

An Analysis of Image Deterioration in Wet-Plate Negatives from the Mathew Brady Studios

Mark H. McCormick-Goodhart

Conservation Analytical Laboratory, Smithsonian Institution, Washington, DC 20560

The deterioration of collodion wet-plate negatives made in the Mathew Brady Studios during the 1860s was investigated. The most seriously degraded plates were found to have saponified varnish coatings. Carboxylic acid metal salts in the varnish layer were determined by Fourier transform infrared spectroscopy. Subsequent identification of the metal ion as sodium by energy dispersive x-ray spectroscopy led to an investigation of the glass composition. Glass composition was measured by electron microprobe analysis, using wavelength-dispersive x-ray technique; the saponified varnish plates had glass substrates of the same composition, characterized by high sodium content.

Journal of Imaging Science and Technology 36: 297–305 (1992)

Introduction

In 1981 the National Portrait Gallery acquired 5445 glass plate negatives made by Mathew Brady's Washington and New York studios during the years 1861–1866. These original negatives were created entirely by the collodion wet-plate process and comprise what is now referred to as the Meserve Collection. Brady's studios produced finely crafted portraits and attracted the affluent and celebrities of the times. The images of many prominent 19th century figures are featured in extraordinary detail within the collection: Abraham Lincoln, Ulysses S. Grant, Jefferson Davis, William Tecumseh Sherman, Henry Wadsworth Longfellow, Oliver Wendell Holmes, Nathaniel Hawthorne, P. T. Barnum, Samuel Morse, and so forth. The plates are compelling testimony to Mathew Brady's genius and to the skills of the craftsmen employed by him. Due to their provenance they also form a unique study group in which to examine the craft and image stability of the wet collodion process. A brief history of the Meserve Collection is included in the Appendix.¹

The need for a better understanding of deterioration mechanisms arose from concerns that appeared at the time the collection was acquired. A small, but significant, number of plates (~1–2%) were set aside from the others because the varnish layers were tacky. Many dirt particles and fibers from the paper enclosures had become embedded. Discoloration, small cracks, and image losses, as well as localized "spotting" or "mottling" patterns in the image silver, were quite apparent. The tacky varnish coatings also exhibited a strong response to relative humidity. After the affected plates had been transferred to their new storage environment, where the relative humidity does not exceed 50%, they did not retain

the high tack level. Figure 1 shows a modern print made from an affected plate, side by side with a plate in excellent condition. Figure 2 illustrates 5 mm × 5 mm area details from the same plates. The macrophotos were recorded using a combination of transmitted and reflected light to reveal both negative transmission density and the present condition of each plate's surface.

Environmental history was ruled out as a cause for differences between the plates. The Washington and New York plates were merged very early, because prints were made for sale to the public by E. & H. T. Anthony in New York. The popular *carte-de-visite* format exploited multiple-exposure camera backs, which yielded several poses on a single large plate. Because each plate was finished in a continuous method of coating, sensitizing, exposing, and processing, the multiple exposures possess equivalent materials and process quality. The large plates were then typically cut apart to *carte-de-visite* size and did not always stay filed side by side. One practice that increased the opportunity for separation was gang printing. Various small plates would be mounted in sequences to a larger backing glass in order to facilitate contact printing. Nevertheless, when mates are located and judged side by side today, the present manner and degree of deterioration are remarkably the same. Thus, the multiple-exposure image mates provided reasonable evidence that the present image quality of individual plates in the Meserve Collection was related to material and/or craft, rather than to microclimate or other environmental differences.

Experimental

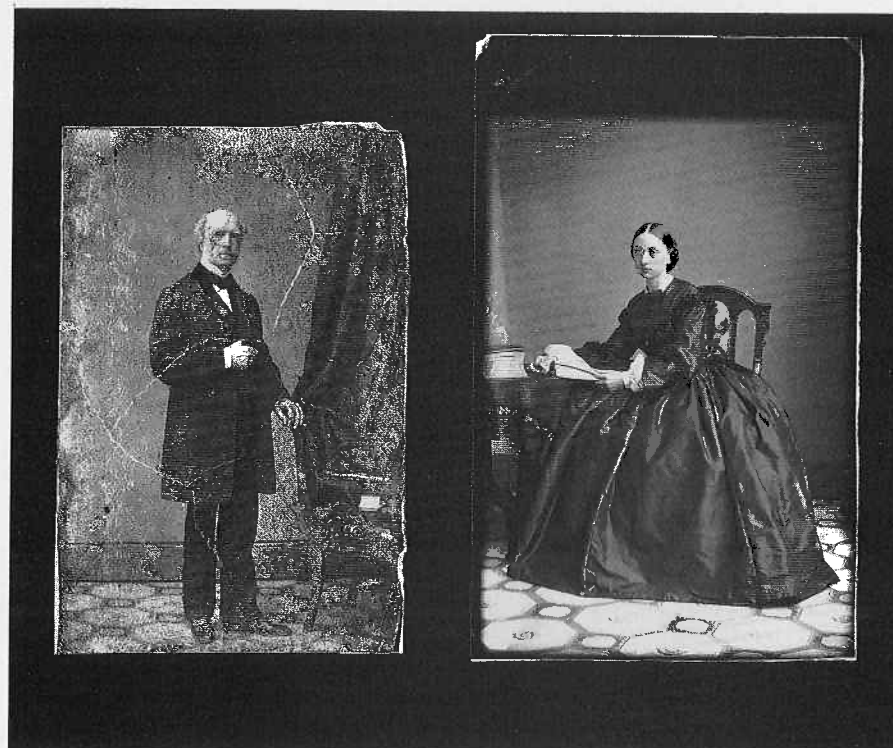
All negatives in the collection have varnish overcoats. Varnishing was a customary and indeed essential aspect of wet collodion craft. An unvarnished wet-plate negative did not survive contact printing procedures very long before severe scratches and abrasion occurred, because the collodion binder (cellulose nitrate) is about $2 \pm 1 \mu\text{m}$ thick and the developed silver particles are concentrated at the collodion surface. The varnish thickness is typically 4–8 μm .^{2,3} A scanning electron micrograph cross-sectional view of a wet-plate negative's collodion-silver binder and varnish layers is shown in Fig. 3. No distinct boundary is evident between the varnish and collodion, although some vertical fracture lines seem to be characteristic of the varnish layer's cross-sectional face. Figure 3 also reveals that some of the silver particles are only loosely bound and can be freed into the varnish region when the varnish is poured. This situation is not surprising when the close solubility parameters of the varnish and the collodion binder layer are considered.

Varnish Analysis. Varnish condition was examined by Fourier transform infrared (FTIR) spectroscopy. Microgram samples of varnish were removed with a dissecting needle from three plates exhibiting once-tacky var-

Original manuscript received July 22, 1991.

© 1992, IS&T—The Society for Imaging Science and Technology.

Figure 1. Contact print from a deteriorated Brady Studios negative (NPG 5296:185, *Rev. Farley*), left, and one in excellent condition (NPG 3050:102, *Unidentified female*), right. Heavily embedded paper fibers and opaque re-touched cracks on the deteriorated negative appear as low density values in the contact print. The bright streak seen on the good plate is a typical edge nonuniformity from the hand-coated sensitization method of wet-plate photography. It is not a sign of age or deterioration.



nish layers and from four randomly selected plates wherein the varnish coatings appeared to be in fine condition. The varnish was separated from the collodion-silver region with the aid of a 35–50 × stereo microscope focused on a high-image-density area. A sufficiently pure sample of the varnish resin was removed by taking care not to disturb the silver image. The deteriorated plates presented more difficulty, because the silver matrix had started to break up and disperse, which accounts for much of the mottled and clumped-grain appearance of the affected plates. Transmission IR spectra were obtained using a Cygnus 100 FTIR spectrometer fitted with a Spectra Tech IR-Plan™ microscope accessory. It was thus possible to keep the amount of varnish required for analysis to microgram levels, and vital image content was undisturbed.

The FTIR spectra of varnish extracts from the good quality plates all displayed a characteristic signature of shellac. The Brady studios choice of a shellac formulation is in agreement with the apparent popularity of shellac at the time. During the Collodion Era of photography many natural resins, such as shellac, sandarac, copal, dammar, mastic, benzoin, elemi, etc., were recommended in photographic varnish formulas,^{4–8} but recipes made largely of shellac dissolved in alcohol were prevalent.^{9–12} Spirit varnishes were fast drying and preferred over oil-based varnishes, because they allowed the negatives to be contact-printed shortly after varnishing.

FTIR spectra of the degraded varnish samples revealed strong peaks at approximately 1564 cm⁻¹ and 1400 cm⁻¹, which are not associated with natural resin spectra,^{13,14} cellulose nitrate, or potential collodion-era plasticizers, such as camphor, bergamot oil, lavender oil, etc. These peaks are characteristic of carboxylic acid metal salts. Figure 4(a) shows the IR spectrum of varnish from deteriorated plate #NPG 5296:185 and, for comparison, Fig. 4(b) shows the spectrum of a freshly made sample of shellac. The presence of metal ions in the extracted

varnish samples was then confirmed by scanning electron microscopy with simultaneous energy-dispersive x-ray analysis (SEM-EDS). Analyses were conducted on a JEOL 840A SEM with a Tracor Northern 5502 energy dispersive spectroscopy system. The degraded varnish samples contained easily detectable sodium, whereas sodium was not found in the good varnish samples [see Figs. 5(a) and 5(b)]. The presence of sodium in the degraded varnish samples is consistent with the FTIR interpretation of carboxylic acid metal salts. The varnish deterioration involved the alkaline hydrolysis of ester groups in the resin. A carboxylic ester is hydrolyzed to a carboxylic acid, which under alkaline conditions is obtained as its salt. The deteriorated plate varnishes had thus become saponified over time, causing their present hygroscopic nature. With respect to sodium, alkaline hydrolysis of the ester groups may be illustrated:



The interpretation of the FTIR and SEM-EDS data was verified by making freshly saponified shellac coatings to compare with the historical plate samples. Solutions of shellac dissolved in alcohol were prepared and varied amounts of sodium hydroxide were then added. The reaction with the NaOH was immediate and could be observed by the darkening of the shellac color. Films were cast on glass substrates and FTIR analysis of the dry films was accomplished as previously described. With an appropriate amount of NaOH, the spectrum of one freshly saponified shellac sample [Fig. 4(c)] closely matched the IR spectrum of degraded plate #NPG 5296:185 [Fig. 4(a)], providing good experimental proof of the postulated varnish degradation mechanism.

An Alkali Source. Various pathways to an alkaline environment were considered. SEM-EDS detection of both sodium and sulfur suggested high residual fixer might be present. However, it was found that the 1–3 μm collodion layer does not retain the fixer at the levels encountered



Figure 2. 5 × 5 mm area detail of (a) the deteriorated negative NPG 5296:185, *Rev. Farley*, revealing fine coating cracks and image loss as well as embedded dirt and fibers. (b) NPG 3050:102, *Unidentified female*, where the image structure is clean and completely intact, revealing even the grain structure of wood in the back of the chair used by the sitter.



here. Under the poorest conditions, a wet-plate photographer would have at least rinsed the plates, because unrinsed plates presented immediate practical problems. An experiment was undertaken to verify what sodium and sulfur levels would be found by the SEM-EDS instrumentation under these circumstances. A new wet plate

was made and processed, adhering to traditional formulas,¹⁵⁻¹⁷ with sodium thiosulfate as the fixing agent. At the end of the fixing operation only a brief rinse was performed. The collodion-silver layer was then sampled and evaluated by SEM-EDS for the presence of sulfur and sodium, and was found to be below detection limits

Figure 3. SEM micrograph of a wet collodion negative in cross section at 8,000 \times magnification. The sample was a coating flake already separated from its glass support.

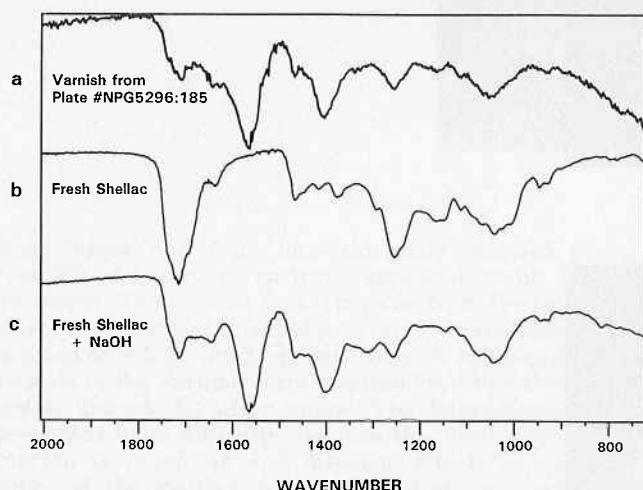
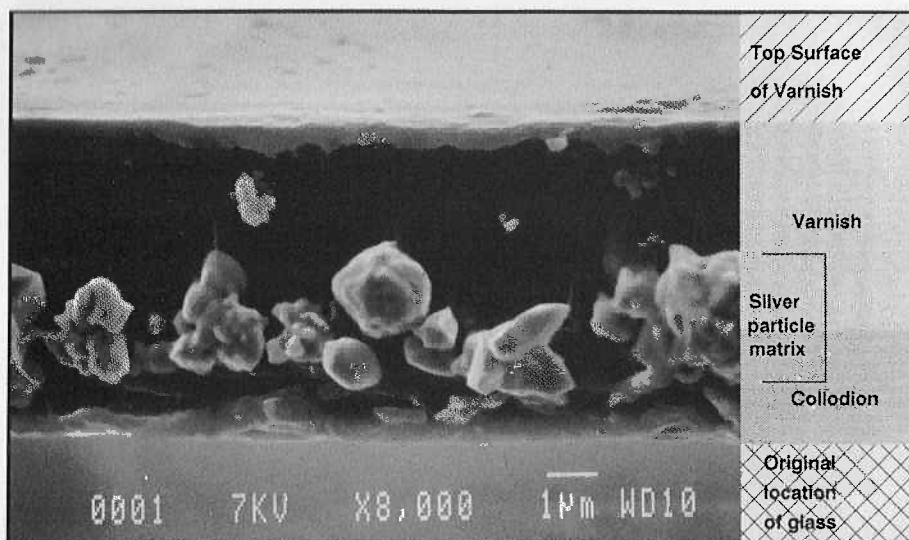


Figure 4. FTIR spectra of (a) deteriorated varnish extracted from the plate NPG 5296:185, (b) a freshly prepared shellac sample, and (c) fresh shellac saponified by the addition of 0.19 g NaOH per g shellac resin.

for both elements. Additionally, a sodium thiosulfate fixer acting alone could not establish the necessary pH level required to saponify the varnish. When sodium thiosulfate was used to fix wet-plate negatives (potassium cyanide was also common), photographers prepared a highly concentrated and unbuffered formula. The pH decreased in contact with the wet plate.

No other process components seemed capable of leading to an alkaline regime, either. Both the silver nitrate sensitizing bath and the pyrogalllic acid or ferrous sulfate developers were adjusted to pH values typically between 4.5 and 5.8 with citric acid, acetic acid, or drops of nitric acid specified in various formulas. Wet-plate technology did not use any alkaline developers. Also, wet-plate photography was a solution physical development process. The silver ions needed for development were supplied by the excess silver nitrate from the sensitizing bath, rather than through the chemical development mechanism associated with modern films and developers. The large, nonfilamentary particle shape, as shown in Fig. 3, can be attributed in part to the physical development activity.

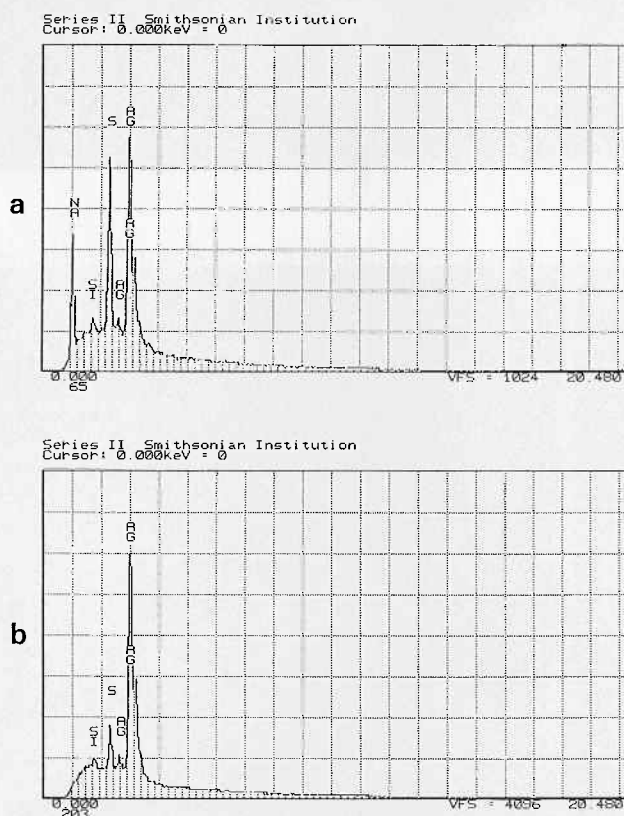


Figure 5. SEM-EDS data for (a) varnish sample removed from a deteriorated plate (NPG 5296:185, *Rev. Farley*) and (b) varnish from a plate in excellent condition (NPG 2999:101, *Emma Webb*).

The cellulose nitrate and the varnish resins were also, by nature, slightly acidic. Because no wet-plate chemistry that might lead to an alkaline environment was identified, and any external sources of sodium would be likely to come into contact with the plates in a more non-uniform manner, the probable source of the sodium and corresponding high pH level was reasoned to be from interaction with the collodion negatives' own glass substrates.

Simple, nondestructive screening methods utilizing UV fluorescence and x-ray fluorescence (XRF) spectroscopy were then undertaken to look for a correlation between glass composition and coating deterioration. Twelve plates with saponified varnish were compared with 15 randomly selected plates in good condition. UV fluorescence proved inconclusive, because both varnish coatings and glass substrates fluoresced simultaneously, making it difficult to sort varying glass compositions into any defined categories. XRF (United Scientific Dubois Object Analyzer with Tracor-Northern 5502 instrumentation) was used without vacuum to examine the uncoated sides of the plates. The spectra revealed a unique "signature" for the deteriorated plates. Two aspects of this signature can be seen by comparing Figs. 6(a) and 6(b); Fig. 6(a) shows a strong arsenic peak and an apparently lower calcium signal than that of Fig. 6(b), the nonsaponified plate.

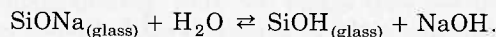
The method is semiquantitative. Relative peak heights of different elements do not indicate elemental quantity ratios. For example, As_2O_3 is not a larger component than CaO with respect to its actual percentage of the bulk glass composition. The strong signal simply reflects the higher XRF detector sensitivity to arsenic than to calcium. Nevertheless, a 100% correlation between the XRF pattern and a saponified coating on the reverse side of the glass was determined. All saponified-varnish plates could be sorted from plates with good varnish by simply observing the consistent XRF signature. It must be noted that sodium is not a detectable element with the nonvacuum-mounted XRF apparatus used, but potassium

is. No major potassium peak was detected by XRF in any of the test samples, which implied that Brady studio plates were predominantly soda lime glasses. One specialty glass was detected by UV fluorescence among 27 samples and confirmed by XRF to have a high lead oxide component.

Glass Composition Analysis. Accurate glass composition data were determined by wavelength-dispersive electron microprobe analysis. An ARL SEMQ Electron Microprobe was used. Beam size was defocused to $40\ \mu\text{m}$ to improve bulk composition statistics. Small chips of glass were removed from corners of six saponified varnish plates and six plates with good varnish. The six plates with good varnish were randomly selected from the population of plates in good condition, although multiple-exposure image mates were not allowed, because they would obviously have the same glass composition. The saponified varnish plate samples were also randomly chosen, but with one exception. An encampment scene was deliberately included, because it had been processed outside the studio environment, yet was exhibiting the same mode of deterioration. The glass chips were cut using a diamond-studded copper wire, embedded in epoxy, and polished to expose a fresh surface indicative of bulk composition. A chip from an NBS #620 soda lime flat glass standard was also prepared at the same time and analyzed at the beginning, middle, and end of machine time to verify accuracy and repeatability of the results. The glass composition results are listed in Table I. The varied compositions were then plotted on a ternary phase diagram, as shown in Fig. 7, by grouping appropriate species and normalizing the percentages to total 100%. Such graphical representation clearly reveals how the glass substrates of "good" images versus those with deteriorated images cluster in different compositional regions. Two good plates roughly matched the modern soda lime glass formulation, and the other good plates had higher alkaline earth oxide (CaO and MgO) and lower alkali oxide (Na_2O and K_2O) quantities than did modern plate glass. Within the limits of experimental accuracy, all saponified varnish plates tested had the same bulk composition, characterized by higher alkali oxides and lower alkaline earth oxides in the glass formulation. The standard deviation associated with the electron microprobe analysis is small and accounts for the minor compositional variances of the saponified samples reported in the table.

The chemical durability of silicate glasses has been investigated.¹⁸⁻²² Numerous factors, such as glass homogeneity, surface roughness, thermal history, etc., make the issue of durability more complex than can be expressed solely in terms of bulk composition. However, in general, the addition of alkali oxides reduces the melting temperature and improves manufacturing economics, but corrosion resistance rapidly decreases as the alkali oxide concentration is increased. On the other hand, the addition of alkaline earth oxides improves the glass durability. It can be seen that the condition of the image coatings correlates with the chemical durability of the glass substrates as influenced by the bulk glass composition.

Corrosion of soda-silica glass has been characterized in two basic stages by the following general equations.²³ In Stage 1 sodium leaches from the glass in an ion exchange process, resulting in a "silica-rich" layer with hydrated micropores:



During Stage 2 breakdown of the silica network occurs,

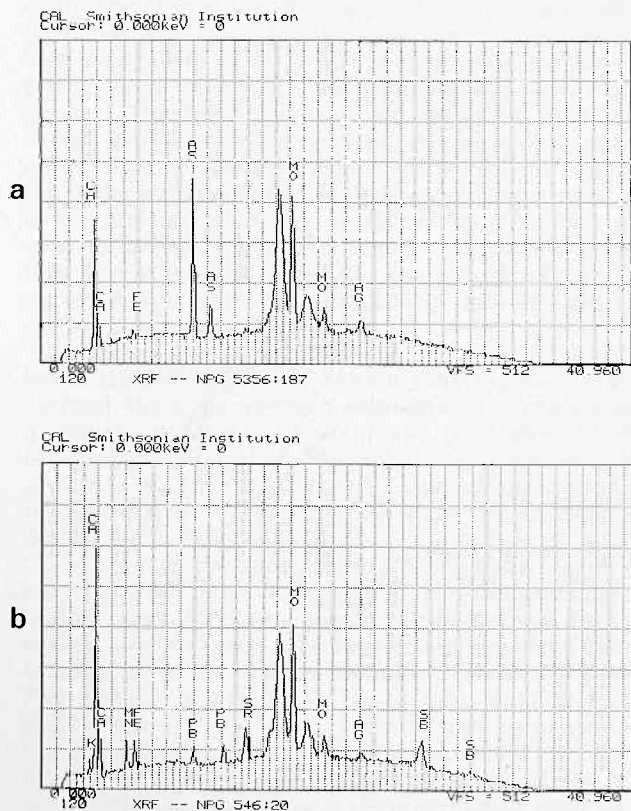


Figure 6. XRF "signature" of the uncoated glass surface for a negative (a) with saponified varnish coating (NPG 5356:187, *Alpheus Hyatt*) and (b) with a coating in excellent condition (NPG 546:20, *David G. Farragut*). Molybdenum peaks are an artifact of the x-ray emission source.

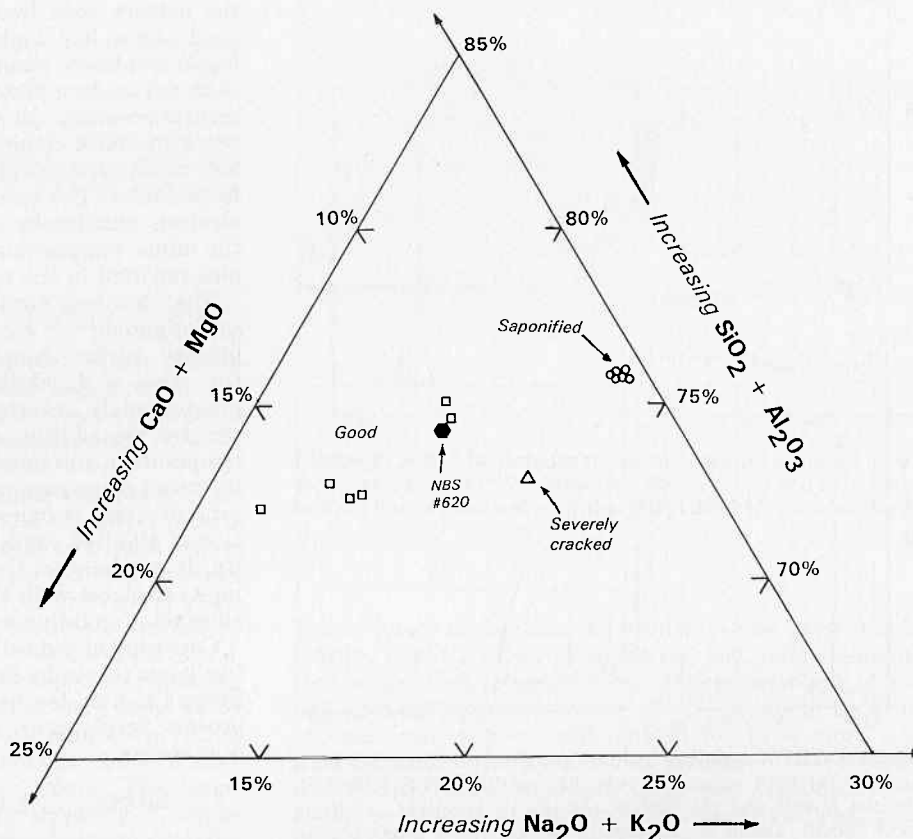
TABLE I. Glass Composition Data (Wt %)*

SAMPLE (Condition)	SiO ₂	Al ₂ O ₃	FeO	MgO	CaO	K ₂ O	Na ₂ O	Total
NBS # 620 Glass Standard <i>Specifications</i>	72.1	1.8	0.04 <i>Fe₂O₃</i>	3.7	7.1	0.4	14.4	99.54
NBS # 620 Glass Standard <i>Microprobe data</i>	71.0 (0.59)	1.7 (0.09)	BDL	3.9 (0.10)	7.3 (0.12)	0.4 (0.02)	14.9 (0.21)	99.2
NPG 951:33 (Good) <i>Lee, Henry W.</i>	71.0 (0.59)	0.5 (0.04)	0.3 (0.02)	BDL†	14.1 (0.14)	0.1 (0.02)	12.6 (0.16)	98.7
NPG 546:20 (Good) <i>Farragut, David G.</i>	73.3 (0.59)	0.9 (0.09)	0.1 (0.02)	0.3 (0.04)	9.8 (0.10)	1.3 (0.08)	13.2 (0.19)	99.0
NPG 1993:69 (Good) <i>Newell, Major Edward, and another</i>	70.2 (0.59)	0.6 (0.06)	0.1 (0.02)	0.2 (0.02)	15.9 (0.18)	0.3 (0.03)	11.0 (0.15)	98.3
NPG 3050:102 (Good) <i>Unidentified female</i>	70.6 (0.54)	0.3 (0.06)	0.2 (0.02)	BDL	13.8 (0.18)	0.1 (0.02)	13.2 (0.19)	98.3
NPG 1240:43 (Good) <i>Patton, John</i>	70.8 (0.53)	0.4 (0.03)	0.2 (0.03)	BDL	13.5 (0.2)	0.1 (0.02)	13.4 (0.20)	98.4
NPG 3168:109 (Good) <i>Joseph, the French Giant</i>	72.1 (0.68)	0.8 (0.05)	0.1 (0.02)	0.3 (0.05)	9.9 (0.19)	1.9 (0.07)	12.8 (0.17)	97.8
NPG 2617:89 (Saponified) <i>Unidentified male</i>	74.5 (0.77)	BDL	BDL	BDL	5.6 (0.13)	0.1 (0.02)	18.1 (0.18)	98.3
NPG 5330:186 (Saponified) <i>Camp Scene / NY 7th Region</i>	74.9 (0.72)	BDL	BDL	BDL	5.8 (0.09)	0.1 (0.02)	18.3 (0.16)	99.1
NPG 5359:187 (Saponified) <i>Lamon, Ward Hill</i>	75.6 (0.61)	BDL	BDL	BDL	5.4 (0.09)	0.1 (0.02)	18.5 (0.18)	99.6
NPG 5061:187 (Saponified) <i>Lefferts, Marshall</i>	74.9 (0.63)	BDL	BDL	BDL	5.4 (0.07)	0.1 (0.02)	18.1 (0.37)	98.6
NPG 5356:187 (Saponified) <i>Hyatt, Alpheus</i>	74.8 (0.73)	BDL	BDL	BDL	5.9 (0.10)	0.1 (0.02)	18.0 (0.23)	98.9
NPG 5296:185 (Saponified) <i>Farley, Rev.</i>	74.7 (0.70)	BDL	BDL	BDL	5.4 (0.11)	0.1 (0.02)	18.4 (0.19)	98.6
NPG 5306:186 (Severe cracking) <i>Ingraham, D. P., Jr.</i>	71.1 (0.48)	0.2 (0.05)	0.1 (0.02)	0.2 (0.03)	9.0 (0.11)	0.4 (0.04)	16.8 (0.26)	97.7

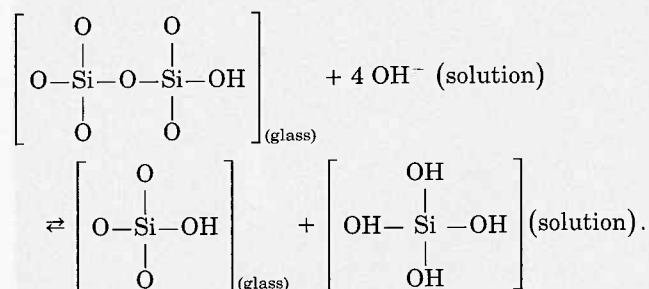
*Data in parentheses = standard deviation.

†BDL, below detection limit.

Figure 7. Bulk composition data from Table I plotted on a ternary phase diagram. Weight percent values were normalized to total 100%. FeO was divided equally between glass formers and alkaline earth oxides.



resulting in dissolution:



Because the OH^- ion excess at the glass surface promotes Stage 2, pH values higher than 9 at the glass surface have been found to be a basic threshold for the onset of Stage 2. When Stage 1 predominates, the thickness of the hydrated surface layer continues to increase, and when the Stage 2 reaction occurs congruently the ratios of the dissolving species approach that of the bulk composition. The extents of Stage 1 and Stage 2 reactions are also a function of the environmental conditions to which the glass surface is subjected. Glass corrosion studies often model one or more of four common environmental regimes: static aqueous corrosion, dynamic aqueous corrosion, static weathering, or dynamic weathering. For example, the glass surfaces in a tightly enclosed space, such as found on plates that were attached to backing glasses in the Meserve Collection, undergo primarily static weathering. Stage 2 of the reaction is accelerated, because high pH corrosion products from Stage 1 remain trapped at the glass surface. The packaging construction of daguerreotypes is another example of this environment, and the corrosion products of 19th century daguerreotype cover glasses have been characterized.²⁴ The weathering of the glass is recognized by localized pitting, haze, and other dendritic deposits on the glass surface. The saponified varnish plates did exhibit an overall haze on the rear surface, but corrosion products on the back of collodion negatives in excellent condition could also be identified. Weathering on the uncoated side of the glass negative was therefore found to offer only indirect, but not conclusive, evidence of image deterioration due to the glass support. The coated side and the uncoated side represent significantly different potential corrosion environments.

As long as the varnish and collodion layers are adhered (i.e., no cracks or flaking that expose the glass surface), the glass corrosion environment is analogous to a static aqueous environment. Corrosion at the collodion-glass interface was apparently confined to the growth of a hydrated glass layer, and corrosion products associated with weathered glass were not observed underneath adhered coating areas.

The average thickness of the hydrated glass layer was not measured in this investigation. However, an approximation of the thickness, which can be derived from the shellac saponification experiment, provides some insight into the extent of the glass corrosion. The freshly saponified shellac samples were mixed with 0.03 to 0.19 g sodium hydroxide per g of shellac. These concentrations are equivalent to sodium amounts that could be supplied by the 18% Na_2O (13.4% Na) component of the bulk glass material from leaching depths ranging from 0.5 to 3- μm and taken up uniformly by 2- μm collodion and 6- μm varnish layers. The spectrum shown in Fig. 4(c) contained the sodium concentration that would be available from a fully leached 3- μm glass layer, and lower concen-

trations produced smaller, but easily detectable, carboxylic acid metal salt peaks in the shellac IR spectra. Hydrated surface layers on the order of a few micrometers thick do not represent large amounts of glass corrosion on soda lime plate glass. For example, Clark, Pantano, and Hench²³ reported the formation of a 12.7- μm hydrated silica layer in a ternary soda-lime-silica glass (20 Na_2O -10 CaO -70 SiO_2 mol%) from static aqueous attack at 100°C in a 3-hr reaction time. The thickness increased to 29 μm after 12 hr at 100°C.

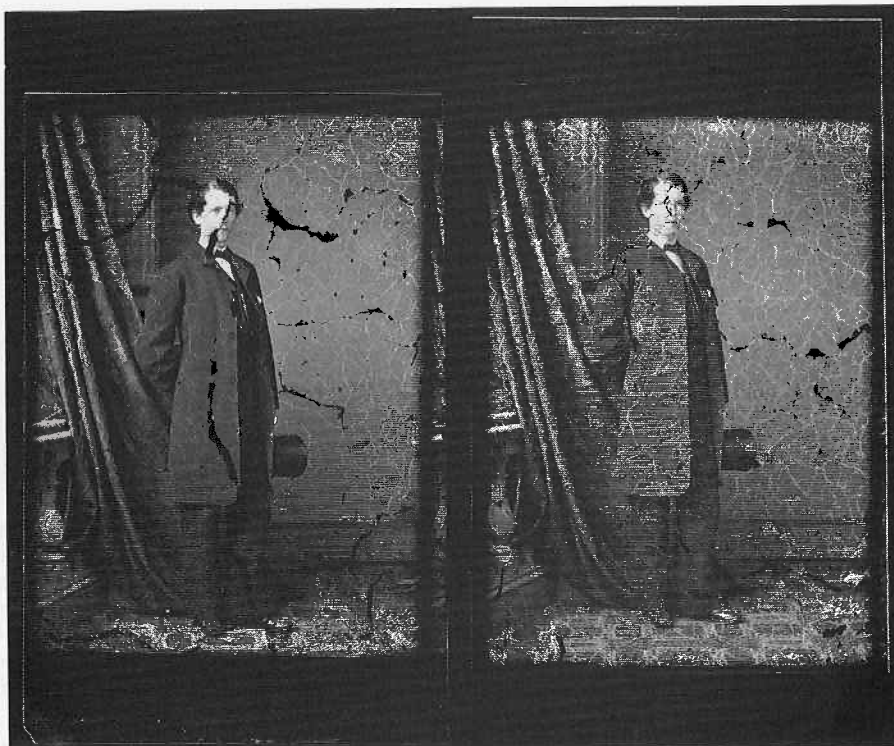
Conclusions

The most severely deteriorated wet plates in the Meserve Collection were concluded to have high sodium glass substrates of the same bulk composition. Over time, enough sodium leached from the glass to cause considerable saponification of the varnish. Despite our 20th century views about the handcrafted variability of the wet-plate process, the most chemically deteriorated Brady studios negatives had poor image stability through no fault of the photographers nor one that they could have easily foreseen. The glass analyses indicate some significant manufacturing variability in 19th century soda lime glass, but the lot-to-lot variability from a single manufacturer is not known. Still, the fact that all saponified plates share identical glass composition suggests that one of the Brady studios purchased this high-sodium glass as stock from a single lot. NPG 5330:186 is especially interesting because it is one of a few Civil War encampment scenes in the Meserve Collection. The collodion craft was performed at a remote location away from either studio; yet this plate has shared the same fate as its studio-made counterparts, because of its glass substrate.

Although the poorest quality plates in the Meserve Collection might be regarded as an isolated bad batch of glass, one additional sample from the collection that was included in the analyses suggests that glass substrate compositions may have a larger role in collodion wet-plate image stability. This sample, NPG 5306:185, differed from the saponified varnish plates. It did not show overall discoloration or tackiness. Instead, severe cracking and flaking of the coating layers had occurred. A modern print from this plate and one of its multiple-exposure image mates is reproduced in Fig. 8. Due to the tenuous adhesion of the image to the substrate, sampling the varnish for FTIR analysis was not attempted. The glass composition of NPG 5306:185 is identified on the ternary phase diagram of Fig. 7 by the notation "severely cracked." At 16.8 wt% Na_2O , the sodium content is higher than found in any of the plates with coatings in excellent condition. Nineteenth century glass procured for wet-plate photography may have a range of compositions that directly influences long-term coating adhesion characteristics through the rate of hydrated glass formation and corresponding alkali leaching at the collodion-glass interface.

More samples in various stages of cracking and adhesion failure definitely exist in the Meserve Collection. During a recent project to rehouse the negatives in acid- and lignin-free quality paper envelopes, the curatorial staff made a conscientious effort to note the present condition of each item in the collection. Sixty-eight percent of the negatives were found to be in very good condition and demonstrate the inherent stability of the wet-plate process. Fifty-two plates (1%) are broken, an often lamented disadvantage of glass substrates. Thirteen percent were listed as "damaged," meaning me-

Figure 8. NPG 5306:185 and 5307:185, *D. P. Ingraham, Jr.*, exhibiting severe cracking and flaking. Fine cracks appear bright in print because of collected dirt and preferentially discolored varnish at the exposed crack edges on the negative. Larger area image losses from coating adhesion failure appear black in the print. Note the striking similarity of the deterioration shown by both plates.



chanically scratched, abraded, etc. Eleven percent were judged to be "deteriorated," whereas another 6% were reported as "deteriorated and flaked" or "deteriorated, flaking, and might benefit from immediate conservation measures." The survey therefore indicated that 17% of the collection had some coating problems associated with chemical deterioration, cracking, and adhesion problems. Additional glass analyses from samples in this group of wet-plate negatives are required in order to validate whether a more subtle correlation exists between glass composition and coating adhesion.

Acknowledgments. The author thanks Eugene Jarosewich and Joseph Nelen (Department of Mineral Sciences at the Museum of Natural History) and Pamela Vandiver (Conservation Analytical Laboratory) for their assistance with the electron microprobe analyses. Walter Hopwood and Melanie Feather (Conservation Analytical Laboratory) provided invaluable help with the FTIR spectroscopy and SEM-EDS analyses. The author also thanks Will Stapp (International Museum of Photography at the George Eastman House) and Ann Shumard (National Portrait Gallery) for their knowledge of and assistance with the Meserve Collection materials.

Appendix: The Meserve Collection—A Brief History

Frederick Hill Meserve (1866–1962) first became interested in historical photographs while searching for images with which to illustrate the Civil War memoirs of his father, a Union army veteran. In 1897 Meserve purchased a small packet of salt print photographs for \$1.10 at a New York auction house and thereby embarked on a course that ultimately led him to amass one of the largest and most important private collections of historical 19th century American photographs. The core of this collection was a large group of Mathew Brady *carte-de-visite* negatives, which Meserve purchased in 1902, still in their original wooden storage boxes, from Anthony,

Scovill and Company, the successor firm to E. & H. T. Anthony, which had acquired the negatives from Mathew Brady himself. Meserve, a dedicated amateur historian, spent the remainder of his life working with these negatives, organizing and studying them, as well as printing them, to produce the illustrations for *Historical Portraits*—his privately published 28-volume iconography of notable 19th century American subjects. When Frederick Hill Meserve died at the age of 96, his extensive collection was inherited by his daughter, Dorothy Meserve Kunhardt, who shared her father's passion for the material and continued his work.

In 1981, with the assistance of the United States Congress, the National Portrait Gallery purchased a group of more than 5400 Meserve Collection negatives from the Dorothy Meserve Kunhardt Trust. These original collodion glass-plate negatives, nearly all of which were made in Mathew Brady's New York or Washington galleries, comprise a remarkably comprehensive pictorial index of the prominent personalities of the Civil War era, including Abraham Lincoln and many of his contemporaries. With the acquisition of this portion of the original Meserve Collection, the National Portrait Gallery joined the Library of Congress and the National Archives as a major repository for original Brady negatives. ▲

References

1. A. Shumard, reprinted by permission from exhibit brochure, "*Lincoln and His Contemporaries*," National Portrait Gallery, Washington, DC, 1990.
2. M. McCormick-Goodhart, *9th Triennial Meeting*, Dresden, Germany, August 26–31, 1990, Preprints vol. I, ICOM Committee for Conservation 262(1990).
3. M. McCormick-Goodhart, *Topics in Photographic Conservation, AIC Photographic Materials Group 3*: 135(1989).
4. M. S. Barger, *Bibliography of Photographic Processes in Use before 1880*, Graphic Arts Research Center, Rochester, New York, 1980.
5. J. Martin, *Brit. J. Photogr.* **8**: 304(1861).
6. J. G. Vail, *Photographic Mosaics* 32(1878).
7. J. Sang, *Photogr. J.* **5**: 226(1859).

8. H. R. Nicols, *Photogr. News* **6**: 17(1862).
9. M. Carey Lea, *Philadelphia Photogr.* **4**: 167(1867).
10. Anonymous, *Photogr. News* **14**: 522(1870).
11. Anonymous, *Brit. J. Photogr.* **24**: 279(1877).
12. Anonymous, *Brit. J. Photogr.* **25**: 575(1878).
13. M. Derrick, *J. AIC* **28**: 43(1989).
14. *The Sadtler Standard Spectra*, Sadtler Research Laboratories, Philadelphia, PA, 1965.
15. J. Towler, *The Silver Sunbeam*, Facsimile 1864 Edition, Morgan & Morgan, New York, 1969.
16. F. S. Archer, *The Collodion Process on Glass*, 2nd ed. (printed for the author), London, England, 1854.
17. T. F. Hardwich, *A Manual of Photographic Chemistry, Including the Practice of the Collodion Process*, 6th ed., J. Churchill, London, England, 1861.
18. F. R. Bacon, *Glass Ind.* **49**: 438(1968).
19. A. K. Lyle, *J. Amer. Ceram. Soc.* **26**: 201(1943).
20. R. W. Douglas and T. M. El-Shamy, *J. Amer. Ceram. Soc.* **50**: 1(1967).
21. T. M. El-Shamy and R. W. Douglas, *Glass Technol.* **13**: 77(1972).
22. S. Tsuchihashi and E. Sekido, *Bull. Chem. Soc. Jpn.* **32**: 868(1959).
23. D. E. Clark, C. G. Pantano, Jr., and L. L. Hench, *Corrosion of Glass*, Magazines for Industry, Inc., New York, 1979.
24. M. S. Barger, D. K. Smith, and W. B. White, *J. Mater. Sci.* **24**: 1343(1989).