Bull. Soc. Photogr. Imag. Japan. (2014) Vol. 24 No. 1: 6–11

Original Paper

Method for Increasing the Durability of Transcribed Gold-Layer Photographs

Ken'ichi KUGE* and Kenta NOJO*

Abstract: Baking conditions for the preparation of gold-layer photographs via transcription on a porcelain base were investigated with the aim of increasing the durability of the photographs. It was found that increasing the maximum baking temperature increased the durability of the gold layer against scratching. This increase, however, brought about a reddening of the image and a decrease in the maximum optical reflection density. Images from the photographs that were baked above 900°C were retained even after scratching the photograph with sandpaper or dissolution of the gold layer in a tincture of iodine. It is proposed that the glaze layer on the porcelain base softened up after baking at temperatures above 800–900°C and that the gold layer gradually sank into the glaze layer. At the same time, the boundary between the gold and glaze layers fused, increasing the adherence of the gold layer to the glaze layer.

Key words: Silver-salt photography, Image preservation, Photographic printing paper, Gold, Baking

1. Introduction

Photographs are created with the aim of preserving images so that the images can be viewed later. The progress of photographic technology has always been associated with problems in image preservation. Recently, the development of digital photographic system has given rise to a new problem of digital data preservation [1]. The fact that black-and-white photographs taken in the early stages exist today has shown their high capability for preservation, and it is expected that the lifetime of these photographs is more than 500 years [2) 3)]. However, as of now, it is not possible to preserve these photographs for extremely long periods of time, e.g. beyond 1000 years, as is observed in the case of stone monuments such as the Rosetta stone.

To address this problem, we developed the gold-deposition development method [4)–10)] and created a gold-layer photograph by altering the image with gold particles deposited on a ceramic base through baking [11)–15)]. Because they consist of a gold layer and a ceramic base, which are both chemically stable, these gold-layer photographs are expected to be preserved for extremely long periods. Moreover, we developed a method for creating a transcribed gold-layer photograph by pasting printed paper with an image made of gold particles onto a heat-resistant base and baking it [16)]. This method does not require the initial preparation of photographic materials with heat-resistant bases. Further, this method also generates chemically stable photographs because these photographs consist of only a gold layer and a stable base.

The gold-layer photographs and the transcribed gold-layer photographs prepared by the above-mentioned methods had a drawback, however: the adhesion of the gold layer to the base was not strong enough, and the image could easily be damaged by scratching. Moreover, when such a gold-layer photograph is immersed in water for long periods of time, the gold layer is gradually exfoliated from the base [17)]. Unless these shortcomings are overcome, these photographs cannot be preserved for extremely long time periods. In this study, we investigated the baking conditions used in preparing a transcribed gold-layer photograph on a porcelain base. The aim was to determine the conditions under which the gold layer would firmly adhere to the base, so that transcribed gold-layer photographs with high durability can be produced.

2. Experimental method

Baryta printing paper (Lodima Photo Paper) was used to prepare photographic images composed of gold particles*. Gold deposition was performed on the papers with either stepwise exposure or uniform exposure. In the stepwise-exposure process, the area to be exposed was divided into several parts and the light exposure for each part was increased in a stepwise fashion. The conditions used for the gold-deposition development were the same as reported previously [16)]. The formula for the development is shown in Table 1.

The printing papers were pasted on a base of white porcelain tile by using 0.8–2% gelatin solution as an adhesive. Normally, we used the 0.8% solution, but we increased the concentration gradually to 2%, when a warp in the paper increased. The printed side of the paper was kept in contact with the base. After baking in an electric furnace, the paper base and the gelatin in the emulsion layer burned out and the gold particles melted, thus a transcribed

Received 10th, September 2013; Accepted 8th, May 2014

*Graduate School of Advanced Integration Science, Chiba University, 1-33, Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

Table 1. Formula for gold deposition development

Reagent solution	Concentration	Amount
Solution A		
KSCN	0.1 mol/L	40 mL
$NaAuCl_4 \cdot 2H_2O$	0.05 mol/L	20 mL
KBr	0.8 mol/L	10 mL
Water to make		900 mL
Solution B		
Ascorbic acid	0.1 mol/L	100 mL

The solutions A and B were mixed and immediately used for development.

gold-layer photograph was created. The temperature inside the furnace was raised in two steps, as described previously [13]. In the first step, the rate of temperature increase and final temperature were 60°C/h and 420°C, respectively. This final temperature was maintained for 1 h before starting the second step. In the second step, the rate of temperature increase was 120°C/h and the final temperature varied from 700°C to 1100°C. The samples were allowed to cool down in the furnace after being held at the final temperature for 3 h.

The durability against scratching of the gold layer on the photographs was evaluated by two methods. In the first method, the gold layer was rubbed 50 times with a wet, hard scourer by hand at a constant power throughout**. In the second method, the gold layer was scratched 50 times with sandpaper (No. 1500) with the same procedure as the first method.

The durability of the images in water was evaluated as follows. The photographs were immersed in warm water at 60°C for a certain period of time. Their optical reflection density (OD) was then measured, and then the gold layer was rubbed with a scourer and the exfoliation of the gold layer was examined visually. The durability of the images in other solutions, including acetic acid, sodium carbonate, and surfactant (Drywell, Fujifilm) solutions, were also evaluated by the same method. The ODs of the gold-layer photograph on the printing paper before baking and the transcribed gold-layer photograph after baking were measured with a densitometer (Model 2119, Abe Design). The reflection spectra of the photographs were measured with a spectrophotometer (UV-2550PC, Shimadzu).

The dissolution of the gold layer was examined by immersing the photograph in a tincture of iodine, which can dissolve gold. This iodine tincture was prepared by dissolving 6 g of iodine and 4 g of potassium iodide in a mixture of 70 mL ethanol and 30 mL water.

3. Experimental results

The photographic characteristic curves for the gold-particle photographs on printing paper before baking and the transcribed gold-layer photographs after baking are shown in Fig. 1. The final baking temperature was varied between 700°C and 900°C. The maximum OD of the gold-layer photographs was lower than those of the images on the printing paper measured before baking. This decrease in the maximum values of ODs after baking became notable as the baking temperature was increased. Moreover, this decrease in OD resulted in a reduction in the contrast of the photographs. The surface of glaze layer in areas without gold layer coverage became rough after baking at 900°C or higher, resulting in a decrease in surface luster.

Changes in OD of the transcribed gold-layer photographs baked at 700–1100°C caused by rubbing with a scourer or scratching with sandpaper for 50 times are shown in Fig. 2. The higher the baking temperature was, the lower the OD measured after baking became. Thus, the largest decrease in OD was observed for the sample baked at 1100°C. No significant decrease in OD was observed after rubbing the baked photographs with a scourer. On the other hand, the OD drastically decreased after scratching with the sandpaper for the samples baked at 700–750°C. In this case, the gold layer was removed upon scratching, revealing the white surface of the tile base. The decrease in OD due to sandpaper damage became smaller with increasing baking temperature. The OD hardly changed for the sample baked at 1100°C, although the OD of this sample was already decreased significantly due to the baking.

Images of the photograph surfaces observed with an optical microscope are shown in Fig. 3. It can be seen that the gold layer of the photograph baked at 700°C was almost completely removed down to the white surface of the tile base after scratching it with the sandpaper. In contrast, a large part of gold layer still remained and the area of white base was smaller for the sample baked at 800°C. The white base is not visible for the sample baked at 900°C and the gold layer remains on the all observed areas.

The ODs of the samples baked at 700–900°C observed after various repetitions of sandpaper scratching are shown in Fig. 4. The OD decreased more rapidly for the sample that was baked at 700°C than the sample baked at 800°C. Compared to these results, the OD for the sample baked at 900°C decreased only slightly with increasing sandpaper scratching times. This tendency is similar to the trend observed in Fig. 2.

The reflection spectra before and after scratching with sandpaper 50 times are shown in Fig. 5. Reflectance increased as baking temperature rose. Relatively higher reflectance was observed in the wavelengths region of longer than 550 nm. These spectral

* When the printing paper of a resin coat (RC) is used, a thin layer of titanium oxide, which is included in the paper base [19], is formed upon baking. This layer emits interference light, and the gold-layer image is hidden by this light. On the other hand, barium sulfate contained in the base of the baryta printing paper [20] is in a powder form and is removed easily by baking.

** The loads applied upon rubbing or scratching were not measured because these treatments were carried out by hand. However, the same person always carried out this process to ensure the same load was applied each time.

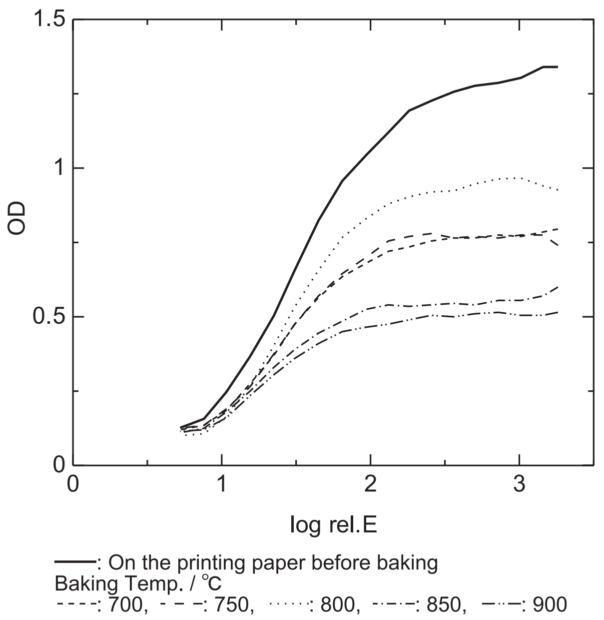

Fig. 1. Photographic characteristic curves of transcribed gold-layer photographs baked at different temperatures. The solid line shows the curve for the printing paper before transcribing and baking; the dashed lines are for after transcribing and baking.

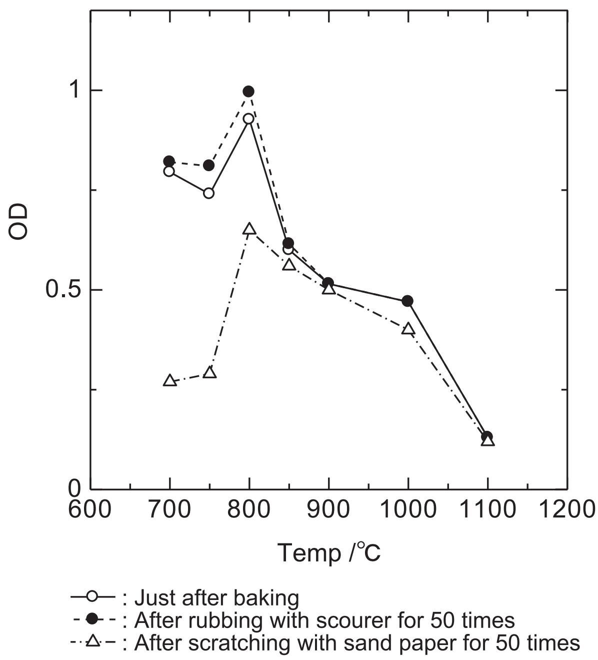

Fig. 2. Changes in optical density of the transcribed gold-layer photographs prepared at different baking temperatures caused by rubbing with a scourer or scratching with sandpaper for 50 times.

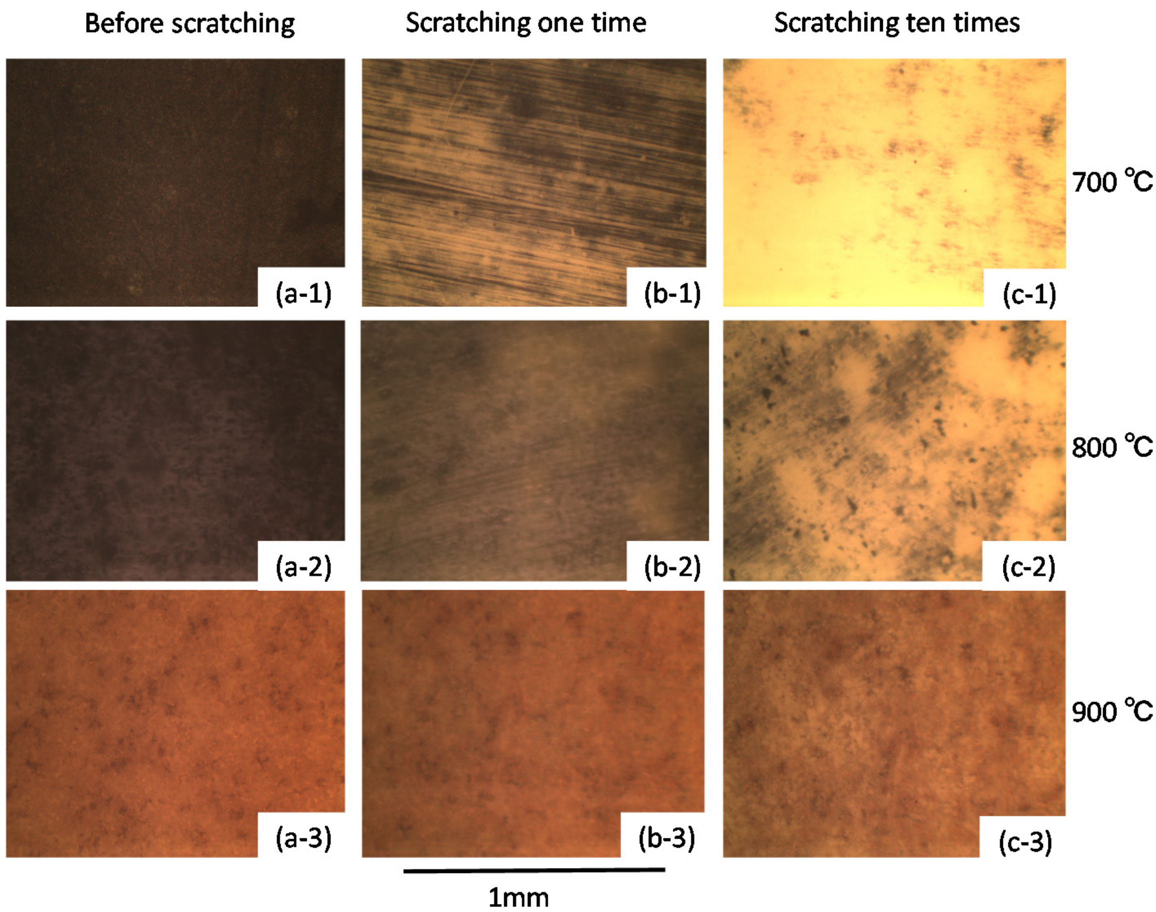

Fig. 3. Optical micrographs of the surface of transcribed gold-layer photographs. The gold-layer photographs were prepared at different baking temperatures. The images on the left (a), center (b), and right (c) columns show the results before scratching with a sandpaper (a), after one-time scratching (b), and after 10-times scratching (c), respectively. The top (1), middle (2), and bottom (3) rows show the results for baking at 700, 800, and 900°C, respectively.

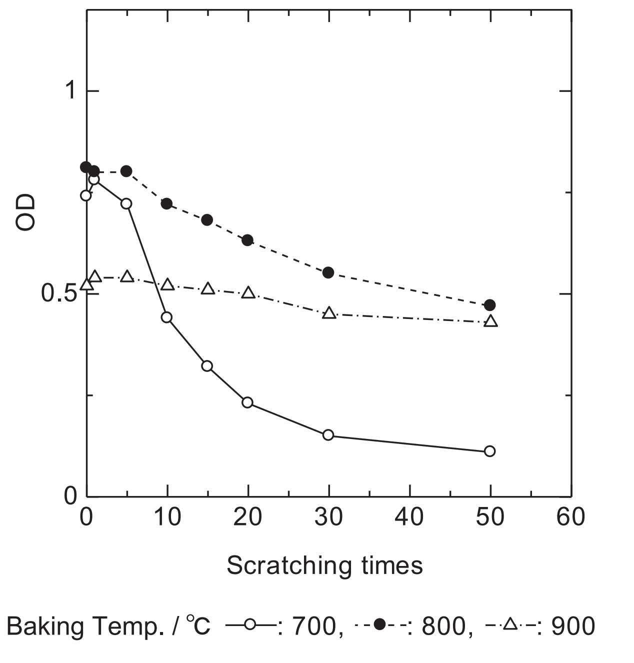

Fig. 4. Resistance of transcribed gold-layer photographs prepared at different baking-temperatures to sandpaper scratching represented as a change in optical density with sandpaper-scratching times.

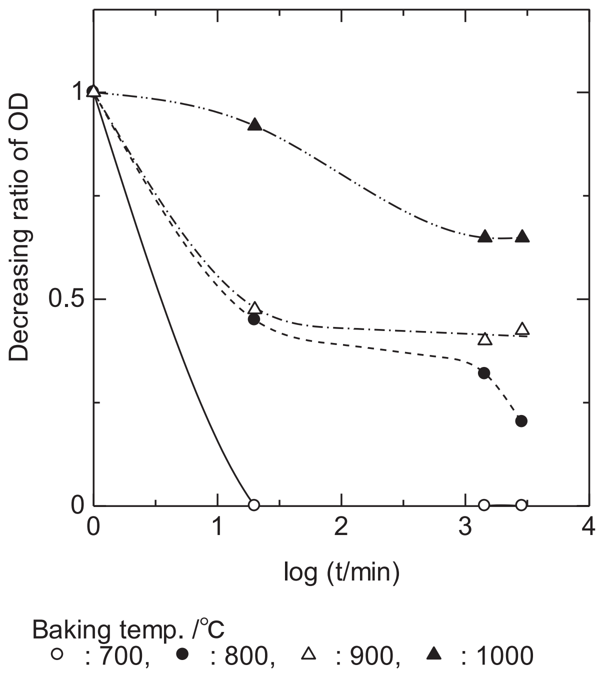

Fig. 6. Decrease in the optical density of transcribed gold-layer photographs baked at different temperatures after immersion in the tincture of iodine for different periods. The decrease is represented as the ratio of OD before and after immersion.

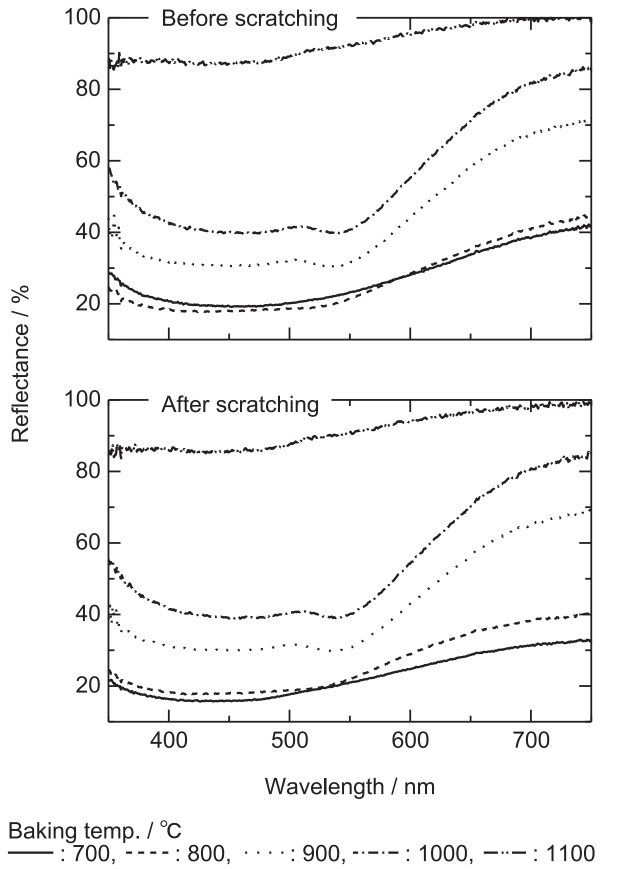

Fig. 5. Reflection spectra of transcribed gold-layer photographs baked at different temperatures. Top: before scratching; bottom: after sandpaper-scratching for 50 times.

characteristics contributed to the decrease in overall OD for samples baked at higher temperatures. Scratching did not result in a large change in the spectra, and therefore, the hue of photographs did not change after scratching.

The results of the analysis of gold layer dissolution by the tincture of iodine are shown in Fig. 6. The tincture dissolves the gold layer if any part of it is uncovered, and when that happens, the white surface of the tile base is revealed. However, if the gold layer is covered with or buried under a protective layer, the immersion in the tincture will not cause any change to the gold layer. Figure 6 shows the ratio of OD before and after immersion versus the immersion period represented on a logarithmic scale. The ratio of OD decreased with time immersed in the tincture of iodine. The gold layer for the sample baked at 700°C almost disappeared after 20 minutes of immersion. For samples baked at higher temperatures, the decrease in the OD ratio became smaller with time and the gold layer was not completely removed.

The characteristic curve for the sample baked at 700°C and immersed for 5 months in warm water is shown in Fig. 7. The OD did not significantly change after immersion in water for this sample. The gold layer on the transcribed photograph did not exfoliate by immersion in pure water. This is contrary to the previous studies [17], in which the gold layer was exfoliated upon immersion in water for a gold-layer photograph prepared directly on a glass plate. Therefore, the method used to transcribe photographs in this study has increased the durability of gold-layer against the immersion in water.

The results of durability of samples baked at different temperatures against the immersion in warm water for certain periods of time are listed in Table 2. For samples baked at 700 and 750°C,

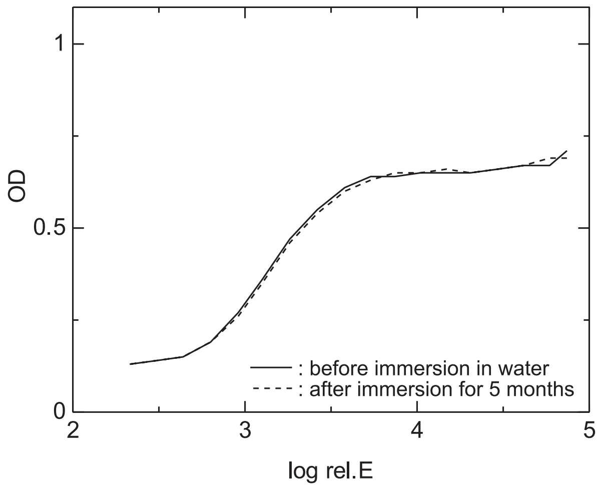

Fig. 7. Photographic characteristic curves of transcribed gold-layer photographs before and after immersion in water at 60°C for 5 months. The gold-layer photographs were baked at 700°C. Solid line: before immersion, dashed line: after immersion.

Table 2. Exfoliation of gold-layer on the photographs by immersion in a water at 60°C for one day or half a year

Baking temperature/°C	Treatment	
	Immersing 1 day and rubbing with a finger	Immersing for a half year and rubbing with a scourer
700	×	—
750	×	—
800	○	△
850	○	○
900	○	○

×: exfoliation, —: no data
△: decrease of density, ○: no change

after one day immersion in water, the gold layer was exfoliated even by soft rubbing with a finger. In contrast, the OD of the samples baked at 850 or 900°C did not change by rubbing with a scourer even after immersion in water for half a year, although a small decrease in OD was observed for the sample baked at 800°C. The immersion in the other solutions examined in this study also showed similar results. It can be stated that high-temperature baking of transcribed gold-layer photographs results in the gold layer adhering strongly to the ceramic base.

4. Discussion

By increasing the baking temperature, resistance to both scratching and immersion in water increased and the durability of the gold layer was enhanced. Normally, porcelains consist of two parts: a porous base and a glassy glaze layer covering the base. The base has high thermal stability, while the glaze layer softens up and then melts above 800–900°C, as evidenced by the increase in roughness and decrease in luster of the surface of glaze layer. However, the glaze layer does not have a definite melting point owing to its glass-like properties.

The gold layer deposited on the glaze layer is not uniformly flat.

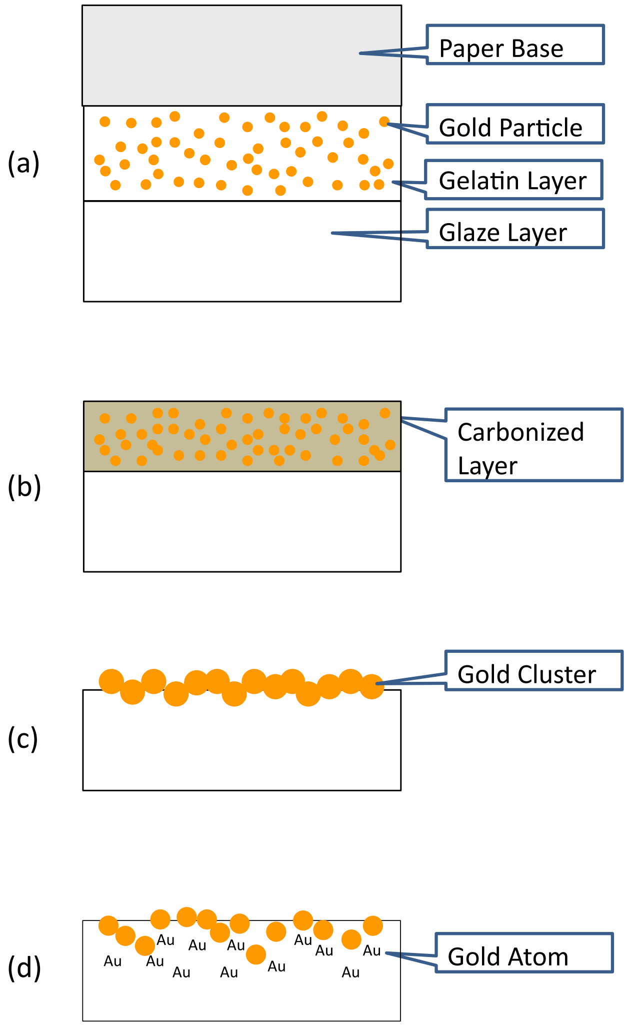

Fig. 8. Schematic diagram of the transcription process for preparing gold-layer photographs, (a) before baking, (b) below 420°C in the first baking step with raising temperature of 60°C/h, (c) above 420°C in the second baking step with raising temperature of 120°C/h, (d) above 800°C after softening up and melting of the glaze layer.

The layer consists of aggregates of gold clusters, which are formed upon sintering of the gold particles [12]. The gold layer has high electric conductivity, and hence the gold clusters are in contact with each other through partial melting at the contact points.

The schematic diagram in Fig. 8 shows the assumed baking process that leads to the formation of transcribed gold-layer photographs. This formation process helps us better understand the mechanisms that lead to an improvement in the durability of the transcribed gold-layer photographs. First, when the sample is baked below 420°C, both the paper base and the gelatin in the emulsion layer are carbonized. Gold particles are dispersed in the carbon layer as well. In the second baking process above 420°C, the carbon layer gradually burns out completely. As the carbon layer decreases in thickness, the gold particles come to contact with each other and form clusters by sintering. Above about 700°C, the clusters melt and begin contacting each other to make a gold layer composed of the aggregates of clusters. At the same time, the glaze layer begins to soften up and some gold clusters sink into the glaze layer. The clusters that are not dissolved in the tincture of iodine increase with the increase in the number of clusters buried in the glaze layer.

At temperatures above 800–900°C the gold layer sinks into the glaze layer and a part of it breaks up into gold clusters. These gold clusters are dispersed in the glaze layer and result in the red color in the photographs, due to the plasmon absorption of the clusters. This results in the increase in the stability of the gold layer or clusters against damage caused by scratching or dissolving. At the same time, some gold atoms in the layer or clusters are gradually dissolved into the glaze layer, because the liquid glaze is a solvent of gold atoms [18]. This dissolving increases with increasing baking temperature. The dissolved atoms do not show any color and this brings about the decrease of OD that is seen for samples baked at higher temperatures. If a layer of a solid solution of a high concentration of gold atoms in the glaze forms at the interface between the gold and the glaze layers, then the boundary between these two layers becomes fuzzy. This lack of a clear boundary between the gold and the glaze layers is indicative of enhanced adherence.

References

1) http://www.oscars.org/science-technology/council/projects/digitaldilemma/ (accessed on line 2013/9/6)
2) K. Ozeki, J. Soc. Photogr. Sci. Tech. Jpn., **71**, 400 (2008) [in Japanese].
3) Y. Teshima, K. Ozeki, J. Soc. Photogr. Sci. Tech. Jpn., **76**, 487 (2013) [in Japanese].
4) K. Kuge, M. Arisawa, N. Aoki, and A. Hasegawa, Jpn. J. Appl. Phys., **39**, 6550 (2000).
5) K. Kuge, K. Kimijima, M. Arisawa, N. Aoki, A. Hasegawa, J. Soc. Photogr. Sci. Tech. Jpn., **64**, 242 (2001) [in Japanese].
6) K. Kuge, K. Suzuki, N. Aoki, A. Hasegawa, J. Soc. Photogr. Sci. Tech. Jpn., **65**, 536 (2002) [in Japanese].
7) K. Kuge, M. Arisawa, N. Aoki, A. Hasegawa, Imaging Sci. J., **52**, 176 (2004).
8) K. Kuge, N. Aoki, S. Saito, O. Hikosaka, A. Hasegawa, J. Imaging Sci. Tech., **51**, 96 (2007).
9) K. Kuge, X. Chen, T. Sakai, A. Hasegawa, J. Imaging Sci. Tech., **54**, 10507 (2010).
10) K. Kuge, Y. Yu, K. Fuma, R. Ito, T. Sakai, Bull. Chem. Soc. Jpn., **84**, 947 (2011).
11) K. Kuge, Y. Goto, T. Nakao, H. Hikosaka, T. Sakai, A. Hasegawa, J. Soc. Photogr. Sci. Tech. Jpn., **67**, 490 (2004) [in Japanese].
12) K. Kuge, Y. Nakanishi, T. Sakai, A. Hasegawa, J. Soc. Photogr. Sci. Tech. Jpn., **71**, 86 (2008) [in Japanese].
13) K. Kuge, A. Takahashi, T. Harada, K. Doi, T. Sakai, J. Soc. Photogr. Sci. Tech. Jpn., **73**, 319 (2010) [in Japanese].
14) K. Kuge, T. Nakao, Y. Goto, T. Omatsu, A. Hasegawa, J. Appl. Phys., **100**, 013102, (2006).
15) K. Kuge, M. Ohki, T. Kobayashi, T. Sakai, T. Nakao, A. Hasegawa, J. Soc. Photogr. Sci. Tech. Jpn., **69**, 276 (2006) [in Japanese].
16) K. Kuge, T. Sakai, K. Doi, J. Soc. Photogr. Sci. Tech. Jpn., **74**, 12 (2011) [in Japanese].
17) K. Kuge, J. Soc. Photogr. Sci. Tech. Jpn., **75**, 416 (2012) [in Japanese].
18) S. Onishi, "Togei no dentou gihou", Rikogakusha, Tokyo, 1978, Chap. 6 [in Japanese].
19) I. B. Current, "Neblette's Handbook of Photography and Reprography", 7th ed., by J. M. Sturge, Van Norstrand Reinhold, New York, 1977, p. 149.
20) I. B. Current, "Neblette's Handbook of Photography and Reprography", 7th ed., by J. M. Sturge, Van Norstrand Reinhold, New York, 1977, p. 151.