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EXAMINATION AND INVESTIGATION OF 19th CENTURY PAPER NEGATIVES
A Study of the Process, Materials, and Deterioration Characteristics

Lee Ann Daffner

INTRODUCTION

The earliest extant paper negative was made in 1853 by the English scientist, William Henry Fox Talbot. The first public announcement of his photographic drawing process was made by Fox Talbot in 1839, and within the next two years he had refined and patented his most stable and workable photographic system, the Calotype negative. By the 1860's, the positive salt print processes reached their highest level of technical and artistic perfection. To arrive at this level of perfection, photography on paper went through an extremely rapid stage of expansion, yielding a staggering progression of ideas and developments. Technical procedures inherited from the traditional fine art fields are present in these negatives, such as the use of resins and waxes. Every aspect of the preparation and sensitization of the negative was executed by the photographer, making each negative a unique creation. Consequently, these handmade artifacts are extremely individual and sometimes difficult to interpret. Previously, there has been limited inquiry into the material aspects of early paper negatives although it is one which deserves attention and discussion.

This study reviews the three primary methods employed by photographers in the 19th century for making paper negatives and summarizes the distinguishing characteristics of each process. The basis of this study was a survey conducted during a research internship project at the George Eastman House in Rochester, New York. The subject was a collection of 265 paper negatives by the Irish photographer John Shaw Smith produced in 1852. Other groups of paper negatives were also examined from various private collections, the Metropolitan Museum of Art, and the Museum of the City of New York.

The paper negatives were examined under normal, reflected and transmitted illumination and through the stereo microscope. Micro-chemical analysis of fibers, transparentizers, and retouch media from five paper negatives was conducted. Selected paper negatives were photographed recto, verso, through transmitted light, and with the stereo microscope to illustrate common deterioration characteristics. The information gathered from this survey has proved vital to an understanding of the working methods and techniques of photographers working during the 19th century.

This preliminary investigation was presented at the American Institute for Conservation of Historic & Artistic Works' annual conference in Nashville, Tennessee, in June of 1994. Deterioration characteristics of paper negatives will be mentioned and discussed in this paper, however, the conservation and preservation of these negatives materials is an area of ongoing study, and will be presented in future presentations and publications.

THE PAPER NEGATIVE: HISTORY, TECHNIQUES AND MATERIALS

There are three primary methods of producing paper negatives described in the 1840's and 1850's, although photographers were continually experimenting with and producing variations. The following list summarizes the three methods for producing paper negatives addressed in this report, one 19th century photographer who worked in that process, and mentions several variant methods.

I **The Calotype and Plain Paper Process**
The Plain Paper Negative, waxed post processing.
(William Henry Fox Talbot)

II **The Wet Paper Process**
Waxed postprocessing.
(Louis Blanquart-Evrard)

III **The Waxed Paper Negative**
Waxed before sensitization.
(Gustave Le Gray, after 1851)

Variant Methods
The turpentine waxed negative (Maurice Lespiault)
Collodion on paper (Stephane Geoffroy)
Gelatin on paper (Edouard Baldus)

The Calotype and Plain Paper Process

In 1841 Talbot coined the phrase "Calotype" to describe his photographic process on paper based on a physically developed-out latent image. As he states to the Royal Society of London in 1841, "I have named the paper thus prepared Calotype paper ... the picture is a *negative* one ... the copies are *positive* .... " Talbot recommended that the positive proofs be made with the plain salted paper method, and not the Calotype process. Therefore, suitable terminology for the positive proofs are Calotype Positives or simply, salt prints. Negative images made from Talbot's exact formula are Calotype Negatives.

In Talbot's patented Calotype process, high quality writing papers were coated with silver halide solutions of either sodium chloride or iodine. The sensitizing solution is applied directly to a sheet of paper by brushing, and the light-sensitive silver salt solution is carried into the matrix of the paper fibers. The sensitized paper was

ready for exposure in the camera. These papers were best used as soon as possible, as their sensitivity diminished after 24 hours. Many innovations were made on Talbot's Calotype Negative process in the succeeding years, however, the common feature in all is the application of sensitizing solutions directly to plain paper. These negatives are commonly referred to as Plain Paper Negatives in the photographic literature, and they were often rendered more translucent with warm wax, or left unwaxed, for contact printing positives. For photographers in the 19th century, transparentizing negatives decreased printing times significantly, although it is important to note that they did not always transparentize their negatives.

The Wet Paper Process

Louis Blanquart-Evrard was a tobacco merchant who studied chemistry and learned the Calotype Process from one of Talbot's followers. He has been called the "Gutenberg of Photography" due to his early recognition of the potential for photography's mass production. Among the contributions he made in his long career was the promotion of albumen on paper for positive prints.

In January 1847, Blanquart-Evrard introduced a wet-paper process to the French Academie of Sciences. His adaptations of Talbot's Calotype process included floating the paper on the solution, instead of brushing the surface. However, he also altered the process by pouring the sensitizing solution onto a sheet of glass and evenly pressing the iodized side of the paper to the glass. The sheet was backed by several layers of moist paper to keep the chemicals in solution. Another sheet of glass was put on top of this, and the whole inserted into the camera and exposed moist. Talbot also worked with moist paper, but Blanquart-Evrard's combined innovations distinguished his process from Talbot's.

Paper prepared from the wet paper process would remain sensitive for one day and had to be developed in the evening. In particular, the early traveling photographers in the Near East used the wet paper process where extremely high temperatures restricted the use of other photographic methods, such as the waxed paper negative described below. Maxime du Camp and John Shaw Smith were two such photographers who used the wet paper process.

The Waxed Paper Negative

Le Gray was a painting student of the artist Paul Delaroche when he became involved in photography. He was a founding member of the first photographic society in the world, the Societe Heliographique. In 1851 Le Gray introduced his waxed paper negative process to the French Academie of Sciences in Paris. The most important and innovative procedure he introduced was saturating the paper with wax before sensitizing. Le Gray's method was recognized for its excellent rendition of detail.

The steps in the wax-paper technique are as follows:

1. High quality paper is impregnated with warm wax.
2. The waxed paper is "salted" or "iodized".
3. The prepared paper is stored until ready for total sensitization.
4. The paper is sensitized with silver nitrate. A binding medium was used by Le Gray and his followers in this procedure: "whey", albumen, isinglass, or rice water act as a binder between the waxed surface and the chemistry. (Hannavy 1981)
5. The sensitized paper is exposed in the camera.
6. The exposed negative is developed in gallic acid and fixed.

Variant Methods

An example of the many variant methods of the waxed paper process is the "Turpentine Waxed Paper Process", in which light sensitive solutions were added directly to a wax and solvent mixture. The liquid wax mixture was applied directly to the paper and exposed in the camera. (Hannavy 1981) Other variant methods employed albumin, collodion or gelatin as a binder layer for the image silver. These interesting variations are encountered in the photographic literature, and deserve further study, but will not be addressed in this report.

The Image Silver

In the 19th century, chemicals were available in different grades of purity, as they are today. The photographic manuals always encouraged the amateur to use the "purest possible" (Sutton 1855), however, photography was not yet an exact and distinct science. Without written documentation, it is not possible to determine which processing solutions were used to create a given negative.

The color of the image layer in paper negatives examined in this study ranges from red and yellow tones to brown and neutral tones. This color variation is due in part to differences in the particle size of the final image silver, to the specific chemical formulations and to the paper employed as primary support. Images made from the Calotype and Plain Paper Process are slightly diffuse with softer details, while the waxed paper negatives are surprisingly sharp, due to the initial reduction of light scattering interfaces within the fiber matrix by the transparentizing agent. Sometimes the paper negative image is clearly visible in normal reflected light. Other times the image is only clearly visible through transmitted light. Many of the waxed paper negatives examined appeared flat grey under normal reflected illumination.

Because these photographic negatives are handmade, signs of the operator's techniques and the history of the artifact can be found in their imperfections and aging characteristics.

Some common characteristics associated with the image silver are:

- Spots and stains were caused by fingers and hands contaminated with processing chemicals.
- Pin holes are often present in the center of dark stains at the corners of the print where the photographer may have secured the paper to a hanging line to dry. A black uneven line or spot resulted from the reaction of metal pins with moist, sensitized paper.
- White or black spots occur in the image where metal inclusions in the paper support have reacted with the silver image.
- Mottling of the image is a result of an uneven absorption of the solution in the paper.
- Marbling of the final image material was encountered, and is attributed to contamination of the processing solutions or containers. If marbling is present on only one side of the negative, it is likely that the photographer floated the paper on the solution instead of using an immersion technique.

The Paper

The final image of a photograph is greatly affected by the individual qualities of the paper used as the primary support. A smooth, lightweight paper will absorb the chemicals differently than a soft, thick paper. The sizing of the paper will also affect the appearance and hue of the final image. Some papers will readily accept transparentizing agents while other papers are not easily saturated. The early practitioners of paper negatives processes were constantly in search of papers which had specific characteristics to suit their individual needs.

Locating a dependable supply of high quality papers was a primary concern for the early photographers. Paper impurities could ruin the image by reacting with the photographic chemistry. Usually these impurities were bits of metal particles left over from the initial paper processing. The resulting flaws in the image are in the form of local silver accumulation, or oxidation. Uneven sizing in the paper could result in uneven sensitizing.

The scarcity of good quality papers can be traced to the historic and significant change in the papermaking industry in the late 1820's. The industrialization of mechanical printing and mechanical papermaking process changed the course of the papermaking industry. With paper mills producing large amounts of machine-made paper, the demand for linen and cotton rags rose. Consequently, the hand-made paper production fell sharply. The early photographers were faced with the challenge of locating papers suitable for photographic use. By the late 1850's paper mills such as Chafford Mills in England and Canson's in France were producing papers specifically designed and produced for use as photographic negatives.

High quality wove papers were preferred by 19th century photographers because they do not have laid and chain lines. Talbot recommended using "the best writing-paper, having a smooth surface, and close even texture", and states: "The watermark, if any, should be cut off, lest it should injure the appearance of the picture." (Talbot 1841) Watermarks are encountered in the surviving negatives, and often are aesthetically placed within the composition. During this study, the "J WHATMAN / TURKEY MILL / 18..." watermark was observed in paper negatives produced by both English and French photographers. The English photographer, Benjamin Brecknell Turner used paper with the distinct water mark, "R TURNER PATENT TALBOTYPE", which was produced after 1852 at Chafford Mills in England. Most watermarks are missing from paper negatives, thus making positive identification difficult and inconclusive.

The handmade papers tend to be more dense and measure 5 mil in thickness. Despite these slightly thicker papers, photographers using wet paper processes were faced with the challenge of working with wet paper and wet tears are commonly encountered with negatives made with these methods. Due to the increased wet-strength of the Waxed Paper Negative, thinner papers could be employed, some measuring 3 mil in thickness.

The Wax

Beeswax was a familiar and well known material to 19th century artists and craftsmen and was employed for waxing paper negatives. This familiar material is known to have been used by ancient civilizations, and sun bleached wax was used in the Roman Era. The documented use of transparent paper in art date back to 1437 when Cennino Ceninni described several methods of preparing "clear" tracing paper in the Craftsman's Handbook. Tracing papers were often preferred by artists and craftsmen as a less destructive method of copying originals then by tracing with a stylus or by pricking and pouncing (Bachman 1983)

In the 17th century, tracing papers were used by the artist and draftsmen with the camera obscura. Many of the early photographers such as Le Gray had training in the Fine Arts, especially painting and would have been familiar with the techniques and materials used in rendering paper transparent. It is not surprising that they investigated these techniques during their photographic experiments and wax was employed early in the 1840's for rendering photographic images more transparent. Paraffin wax was discovered in 1830, although full scale production was not developed until 1855, thus, it is generally presumed that the wax used for paper negatives is beeswax. (Ivanovsky 1952)

Wax has long been known for its chemical stability. This stability is due to the fully saturated long chain polymer components. There are very few functional groups on the long chain available to react, which also improves its stability. Beeswax is resistant to oxidation, and is an effective moisture barrier. Although it is resistant to biological deterioration, there are fungi which will grow on beeswax. (Kowalik 1984) The development of light spots and cracking is a result of biological attack. Beeswax can become brittle over time due to gradual hydrolysis and oxidation. (Griswold 1992) It is naturally a warm light amber color, although it can be chemically bleached or lightened by the sun. However, after aging, bleached beeswax regains its amber color.

The numerous methods for impregnating papers with wax varied from sprinkling grated wax onto a paper and warming with an iron, to immersing the paper in a tub of molten wax. Excess wax could be removed by placing the paper between blotters and reheating with an iron. The wax could be applied to a paper overall, or selectively, in an effort to increase exposure and detail locally in an image.

Except in extreme examples, it is often not possible to determine if a photographer added resins or gums to his wax, a practise historically associated with wax working. Venice turpentine, the oleo-resin of the European larch tree was commonly combined with wax by artists in the 19th century. The addition of resins can alter the stability of waxes and affect the aging characteristics. Resin additives to wax can cause a variety of changes including embrittlement, darkening, cracking, shrinkage, change in refractive index, increased tackiness, surface efflorescence, and biological growth. The deterioration of each component, namely the wax and resin admixtures, may take place separately or synergistically. (Horie 1987) The addition of resins can alter the stability of waxes and affect its aging characteristics. The oxidation of oils and oleo-resins leads to the formation of colored products, producing a visible darkening of the film with age. To date, the nature of additives in these negatives remains to be identified.

Overall, the condition of the wax in the various negative collections examined was good. All negatives are vulnerable during handling. The deterioration characteristics observed were handling dents and a slight overall darkening and crystallization of the wax. This characteristic was readily apparent against the black retouched sky areas. Creases and handling dents are common, as flexing the wax layer will result in minute breaks and cracks. The change in the light scattering qualities in these broken areas makes them appear white.

Many of the handling dents present in the negatives were made by the photographer, which was apparent when comparing the positive prints to their negatives. Newer dents were observed, as well as impressions made from writing

on the paper portfolios. The early manuals recommend taking great care of the negatives once they are waxed, suggesting they be placed in a portfolio and not handled extensively to " ... preserve them carefully." (Sutton 1855) Although these flaws in the negative may be disfiguring and unsightly, they can provide important historic information about the history of the negative.

Applied Media

Processing flaws in paper negatives were retouched with a variety of methods depending on the process and preferences of the photographer. Original retouch media was observed on many of the negatives examined. In the Shaw Smith collection, most of the paper negatives were retouched on the recto with a dense, opaque black medium, which served to mask out the sky and inscriptions made on the verso. Mold was observed on many of the negatives, usually in the unwaxed areas. The growth appears to be associated with the binding agent, as it is seen especially around large pigment agglomerates in retouched areas where there is excess binder. Cracking and minor flaking were also observed in the retouched areas which were severely creased. Planer deformations in the paper support were evident along the image where retouch media had been applied.

On the other hand, the waxed paper negatives viewed were only occasionally retouched. When they were, it was usually with ink or pencil, as other retouch medium would not adhere to the waxy surface of the paper.

Iron gall ink was employed for both retouch and inscriptions, and presents special concerns due to its aging characteristics. The deterioration of the paper support is a result of the oxidizing action of soluble iron compounds in the ink. Areas where iron gall inscriptions and retouching were present had severely oxidized, resulting in image loss and local deterioration in the paper support.

Wafers

An observation was made during the course of the George Eastman House survey which yields information about the working methods of John Shaw Smith. "Accretions" on the paper corner tabs were present on many negatives in the collection. These accretions occurred in a variety of shapes and sizes, colors and in association with other materials. They are most often seen as small, black, squarish forms, although they also appeared as yellow, green, red, purple and blue. Paper fibers were observed to be attached to them. Conversely, it was observed that sometimes an area of the small paper tab was skinned, and residues of the accretions were present at the edge of the skinned area. Sometimes the attached paper fibers were stained with metallic silver. The accretions always faced outward, towards the recto of the negative.

If the accretion was colored, it contained distinct pigment particles. A small sample tested positive for starch. The paper handling tabs were added before the negative was retouched, so they were clearly part of the later stages of processing. The presence of paper fibers suggested they may have been used during the printing stage, when the negative would need to be held against the paper.

Two citations in the photographic literature on printing calotypes referred to using "wafers" to secure the negative to the positive paper. In Tomlinson's 1854 *Cyclopedia of Useful Arts and Manufacture,* a wafer was described as a small disc of dried wheaten four to which an adhesive property is instantly communicated on the addition of moisture. Wafers were used to seal envelopes and coloring matter was sometimes added, as were perfumes. It was observed on 25 Shaw Smith negatives that two or three colored accretions or wafers were present on a single tab. The frequency of distinct accretions present could indicate how many prints were made from a given negative.

CONCLUSION

This preliminary study of the material components of paper negatives has provided a foundation for understanding the working techniques and materials of 19th century photographers. The investigation has also become the foundation for further, in depth study of the deterioration and preservation concerns of these beautiful and fragile artifacts. These first generation, in camera originals are direct links to the 19th century photographer's experience; untapped sources of insight to our photographic history and development.

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