Article: THE EVALUATION OF FOUR AQUEOUS AND NON-AQUEOUS SURFACE-CLEANING TECHNIQUES ON SILVER GELATIN PHOTOGRAPHS
Author(s): Penley Knipe
Topics in Photographic Preservation, Volume 7.
Pages: 19-27
Compiler: Robin E. Siegel

Topics in Photographic Preservation is published biannually by the Photographic Materials Group (PMG) of the American Institute for Conservation of Historic & Artistic Works (AIC). A membership benefit of the Photographic Materials Group, *Topics in Photographic Preservation* is primarily comprised of papers presented at PMG meetings and is intended to inform and educate conservation-related disciplines.

THE EVALUATION OF FOUR AQUEOUS AND NON-AQUEOUS SURFACE-CLEANING TECHNIQUES ON SILVER GELATIN PHOTOGRAPHS

Penley Knipe

I. Abstract

This project evaluated four solutions used by conservators to surface clean silver gelatin prints, in terms of both success of cleaning and possible damage caused to the image or substrate. It was completed to fulfill the science project requirement of the second-year of the Winterthur Museum/University of Delaware Program in Art Conservation. Aqueous and non-aqueous techniques of surface cleaning of photographs have derived from both photographic processing methods and paper conservation practices, but have been little studied. This project was selected because the investigation and evaluation of surface cleaning techniques has been identified as one of the primary treatment research needs in the field of photographic conservation. It must be emphasized that this project and subsequent paper are very preliminary; they contribute to the understanding of what tools and techniques are and are not useful for the study of surface cleaning. The matter of effective and safe surface cleaning of photographs deserves much further attention.

II. Introduction

Silver gelatin photographs first were developed as a printing-out process (i.e. contact printing) in 1873 and became popular in the 1880s. In 1895, the discovery of chemical development was made. From this point on silver gelatin photographs dominated the market until color photography, introduced in the 1890s, took over in 1965 (1).

While any photographic material that uses silver as the final image material can exhibit image deterioration, silver gelatin prints, especially those that were developed-out, are particularly susceptible to silver degradation, often called 'silver mirroring'. Silver mirroring is the migration of silver to the surface of the gelatin resulting in a reflective surface. The process is believed to be the result of oxidative gases attacking the silver ions; these ions migrate to the photograph's surface and form metallic silver. At the same time, a limited number of silver salts are being formed (2, 3). Silver gelatin prints are the most susceptible to silver mirroring because the gelatin is quite sensitive to moisture and thus can swell and infuse foreign matter more readily than other photographic processes. The reason that developed-out prints, in particular, are the most susceptible to silver mirroring is not known, as compared with those that are printed-out, though differences in morphology and size of the silver particles are thought to be the reasons.

Photographs can exhibit slight to severe surface grime, as well as a host of other surface related damages such as staining from poor processing, light, or handling. The challenge for conservators of photographic materials is to address these problems in an effective, safe, and controllable way. And while both dry and wet surface cleaning are common treatments, little research has been done into the short and long-term effects. Furthermore, while the surface cleaning of a photograph may be considered routine, it is often challenging and problematic due to the layered structure, the tendency of some layers to swell, particularly gelatin, and the risk of altering the surface character essential to the photograph's integrity.

The questions propelling this research were as follows: How effective were these solutions in reducing surface soil? Was silver inadvertently being removed during the process? Did the solutions adversely effect any of the layers, especially the gelatin binder layer? Was there surface disruption after cleaning?

The objective of this experiment was to look at aqueous and non-aqueous solutions commonly used by photographic conservators to treat damaged gelatin prints exhibiting excessive surface grime. The solutions used were water, water and ethanol, ethanol, and water with Photo-Flo. The tools used to evaluate the research were visual examination, microscopic examination with both a stereo-microscope and a scanning electron microscope (SEM), X-Ray Fluorescence (XRF), and spot tests.

Previous related work includes that by Kathryn Henderson (4, 5). Henderson experimented on 50 silver gelatin photographs with seven different solutions, including 1:1 ethanol/water and Photo-Flo/water, as well as five surfactants common to textile conservation. Photo-Flo in water, at pH 7.5, was found to have the most effective cleaning power with no obvious damage through SEM and chromo-meter observation. Henderson also found that the ethanol/water mixture caused no discernible damage, though the cleaning effectiveness was not as good as the solution with Photo-Flo.

There are a number of other publications relating to surface cleaning techniques and possible problems. The Moors have looked at wet surface cleaning techniques and generally advocate the use of water with silver gelatin prints on paper bases under tested and controlled conditions (6, 7). Hendriks and Rempel briefly discuss techniques of wet surface cleaning and both mention the use of Kodak film cleaner as an option. Hendriks also discusses using distilled water or 1:1 ethanol/water for the removal of greasy dirt (8, 9). Other individuals such as Swan state that wet surface cleaning should be avoided on silver-gelatin photographs because of their tendency to swell and soften (10).

This project overlapped with Henderson's research in that two of the five solutions used were the same. However, Henderson was primarily investigating the effects of surfactants traditionally used on textiles and the work at hand was concerned only with solutions currently being used by photographic conservators. While some conservators might use the solutions to reduce both mirroring and grime, the present research focused on the safe and successful reduction of surface grime. Though the potential removal of silver mirroring was of interest, the ultimate goal of this work was to identify solutions that could clean photographs without disturbing any silver, as it is original material, deteriorated or not.

III. Procedure

For this experiment the solutions chosen were filtered tap water from Winterthur Museum's Paper Laboratory (pH 7.2), a 1:1 mixture of water and Ethyl Alcohol (Fisher Scientific), Ethyl Alcohol, and a dispersion of the proprietary surfactant Kodak Photo-Flo 200 Solution in water (1 drop Photo-Flo to 100 ml. water). It should be noted that Photo-Flo is most often used in processing film and prints and is certainly not used as frequently for surface cleaning as the other solutions described. Photo-Flo was used primarily in this experiment to build on the work done by Henderson, and because it is occasionally used for surface cleaning.

Kodak Photo-Flo 200 Solution has a pH of 7.0 and is made primarily of water which accounts for 60-70% of the solution (11). Between 25-30% of the solution is propylene glycol, a humectant used to help retain moisture. The final known component is 5-10% p-tertiary-octylphenoxy polyethoxyethyl alcohol, a surfactant closely related in structure to Triton X. Like all materials, this product breaks down and, among the different degradation products, this surfactant can oxidize to form peroxides (12, 13). However, it is important to remember that it is being used at a dilution by a factor of 2,000 (one drop is approximately 50 microliters (14)).

For this experiment, four historic photographs were chosen as the samples -- the project was one to be completed in a semester, a factor which excluded the use of many samples. The option of artificially aging and soiling photographs was not chosen as historic samples were

available for testing. Moreover, following this course gave a more practical, rather than theoretical, focus to this experiment. The four samples were silver gelatin developed-out prints donated by Debra Hess Norris. The photographs had only slight to moderate surface grime and moderate mirroring and were chosen because they were in the type of condition that could be safely and might be routinely surface cleaned. Two were moderately glossy (Photographs 1 and 2). The other two were thought to be a pair based on size, subject, texture, and printed sequential numbers (4166 and 4186) on the verso (Photographs 3 and 4). These had a pebble-texture surface which was more matte, the result of a thinner, more textured gelatin layer and a thinner baryta layer. The rationale behind choosing a 'pair' was that some of the potential variation in results might be reduced through the use of very similar samples.

The photographs were each assigned a number prior to treatment (1-4). They were then each divided into 5 sections using a polyester overlay to mark the boundaries. Sample size depended on the photograph, but each section was approximately 3/4" wide x 3 - 5" high. Four of the sections were treated with one of the four solutions; the fifth section served as a control. The order of the solutions was randomly determined through a computer program at the University of Delaware's Statistics Laboratory. The treatment order was marked on the back of the photographs in graphite.

The four photographs were treated with swabs (Starline cotton tipped applicators, previously unopened) lightly dampened with the solutions. The swab were gently rolled in the most consistent manner possible, determined with Hess Norris. The technique was to roll down one inch and diagonally up in order to roll down again. The total area covered per swab was about 3/4" x 1" so that approximately three swabs were used per treatment area. One photograph was treated at a time and then put under weight to try to compensate for some of the planar deformation that can occur as a result of wetting. The swabs were all saved in a holder which kept them separated by treatment type and photograph for further testing. The swabs were also covered with small plastic bags to avoid contamination by airborne particulates, etc.

Before and after treatment the areas were examined both visually and with the stereo-microscope at 16 times magnification (Wild M3Z, Winterthur Museum) by the author. The areas were examined before treatment to note surface characteristics, level of mirroring, grime, and any flaws that might have been attributable to the treatment if not noted before. After treatment the photographs were examined for efficacy of grime reduction, surface disruptions, and any other changes from treatment.

The photographs were also examined visually after treatment by Nora Kennedy, Sylvie Penichon, Lyzanne Gann, and Toshiaki Koseki at Kennedy's business, The Better Image. No form was used; rather, general instructions to note difference between sections in the surface characteristics, level of grime, planarity, and mirroring, etc. were given. The examiners worked without knowing which treatments they were evaluating in order to avoid bias. Their remarks were translated to treatment type and consolidated for comparison (see results and discussion).

The energy-dispersive X-Ray fluorescence spectrometer used was Kevex, model K6033S (Winterthur Museum) and the target was Gadolinium at 60 kV and 1.2 miliamps. The distance between the instrument and the sample was three centimeters. Readings of 150 seconds were taken of one spot per each of the five areas on the four samples before and after treatment in order to determine if silver had inadvertently been removed. The areas chosen were of high density and often of mirroring. If any areas were likely to show changes in the level of silver it would be these because here the silver is deteriorated. That is, on the surface there is metallic silver making it possible to remove silver without disrupting other layers.

The swabs were also examined with XRF to look for the presence of silver. As energy-dispersive XRF is not highly sensitive, the possibility that any silver on the swabs would simply

be too low in concentration to detect with this equipment was considered. In part, this portion of the project was an experiment to see if this tool was appropriate to this type of work. If it was determined that such analysis was not revealing any silver on the treatment swabs, as turned out to be the case, this part of the experiment would end, to be replaced by a spot test for the presence of silver.

Because it was important to determine whether non-detection of silver with XRF was indicating that the instrument was insensitive to such low concentrations of material or that silver was, in fact, not being removed, a spot test was used. The swabs were tested for the presence of silver with the Manganese nitrate spot test, which is sensitive to two micrograms (15). The spot test analysis of the swabs was carried out in random order and all testing was done with a blank determination, that is an unused swab, so that any components of the swabs would not confuse the results. Also, known quantities of silver (2, .8, and .04%) were tested for two purposes. The first was to see if either performing the spot test on the actual swab or dropping hydrochloric acid on the swab and rolling it on chromatography paper would work. The other reason was to determine if the test was correctly prepared. Both techniques worked moderately well with the knowns; the results were a purple-black color.

The swabs were also subjected to the Ninhydrin spot test for proteins, namely gelatin, in order to understand whether or not that layer was disrupted during cleaning (16). As before, the spot test was performed on a blank and on known quantities of gelatin (.1, .5, .05, and .025%) to ensure they were being conducted correctly.

The Scanning Electron Microscope (SEM ISO SS40, Winterthur Museum) allowed a much closer examination of the surface morphology of the photographs. SEM also provided a larger depth of field and three-dimensional imaging, capabilities essential to the detection of subtle surface alterations. The magnification used was 310 times. Sample size was approximately 1/4 - 3/8" square. The samples were mounted on stubs using double-sided tape and coated with gold using a SPI gold coating device. One area from each of the five sections of the photographs was examined at 2 kV and a Polaroid photograph was taken of at least one representational area of each section.

IV. Results and Discussion

There were two occurrences during the actual treatment that were noteworthy. First, all of the samples curled due to the introduction of moisture. Because the photographs were not cut into strips, it was impossible to judge which treatments caused more deformation. However, the two textured photographs (3 and 4) reacted more severely to the treatment, bulging as the experiment proceeded. Second, in the areas of mirroring, the swabs tended to be "dirtier," indicating that something was being removed.

The visual observations by the five people yielded few consistent results, due in part to the subtle nature of the grime and the generally non-moisture reactive nature of these particular samples. Also, as there was no form given to the examiners to standardize responses, the comments were quite varied. Some general trends do emerge though.

The photographs curled in the direction of treatment, a known phenomenon thought to relate to the hysteresis of the gelatin caused by the introduction of moisture. Secondly, of the solutions that appear to have disturbed the mirroring, water/ethanol and the Photo-Flo in water were the two most often cited. Ethanol appeared to have affected the mirroring the least.

Because this part of the experiment yielded less than satisfactory results, there are some suggestions for future research that could help avoid some of these problems. First, the examiners should be asked to fill out a form to standardize responses for comparison. Next, if using historic

samples again, the photographs selected should be somewhat more reactive to moisture and more soiled so that the results are less subtle.

X-Ray fluorescence analysis of the first two photographs (1 and 2) showed very little change in silver levels after treatment. The other two photographs showed very interesting and puzzling results for all four treatment types. On photograph 3 there was a decrease in the amount of silver and an increase in the amount of barium (presumably from the baryta layer which consists of barium sulphate) and on photograph 4 the treatments caused the opposite. What is more, on many of the spectra the change in silver corresponded to a similar change in iron. What these consistent but puzzling results indicate is that something is happening to the layer structure of the photographs. That is, the layers are being changed, but as of yet the actual phenomenon is not understood. The opposing results from a 'pair' of prints suggests that these two photographs may not be as similar as first assumed. It is possible that they have existed in very different conditions, as one is significantly more discolored, or were manufactured slightly differently or at different times.

When XRF analysis was done on the swabs, a blank was first analyzed to ascertain a background spectrum. Next, a swab dipped in a silver nitrate solution of approximately a 13% concentration was looked at. The XRF analysis on this swab gave very clear results; at this concentration XRF could definitively detect the metal. The next step was to look at some of the swabs used for treatment. The most soiled swabs were chosen for analysis, as these usually come from the mirrored areas and would therefore be the most likely candidates for the detection of silver. None of the swabs examined showed any evidence whatsoever of silver. All of the spectrum exactly resembled the blank. These results meant one of two things: either XRF was not sensitive enough to pick up this small amount of silver or silver was not being removed in these treatments.

To try to resolve the above question, the spot test for the presence of silver was performed. Though the knowns worked moderately well, the results from the treated swabs were inconclusive -- there were 7 possible positive results out of 32 (21%). The possible positive results came from photographs 1-3. Treatment with plain water yielded one possible positive and the other three treatment types each gave two potentially positive results. Finally, rolling on the chromatography paper yielded less promising results than testing on the actual swabs. However, the real problem lies in that the overall results were not clear -- they were not definite positives.

In the future it is recommended that another, more sensitive spot test be tried, such as the potassium cyanide test which is said to be sensitive to .63 micrograms (18). Also, Richard Wolbers, Associate Professor, Winterthur Museum/University of Delaware Program in Art Conservation, suggested using an electro-chemical test, such as ion-selective electrode for silver. The sensitivity can be between 10^{-7} to 1.0 M, but the test is significantly more expensive ($280-390 in a recent Cole-Palmer catalogue) and requires the electrode to be placed in contact with the object in a drop of water.

This preliminary evidence from the spot test and from the XRF analysis of the swabs and the photographs themselves suggests that silver is not being removed. It is important to remember that this may or may not be true. The results may mean only that the tools tried were not the most appropriate. It may also mean that with these four particular samples with moderate mirroring, the treatments were safe in terms of leaving the image material in place.

The Ninhydrin test was done on some of the swabs to look for the presence of a protein, particularly gelatin, in order to address the question of potential binder layer disruption. The spot test was first performed on knowns and on a blank swab. These tests clearly indicated positive results that corresponded to concentration with the highest concentration of gelatin yielding the

most purple swab. Moreover, there was a negative result from the blank, though the base where the cotton wraps around the stick had a slight purple band, probably due to a small amount of adhesive used during manufacture to hold the cotton in place.

The Ninhydrin testing provided the following results. Photograph 4 reacted the most, followed by photograph 3, and then 2. The swabs from photograph 1 were very light purple, faint enough to cast doubt on whether this was a positive result. It was very interesting that the results of this test were positive by photograph, not by treatment type. That is, all of the swabs from photographs 2, 3, and 4 reacted positively. Comparing the results to the known, it appeared that photograph 4 reacted on par with the swab tested with the .05% gelatin known. If ranked, the water/ethanol swab, followed by the water swab, was the most positive for photograph 4. The Photo-Flo and water swab, followed by the ethanol swab were the most intense purple for photograph 3. The most purple swab from photograph 2 came from the ethanol treatment, followed by the swab from the water treatment.

It is important to remember that dirt can be proteinaceous (though most often it is primarily ash, carbon, and silicon oxides (18)) so the positive reaction may be due, in part, to protein-rich soiling. Also, previous handling of the photographs could have left proteinaceous oils and skin residue behind, which could also account for some of the positive reaction. However, based on the overall intensity of the results for three of the four sample photographs, it is believed that they do indicate some removal of the gelatin layer. The preliminary result that ethanol can affect the gelatin layer was surprising. It may be that in some cases, such as with ethanol, the gelatin is being abraded off rather than solubilized.

The Scanning Electron Microscope results were as follows. For photograph 1, the water and ethanol treatment most resembled the control. The water and Photo-Flo treated sample also appeared to be similar to the control, though the image of it had much more contrast. (It is unclear if the contrast is related to density changes, the appearance of mirroring on such a heightened scale, or a function of the SEM equipment.) The water treated sample appeared more flat and even. The surface that was the most altered was that treated with ethanol -- this treatment appeared to have dehydrated the sample.

Scanning Electron Microscopic examination of photograph 2 revealed the surfaces to all be essentially the same. They were all even and undifferentiated. Again, there were some contrast differences that are not understood, but no surface deformations or alterations were seen on any of the samples.

The SEM results for photograph 3 also showed no significant surface alterations with any of the treatments. A very interesting result was seen on the photograph 4. The sample treated with filtered tap water appeared to have a significant alteration to the surface. There was a much more pronounced paper fiber. It was believed that what was being observed was the swelling of the gelatin with water and then the subsequent shrinking upon drying.

To follow up on these SEM results, it would be interesting to include a swell meter in future research. This equipment might be able to detect alterations to the gelatin layer such as swelling and/or shrinking from treatment.

A final suggestion for future work is to use carefully prepared samples made for the project, rather than historic photographs. It can be very difficult to compare different individual photographs -- an area on one photograph which was tested with one solution can be very different in terms of density, condition, and degree of soiling when compared to another photograph. Creating test samples instead would lend a great deal more consistency. These samples could be artificially aged for silver mirroring. The challenge would be to soil the samples in such a way that would give realistic cleaning results.

V. Conclusions

All four of the solutions appeared to be effective in reducing surface soil. Which treatment type worked with more efficacy could not be determined due to the very subtle differences in results.

Was silver inadvertently removed during the process of surface cleaning? From this preliminary study, it appeared that the four treatments were relatively safe to use on moderately mirrored photographs based on XRF analysis and spot tests. However, visual analysis noted some minor alterations of the mirrored surfaces with water/ethanol and the water and Photo-Flo solution. Silver mirrored surfaces were not visually affected by cleaning with ethanol. That is, the mirroring was not abraded or disturbed. However, SEM analysis indicated that ethanol may, in some cases, dehydrate the photograph's surface.

The question of whether solutions adversely effected any of the layers, especially the gelatin binder layer, was also addressed in this project. Many of the photographs exhibited surface deformation after cleaning, which was probably related to hysteresis of the gelatin binder, a common treatment problem documented in the literature (19). Also, surface cleaning with water on a highly textured surface (i.e. thinner binder) seemed to have significantly changed that surface when examined with SEM (photograph 4). This finding corresponded with the Ninhydrin test which was positive for the swabs used with water on photograph 4. Even a less textured surface, such as photograph 1, appeared to have been altered by water, that is rendered more flat and even. This may, again, be the result of swelling and the subsequent shrinking of the gelatin as proposed for photograph 4.

The use of the Ninhydrin test for looking at soiling vs. gelatin on photographs needs to be explored further. However, the preliminary results that treatments can not only swell, but also perhaps remove some gelatin was very interesting. Even the ethanol treatment seemed to have affected the gelatin layer, which was surprising. Again it may be that, in some cases, the gelatin was abraded off rather than solubilized. It was also useful to note that the Ninhydrin test can be a method to crudely but effectively detect differences in concentrations based on color intensity.

The XRF information and the results of the Ninhydrin test from the two textured photographs revealed that there was clearly something happening to the binder layer. These results merit further consideration. It could be that their layer structure had components from manufacture that were not accounted for or understood.

Analysis of silver loss or removal using XRF was inconclusive. Whether or not this analytical technique is an appropriate tool for the task at hand needs to be ascertained, though from this research it appears that XRF is not an appropriate analytical technique. This question could be answered if a more mirrored and deteriorated photograph was used for the same kind of testing done here.

VI. Acknowledgments

I would like to thank the following people for their kind assistance and encouragement: Nora Kennedy, Photograph Conservator; Sylvie Penichon, Graduate Student at New York University; Lyzanne Gann, Graduate Student at Buffalo State College; Brenda Bernier and Toshiaki Koseki, Graduate Students, Winterthur Museum/University of Delaware Program in Art Conservation; Robert Noble, Statistics Laboratory, University of Delaware; Richard Wolbers, Associate Professor, University of Delaware, Art Conservation Department. I am indebted to Kate

Duffy, Assistant Scientist, Winterthur Museum, for running the SEM and helping interpret XRF data. Finally, special thanks are due to Debra Hess Norris, Associate Professor, University of Delaware, Art Conservation Department and Janice Carlson, Senior Scientist, Winterthur Museum for insightful guidance and invaluable support.

VII. References

1 Reilly, James M., lecture notes, Winterthur Museum/University of Delaware Program in Art Conservation, Photography Conservation Block, 1/10/95.

2 Hendriks, Klaus B. and Lincoln Ross. "The Restoration of Discolored Black-and-White Photographic Images in Chemical Solutions." *American Institute for Conservation Pre-prints*, 1988, 99-117.

3 Nielsen, Ulla Bogvad. "Silver Mirror on Photographs." Royal Danish Academy of Fine Arts Thesis Project, School of Conservation, 1993.

4 Henderson, K. "The Use of Surfactants in Cleaning Silver Gelatine Photographs." *The Imperfect Image; Photographs. their Past, Present and Future.* Centre for Photographic Preservation Conference Proceedings: Windemere, England, 1992, 137-140.

5 Personal communication with Henderson, November 1995.

6 Moor, I.L. and A.H. Moor. "The Effect of Aqueous Treatments on Photographs." Preprints from *Sauvegarde et Conservation Des Photographies Dessins, Imprines et Manuscrits.* Association pour la Pecherche Scientifique sur les Art Graphiques: Paris, 1991, 62-66.

7 Moor, I.L. and A.H. Moor. "An Overview of the Use of Aqueous Treatments on Photographs." *The Imperfect Image; Photographs. their Past, Present and Future.* Centre for Photographic Preservation, Conference Proceedings: Windemere, England, 1992, 236-244.

8 Hendriks, K., et al. "Fundamentals in Photographic Conservation: A Study Guide"; National Archives of Canada: Ontario, 1991.

9 Rempel, Siegfried. "The Care of Photographs"; Nick Lyons Books: New York, 1987.

10 Swan, A. "Conservation of Photographic Print Collections." *Library Trends* 1981, 30, 267-296.

11 Information about the components of Kodak Photo-Flo 200 Solution was gained from Douglas Nishimura and the Material Safety Data Sheet from Kodak.

12 According to Douglas Nishimura, personal communication with Debra Hess Norris, Spring 1996.

13 Personal communication with Janice Carlson, Spring 1996.

14 Personal communication with Richard Wolbers, Spring 1996.

15 Feigel, Fritz. "Spot Tests in Inorganic Analysis"; Elsevier Publishing Co.: New York, 1962, 58-9.

16 "Paper Conservation Catalogue"; American Institute for Conservation, sec. 10, 10-11 & 29-30.

17 Feigel, 60.

18 Wolbers, Richard, lecture notes, Winterthur Museum/University of Delaware Program in Art Conservation, Course ARTC 670, 8/29/94.

19 Calhoun, John M. "Effect of Gelatin Layer on the Dimensional Stability of Photographic Film." *Photographic Science and Engineering* 1959, 3, (1), 8-17.