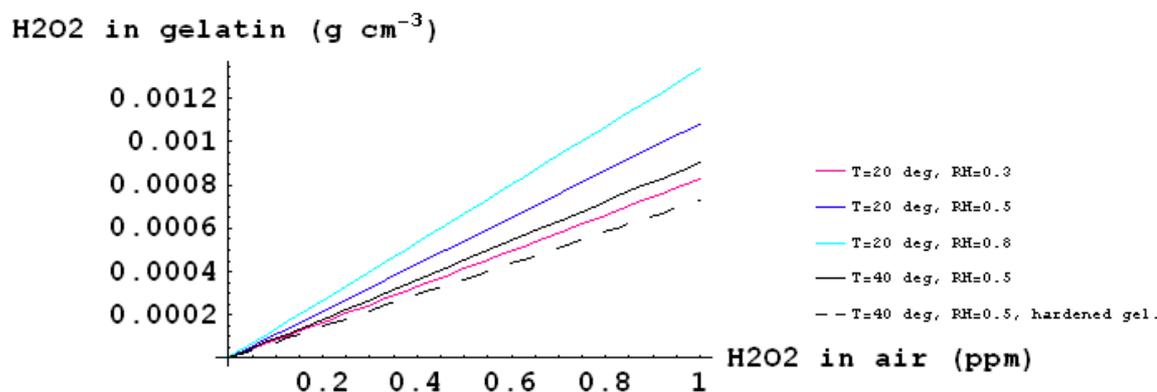


Figure 7. Equilibrium hydrogen peroxide concentration in the emulsion against hydrogen peroxide partial pressure in air for different RH, T and degree of gelatine cross-linking.

### Diffusion of silver ions

The second step in the formation of silver mirroring is the diffusion of silver ions in the gelatine driven by the difference of silver ion concentration between the areas closest to the image silver grains and the emulsion bulk. The diffusion of silver ions in water-soaked emulsions is very fast. Curtis and Leait (1998) report that in wet gelatine gel at room temperature the diffusion constant of silver ions  $D(\text{Ag}^+)$  is  $1.6 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ . However, silver mirroring is formed in normal museum conditions where the moisture content of the emulsion is of the order of 20% maximum. From the work of Tanaka and co-workers (1973) on the conductivity  $K$  ( $\text{ohm}^{-1} \text{ cm}^{-1}$ ) and the silver ions transport number  $\tau(-)$  in silver-silver nitrate ( $\text{AgNO}_3$ ) films kept at 79% RH and 25° C the diffusion constant of silver ions can be calculated (Moore 1972, chapter 10 sec. 13):

$$D(\text{Ag}^+) = \frac{RT}{F^2} \times \frac{K_{\text{tot}} \times \tau}{m(\text{Ag}^+)} \quad [3]$$

where  $R$  is the gas constant ( $R = 8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$ ),  $T$  (K) is the absolute temperature,  $F$  is the Faraday constant ( $F = 96487 \text{ C mol}^{-1}$ ),  $K_{\text{tot}}$  ( $\Omega^{-1} \text{ cm}^{-1}$ ) is the total film conductivity and  $m(\text{Ag}^+)$  ( $\text{mol cm}^{-3}$ ) is the silver ions molar concentration in the film.

Inserting Tanaka's data for  $\tau$ ,  $K_{\text{tot}}$  and  $m(\text{Ag}^+)$  in equation [3], the diffusion constant of silver ions in gelatine films kept at 79% RH and 25 C results as being of the order of  $5 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ .

Assuming a diffusion law of the kind

$$\Delta L = \sqrt{D \times \Delta t} \quad [4]$$

where  $\Delta L$  (cm) is the space travelled in a time  $\Delta t$  (s) by species with diffusion constant  $D$  ( $\text{cm}^2 \text{ s}^{-1}$ ), silver ions in emulsions at 79% RH and 25° C travel 50  $\mu\text{m}$  (typical emulsion thickness in glass plates) in about 6 days. This time is short in comparison with the observed time scale of silver mirroring formation under normal archive conditions, which is of the order of months or few years maximum. This allows us to conclude that, in typical archive conditions, silver ions diffuse rather fast in the emulsion and they can be responsible of the formation of silver mirroring.

### Reaction with external sulphur compounds

Once silver ions are produced and diffuse homogeneously in the emulsion, they will react with external sulphur based compound to produce silver sulphide seeds. Among environmental gases the most probable gas is hydrogen sulphide  $\text{H}_2\text{S}$ , a second possibility is carbonyl sulphide (OCS).

It is possible to envisage the following pathway for the dissolution of hydrogen sulphide in water followed by the reaction with silver ions:

- a)  $\text{H}_2\text{S} \rightarrow \text{H}^+ + \text{HS}^-$
- b)  $\text{HS}^- \rightarrow \text{H}^+ + \text{S}^{2-}$
- c)  $2 \text{Ag}^+ + \text{S}^{2-} \rightarrow \text{Ag}_2\text{S}$

As the solubility constant of silver sulphide is very low ( $k_{\text{sp}} = [\text{Ag}^+]^2 \times [\text{S}^{2-}] = 6.89 \times 10^{-50}$ ), precipitation of silver sulphide will occur as soon as  $\text{S}^{2-}$  ions will be in solution. This, added to the fact that the emulsion surface is the region where the reactants first meet, explains why silver sulphide seeds are produced at the emulsion upper surface and not in the emulsion bulk.

### Growth of silver sulphide particles

The final step in the formation of silver mirroring is the growth of the silver sulphide particles. The silver sulphide seeds grow because of the reaction between silver ions and hydrogen sulphide molecules on them. The reaction does not have a preferential direction, therefore the final shape of the particles is spherical. Further exposure to hydrogen sulphide will provoke the growth of the seeds without increasing of their number. This is supported by two different kinds of studies found in the literature. The first kind of studies is concerned with the tarnishing of silver plates. Bennet and co-workers (1969) have shown that silver sulphide clumps on silver plates nucleated on initial exposure to hydrogen sulphide and that further reaction occurred on the initially formed clumps. Graedel and co-workers (1985) also report the same reaction dynamics.

The second kind of studies is related to the photographic processes called diffusion transfer processes (typically used in Polaroid photographs). In these processes silver sulphide particles are used to catalyse the reaction between the developer and the silver ions (James 1939, Eggert 1947, Shuman and James 1971, Levenson and Twist 1973) either by adsorbing the developer onto the colloidal particles, or by stabilising a single silver atom using the electrical conductivity of the colloidal particle. The

stabilisation of silver atoms by silver aggregates has also been the object of more recent studies<sup>2</sup>. Although diffusion transfer processes differ from silver mirroring because the reaction takes place between silver ions and hydrogen sulphide instead of between silver ions and developer, colloidal silver sulphide particles could play the same catalytic function.

The difference of size between the particles at the interface emulsion-air and the particles underneath can be explained because the particles at the interface grow relatively fast as they are directly exposed to the environmental hydrogen sulphide and the more they grow, the more they fill the emulsion surface hindering the penetration of the gas into the emulsion. When the surface is completely covered, the amount of hydrogen sulphide entering the emulsion is zero and the growth of the particles underneath the surface is blocked.

### Conclusions

This work allows us to conclude that silver mirroring is formed of a surface layer of silver sulphide particles a result of the reaction between silver ions and an environmental sulphur based compound, most probably hydrogen sulphide

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<sup>2</sup> It has been shown (for a review see Henglin (1993)) that the electrochemical potential for the reaction  $\text{Ag}^+ + e^- \rightarrow \text{TAg}^0$  is very low for single ions (-1.8 V) and it increases with the size of the silver aggregates till the value assumed on the solid metal (+ 0.799 V). For small silver aggregates quantum effects have been taken into account (Belloni et al. 1991) while for aggregates bigger than 1 nm a simple surface energy effect explains this behaviour (Plieth 1982).

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