

Article

Understanding Frédéric Flachéron's Paper Negative Process through Experimentation and Specular Reflection FTIR Analysis

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Abstract: Cultural heritage objects present a special set of challenges for chemical analysis. Often micro-sampling or even contacting the object is deemed an unacceptable risk to the object. This study examined if specular reflection FTIR, a non-sampling and non-contact analytical technique, can provide insight into chemical composition of the layered coatings on Frédéric Flachéron's paper negatives (1848–1852) in the Harrison D. Horblit Collection of Early Photography, in Houghton Library, at Harvard University. Specular reflection FTIR data confirmed the identification of beeswax and sandarac as the transparentizing media on Flachéron's paper negatives, as previously published by Lee Ann Daffner. However, specular reflection FTIR analysis also indicated that some negatives had additional localized coatings of orange shellac in specific areas of the images. To understand why Flachéron retouched his negatives with orange shellac, modern experimental replications of the paper negative process were performed. Through modern experimentation with the paper negative technique, it was found that Flachéron's coatings of shellac served as an integral part of his image-altering technique. The color of the orange shellac subtly alters contrast and density, but it does not mask an area the way an opaque watercolor or highly pigmented paint might. The fine adjustments to the negatives with orange shellac were an attempt to perfect the contrast in the print, and better render depth and detail. These discoveries add to a growing body of recent research that points to the historic and art historic importance of negatives and coatings in photography. The specificity with which specular reflection FTIR was able to nondestructively identify the chemical composition of the local coating, and specifically target the analysis on the areas in which it appeared, allowed for an understanding of Flachéron's use of local coatings as a retouching method rather than a protective coating.

Keywords: specular reflection FTIR; Fourier Transform Infrared spectroscopy; cultural heritage chemical analysis; paper negatives; Frédéric Flachéron; negative retouching



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1. Introduction

The French photographer Frédéric Flachéron (1813–1883) became part of a circle of early photographers living in Italy in 1839 [1]. Flachéron was known for dramatic architectural views of Rome. The Horblit Collection at Houghton Library holds 37 paper negatives and more than 80 prints created by Flachéron [1]. Trained as a painter, Flachéron demonstrated skill and imagination in manipulating his negatives. His techniques clearly included masking, retouching, and coating the negatives to block some of the strong Mediterranean sunlight that he was working in to alter the final print. Understanding some of the early photographers' material choices and techniques is important for the art history and conservation of objects that are dated from the dawn of photography.

Twenty-seven paper negatives by Flachéron, taken from the Harrison D. Horblit Collection of Early Photography, in Houghton Library, at Harvard University, were selected for analysis because they exhibited multiple layers of coatings, including localized coatings, which are presumed to be retouched negatives created by Flachéron. In this work, the chemical composition of the localized coatings was determined via reflection FTIR. This occurred after verifying the validity of the information provided by the reflection FTIR, using the coatings on these negatives that were previously identified by Lee Ann Daffner, who also used other analytical techniques [1]. Modern reproduction experiments were performed to attempt to reproduce the effects that these localized coatings would have had on Flachéron's prints to help understand his choice of materials and working methods.

The coatings used by Flachéron to transparentize his paper negatives had previously been identified in 2003 by Lee Ann Daffner [1], providing a known reference against which to evaluate the specular reflection FTIR method. The specular reflection FTIR method confirmed Daffner's identification of beeswax and sandarac on Flachéron's paper negatives. Some of Flachéron's negatives also comprised additional localized coatings, which the specular reflection FTIR measurements identified as orange shellac. The purpose of the localized coating was unclear. If it was for a protective purpose, like the coatings in early salt prints [2], why was it not applied everywhere? If the localized coating was not for protective purposes, was it used to modify the image in the final print?

To probe the reasons why Flachéron might have applied the localized coatings to some areas of his negatives, modern experimental facsimile paper negatives of developed out salted paper prints were made. It was found that Flachéron's coatings of orange shellac served as an integral part of his image-altering technique. The color of the orange shellac subtly alters contrast and density, but it does not mask areas the way an opaque watercolor or highly pigmented paint might. It is assumed that the fine adjustments to the negatives using orange shellac were an attempt by Flachéron to improve the contrast of the print, and better render depth and detail. These discoveries add to a growing body of recent research that points to the historic and art historic importance of negatives and coatings in photography. The specificity with which specular reflection FTIR was able to nondestructively identify the chemical composition of the local coating, and specifically target the analysis on the areas in which it appeared, allowed for an understanding of Flachéron's use of the local coatings as a retouching method, rather than a protective coating.

The nondestructive chemical analysis of cultural heritage objects is a challenge. Micro-sampling, or even just contacting the object in the cases of high gloss photographs and negatives, can be deemed an unacceptable risk to the object. Portable X-Ray Fluorescence (XRF) instruments can meet the no sampling and no contact requirements, but XRF only provides the elemental composition of an object. Elemental analysis can be useful for insights into the inorganic compounds used in the chemical processing of a photograph or negative [3–5], but it is not useful when assessing the organic compounds often used in the coatings. Both Raman spectroscopy and FTIR spectroscopy can provide the molecular composition of the organic (and inorganic) compounds in an object. However, the Raman signal can easily be overwhelmed by any fluorescence from the sample, which is a common problem with organic compounds, such as the paper substrates in paper-based photographs and other works of art. FTIR spectroscopy has long been the go-to analysis technique for organic compound identification, but this occurs either in a micro-sampling modality or by contacting the sample in an Attenuated Total Reflection (ATR-FTIR) modality [6].

The use of non-contact reflection FTIR modes is gaining popularity for cultural heritage object analysis [2,3,7–12]. Non-contact reflection FTIR measurements can be conducted using specular reflection FTIR, diffuse reflection FTIR, or external reflection FTIR (which captures both diffuse reflected light and specular reflected light) modes.

The use of reflection FTIR for the chemical identification of single component coatings on salted paper prints [2], and of general categories of chemicals (i.e., proteins, waxes, cellulose) in paper negatives [3], have previously been published. Reflection FTIR has also been

used for the identification of similar coating materials on historic musical instruments [13]. Reflection FTIR spectral databases are starting to be generated [14,15], but they have a long way to go before they become as comprehensive as the available FTIR-ATR databases. Here, the ability to use specular reflection FTIR identification to specifically identify the components in mixed component coatings or multiple layered coatings is demonstrated, as the working methods of Frédéric Flachéron are rediscovered.

2. Materials and Methods

2.1. Paper Negatives of Frédéric Flachéron, 1848–1852

The Harrison D. Horblit Collection of Early Photography, in the Houghton Library at Harvard University, includes 370 paper negatives [16]. These negatives were first catalogued in 1998 as part of a Getty-funded initiative to catalog the entire Horblit collection. More recently, the paper negatives were included in a Harvard-wide survey of salted paper prints and paper negatives [17]. During that survey, twenty-seven paper negatives by Frédéric Flachéron, taken during a tour of Italy, were identified as excellent candidates for analysis with specular reflection FTIR. These negatives were selected because several paper negatives from this collection, which were taken by Flachéron, had been previously analyzed by Lee Ann Daffner using microsamples for gas chromatography—mass spectrometry (GC-MS) analysis [1]. Daffner also used transmission FTIR analysis attempting to pass infrared light through the paper substrate and the coatings of the paper negatives [1]. This previous study identified the presence of multiple coatings, and therefore, it provided an opportunity to compare findings using different analytical techniques.

As mentioned in the Daffner study, Flachéron's negatives exhibited multiple layers of coatings, including a clear visual indication of an overall transparentizing layer, and an additional localized coating (Figure 1).



Figure 1. This image is representative of the relative glossiness of locally coated areas, as well as the tidelines often visible at the edges of the coated areas, which allowed for the easy visual identification of the coating. Frédéric Flachéron, Untitled, 1851, paper negative, Houghton Library Horblit TypPr 815.F396.075 (N) Sz2.

Flachéron applied an overall coating to his negatives to saturate and transparentize the paper substrate, as was typical with the paper negative process [18]. Photographers of this period often used waxes, oils, and varnishes to achieve a more translucent paper, and these could be applied before or after the negative was prepared and processed. Local coatings were visible as glossy brushstrokes on top of the matte surface of the overall coating, or overlapping edges of the black opaque watercolor layer which was used to mask the sky (Figure 1).

In some cases, the glossy local coating was applied over large areas, as in Figure 2.

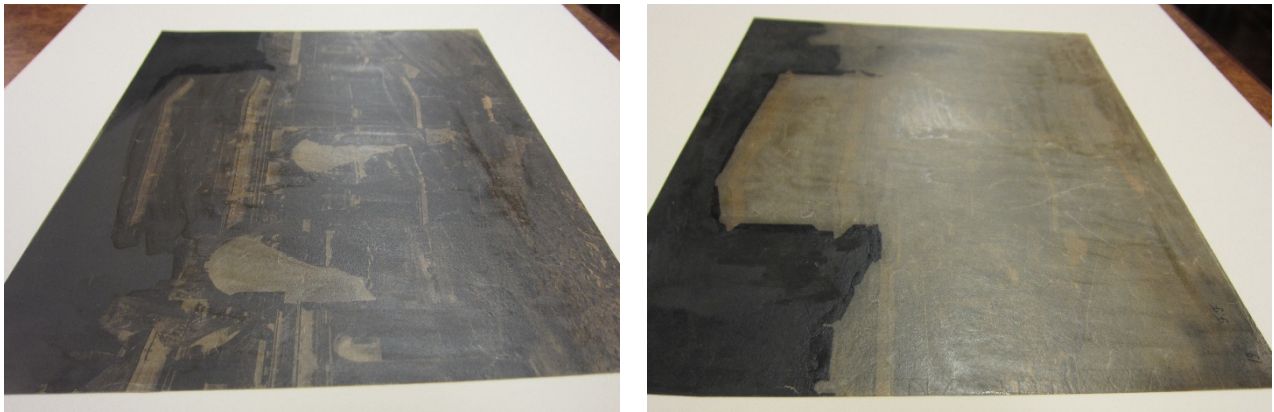


Figure 2. Front and back of negative 063, showing applications of a glossy coating on both sides. Four negatives were found to have similar coatings, either over the entire image area, or in discrete areas only.

In other negatives it was applied to more discrete areas which loosely corresponded with architectural elements in the image (TypPr 815.F396.059 (N) Sz2 outlined in blue in Figure 3).

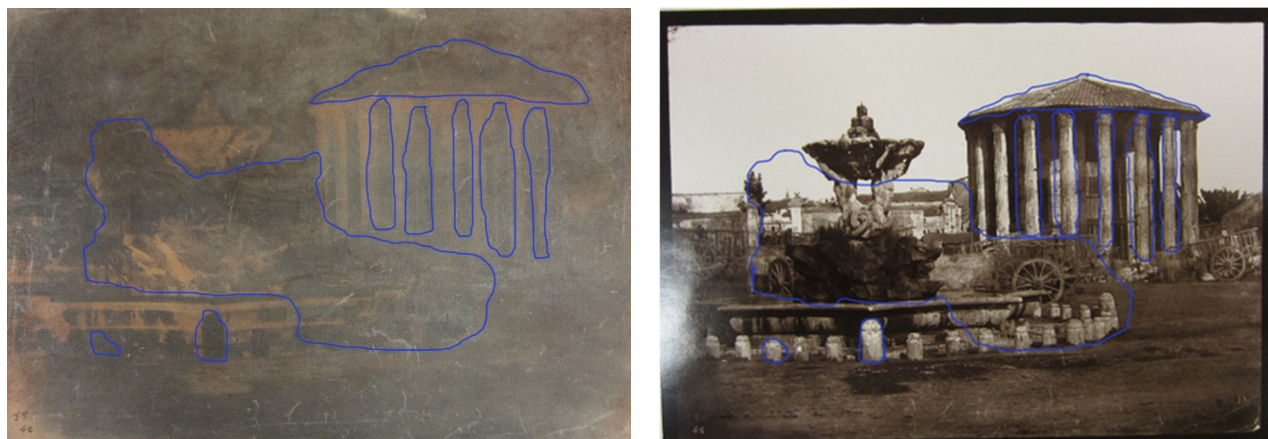


Figure 3. The negative (left) and modern positive (right) of TypPr 815.F396.059, with areas of orange shellac circled in blue. Frédéric Flachéron, Untitled, paper negative, Houghton Library Horblit TypPr 815.F396.059 (N) Sz2.

Daffner's study provided a foundation for the current study. To achieve the first goal of Daffner's study, the specular reflection FTIR modality and the specular reflection FTIR spectral library of single component coatings were used to confirm the presence of beeswax and sandarac, as previously noted [1]. To achieve the second goal, specular reflectance FTIR was used to try to identify any unknown coating components that were previously not identified due to the paper substrate being too thick for transmission FTIR in some important spectral regions and components that may not have been identified because of the destructive sampling of the object that was needed so that GC-MS techniques could be used. This information would shed additional light on Flachéron's working methods and materials.

2.2. Specular Reflection FTIR Analysis

Twenty-seven paper negatives by Frédéric Flachéron from the Horblit Collection were selected for analysis to represent the range of variations based on visual observations. The negatives ranged in date from 1848 to 1852, and fell into two size categories, 10 × 14 in (25.4 × 35.56 cm) and 7 × 8.5 in (17.78 × 21.59 cm). The specular reflection FTIR spectra

were all collected onsite at the Houghton Library with a Bruker Lumos I FTIR microscope with a liquid nitrogen cooled MCT detector, ranging from 4000–600 cm^{-1} . The Lumos has a large open sample stage area, as can be seen in Figure 4. Measurements were taken from areas on the recto and verso that exhibited a glossy local coating, as well as areas that appeared to only have the overall transparentizing coating.



Figure 4. Paper negative undergoing specular reflection FTIR analysis, using the Bruker Lumos I, onsite at the Houghton Library.

The data were collected, processed, and analyzed using OPUS 7.2. The baseline correction was conducted in automatic mode using a rubber band correction. The spectral searches occurred using the standard algorithm setting in OPUS, against the spectral library of single component coatings that were previously published [14]. The spectral contribution of the paper was included in both the reference spectrum and the historic photograph spectrum, so no spectral subtraction was needed for a positive match to occur. The authors believe that this makes the library easier to use, although it does limit the usefulness of the spectral library to only other works on cotton paper. For works on other materials, relevant modern reference samples would need to be taken, and a relevant specular reflection FTIR library would need to be generated.

The OPUS software mathematically matches unknown spectra with reference spectra. This means that the identification of an unknown coating does *not* occur via qualitative visual identification, which is conducted by humans, and concerns certain characteristic stretching bands (e.g., amide I bands for proteins, etc.); rather, it is based on statistical pattern matching of the complete spectrum, which is carried out using a computer.

3. Results

Specular Reflection FTIR Results

The spectra collected from the Flachéron negatives were compared with the single component coating specular reflection FTIR dataset, which was previously developed for the analysis of the coatings used for Harvard University class albums, as previously described [2]. This approach identified a probable mixture of beeswax and sandarac in the areas of the negatives with no apparent localized coating. The spectra from these areas of the negative shared characteristic peaks with the reference spectra for both beeswax and sandarac, therefore, the spectral library search suggested both as possible matches. This confirmed the identifications previously made by Daffner [1] using a complimentary analytical technique.

The spectral library did not encounter issues creating matches when the spectra were collected from either a light or dark region of the photographic image. Human intuition is that a stronger reflected IR signal would occur in the light region of the photograph or

paper negative. This is misleading. This intuition is based on visible light reflectance and is not applicable in the mid-infrared spectral region.

In order to confirm the presence of a beeswax/sandarac mixture, the data from Flachéron's negatives were compared with both mathematical mixtures of sandarac and beeswax spectra, as well as modern reference samples composed of the mixture. The spectral shape of the data collected from the overall coated areas of the paper negatives was similar to a mathematically modeled 1:1 mixture of the modern single component reference spectra of beeswax and sandarac (Figure 5).

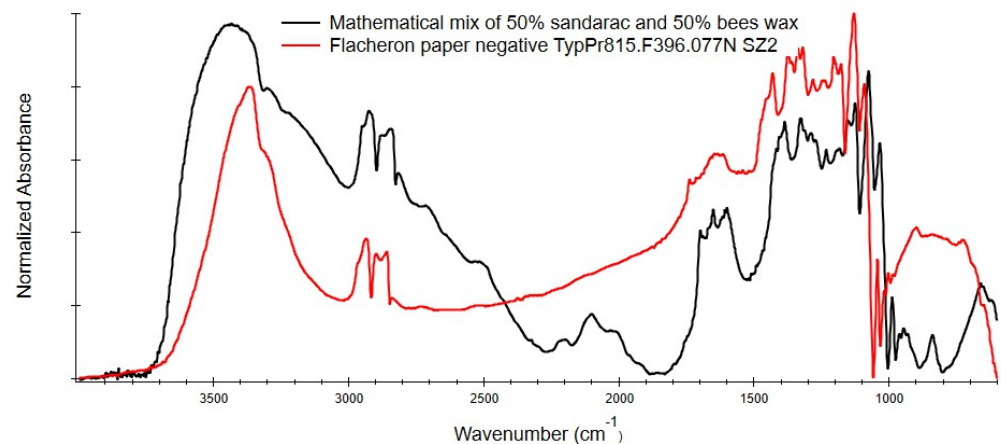


Figure 5. Specular reflection FTIR spectra of the Flachéron paper negative, which showed a match between the historic object and mathematically mixed beeswax and sandarac coatings on salted paper prints.

Modern reference samples of the beeswax and sandarac mixture, composed of equal parts beeswax and sandarac, were created using different application methods for beeswax and sandarac resin in ethanol, all of which are described below. The coated reference samples were analyzed using specular reflection FTIR, and they matched well with the spectra from areas of Flachéron's negatives with no local coatings (Figure 6).

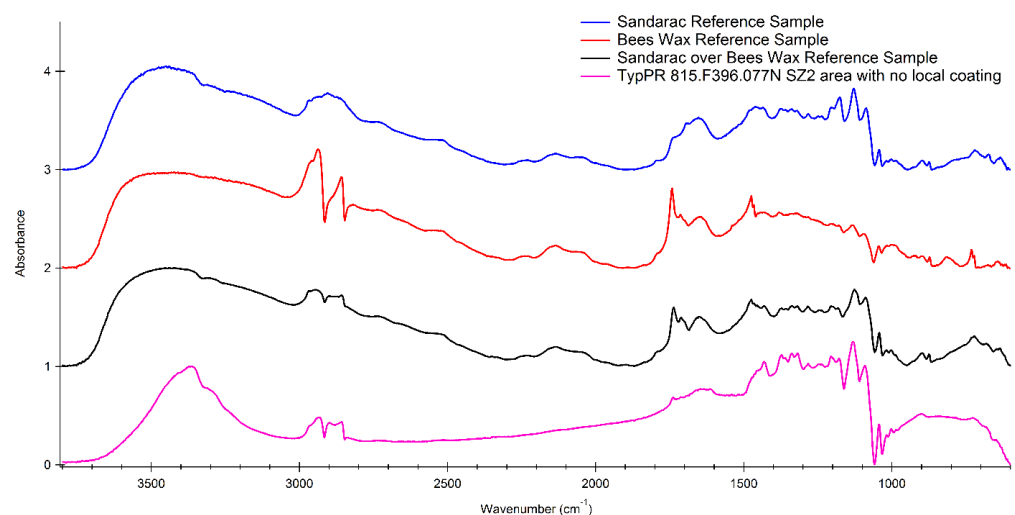


Figure 6. Specular reflectance FTIR spectra of sandarac and beeswax modern reference samples, compared with the Flachéron paper negative, TypPr 815.F396.077N SZ2, on an area with no localized coatings. Note the similarities concerning the spectral shape of the sandarac and beeswax reference sample, and the Flachéron's paper negative; for instance, in the CH stretching region, 2800–3000 cm^{-1} , and in the fingerprint range between 1000 and 1500 cm^{-1} .

Spectra from areas with the visible localized coatings were compared with the specular reflection FTIR library of single coatings. Fortunately, this provided useful findings, indicating a roughly equal mixture of beeswax, sandarac, and shellac in the locally coated areas of Flachéron's paper negatives. Mathematically modeled spectra of mixtures were generated based on the suggestions from the spectral library search; again, modern reference samples were produced based on matches.

To produce the modern reference samples, beeswax and sandarac were coated onto salted paper photographs, created using Crane Pearl White paper by Crane & Co. Paper. Three different application methods for coating the paper prints were tested, as follows:

- Method 1 Mixing melted wax and sandarac together before applying the mixture to the paper. This was unsuccessful. When the sandarac in the alcohol solution was added to the heated wax, the alcohol immediately vaporized and left a very heavy waxy substance.
- Method 2 Waxing a salted paper print over heat, then brushing on a solution of sandarac in alcohol. This was significantly more successful than Method 1. Applying the wax over a heated surface caused it to sink into the paper. The sandarac solution was very easy to apply to the waxed paper surface. It adhered well to the wax, and it made the waxed paper more transparent.
- Method 3 Brushing on a solution of sandarac in alcohol, then rubbing heated wax into the paper surface. The sandarac solution was easily absorbed into the paper, and the wax melted well on top of it.

Despite sandarac and shellac both belonging to the larger general category of resins, they have dramatically different reflection FTIR spectra (Figure 7); therefore, distinguishing between them is not a problem with FTIR.

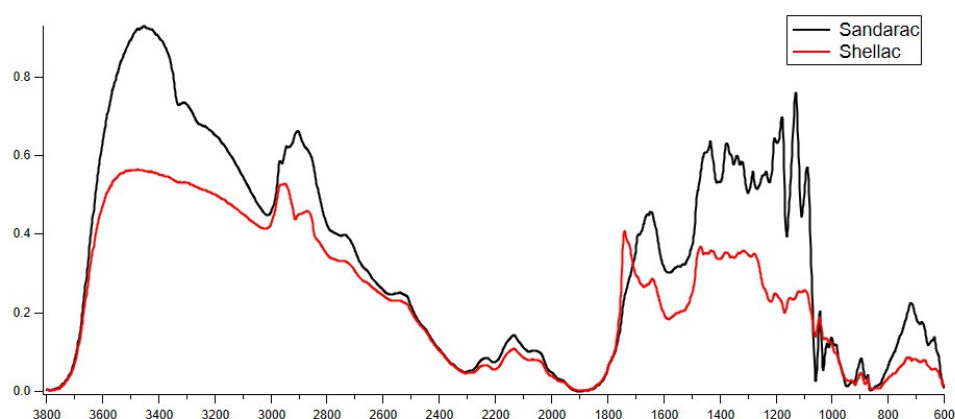


Figure 7. The comparison of sandarac and shellac reflectance FTIR spectra demonstrate that they are easily distinguishable from one another with specular reflection FTIR data, despite both belonging to the larger common category of resins.

Orange shellac is a resin made from secretions of the lac insect, from which, lac dyes are also produced. Shellac is produced to different levels of refinement. Orange shellac retains erytholaccin, which is responsible for its dark orange-brown color. Less colored versions can be produced by processing the orange shellac with charcoal, or by bleaching it with chlorine until fully decolorized [19]. Terminology for shellacs can vary tremendously depending on the vendor. This paper uses Sutherland's definition of "orange shellac" as the darkest orange-brown variety. Different terminology was used by the vendor, from whom, samples were purchased for the analytical and experimental components of this research. Figure 8 shows examples of the raw materials used.



Figure 8. Samples of blonde shellac (left) from Kremer and orange shellac (right) from Talas, which were purchased for this research. They were identified by the manufacturers as “shellac, very light” and “Shellac #1 Lemon,” respectively.

Reflection FTIR data, from coatings of pure blonde shellac and pure orange shellac on paper, were collected to see if we could distinguish between blonde shellac and orange shellac (Figure 9). The bleaching process changes the chemistry of the shellac, such that the different coatings have distinct reflection FTIR spectra.

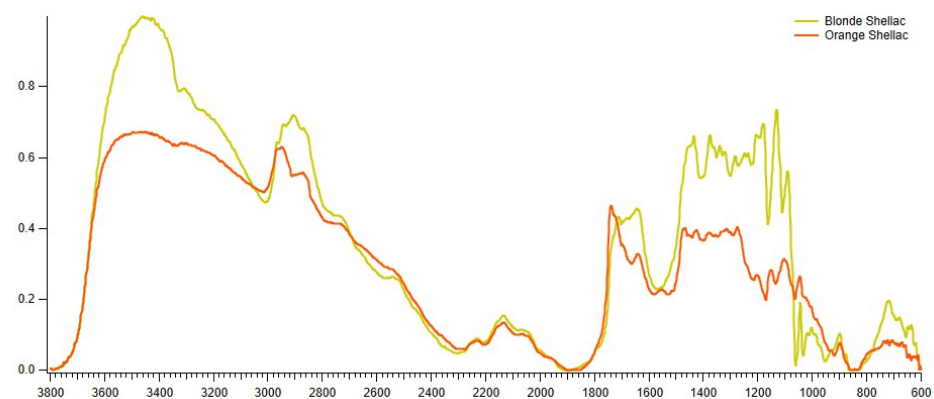


Figure 9. The bleaching process chemically changes the shellac, such that the blonde shellac and orange shellac have distinct reflection FTIR spectra.

Specular reflection FTIR spectra were collected from the reference samples that were prepared in the different ways, and the spectra were added to the spectral reference library. Method 1, which attempted to mix sandarac directly into the beeswax, failed. Figure 10 shows the reflectance FTIR spectra from Method 2, wherein sandarac was coated over beeswax. Method 3 involved beeswax coated over sandarac in order to compare it with an uncoated area of one of Flachéron’s negatives. When using the correlation function of the FTIR library search in the OPUS software, the spectrum in Method 2 was a much better match than the spectrum in Method 3.

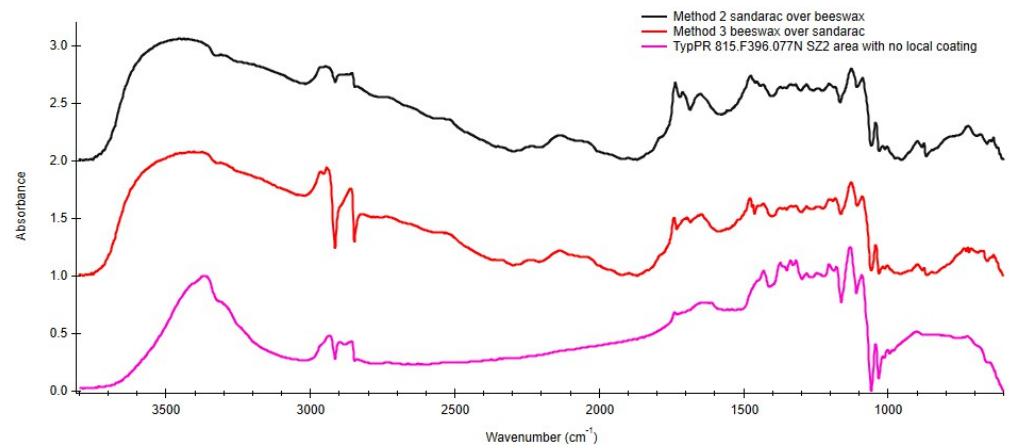


Figure 10. Spectra from Method 2 (sandrac over wax) and Method 3 (wax over sandrac) were compared with Flachéron’s negatives in areas with no local coatings. The library search algorithm strongly suggested that Method 2 was a better spectral match for the historic negatives.

The spectra taken from the locally coated areas of Flachéron’s negatives were matched to the spectra from reference samples coated with wax and sandrac, as well as orange shellac, using the computer. As can be seen in Figure 11, the historic sample and the modern reference sample had very similar spectral shapes.

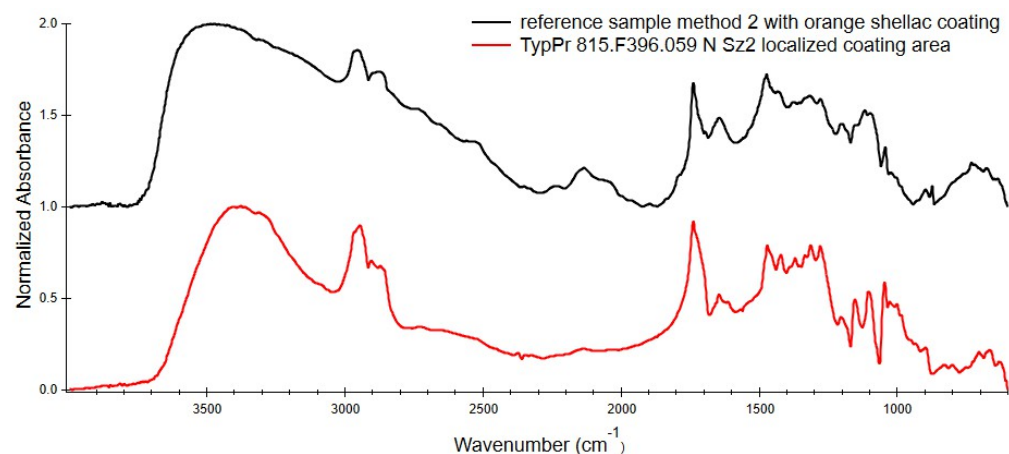


Figure 11. Specular reflection FTIR spectra of a modern reference sample compared with shellac, sandrac, and beeswax, in addition to the TypPR 815.F396.059 N Sz2 Flachéron negative area with a localized coating.

This confirmed the overall mixture of beeswax and sandrac, and it identified the additional coating as orange shellac. Of the twenty-seven negatives analyzed, all were found to have an overall coating of beeswax and sandrac, and four were found to have a coating comprising of locally applied shellac. The twenty-three negatives without shellac had no visible local coatings. The identification of orange shellac as the localized coating material is new information.

In the case of the Flachéron negatives, a visual examination indicated that the localized coating was applied as a layer over the transparentized paper negative, and so differentiating between mixtures and multiple layers was not an issue. The production of reference samples also pointed to the difficulty in preparing a beeswax–sandrac mixture. Furthermore, of the reference samples produced, Method 2, in which a solution of sandrac in ethanol was brushed on top of beeswax-saturated paper, was the best match for spectra taken from the coatings of Flachéron’s negatives.

The new identification of orange shellac on Flachéron's negatives raised the question concerning why he would have applied this local translucent coating in addition to the transparentizing layer of wax and sandarac. Daffner raised similar questions concerning Flachéron's local coatings [1], suggesting that they may have been intended to protect the image material, or to further transparentize certain areas [1]. The new identification of the local coatings as orange shellac led authors to hypothesize that Flachéron used orange shellac for its orange color, rather than for its transparentizing effects.

Yellow, red, pink, and orange colorants were used to retouch negatives throughout the 19th century because these colors preferentially blocked blue light, to which the silver halides in 19th century photographic papers were particularly sensitive. The authors hypothesized that the orange shellac was intended to reduce light passing through the negative, based on the assumption that the orange tint of the shellac would absorb some blue wavelengths of light. Daffner described in detail how Flachéron masked some areas of his negatives with black opaque watercolor, before retouching them with graphite to reduce density without completely masking the image [1]. The application of orange shellac to certain parts of the negative could have produced a subtle reduction in density, like the graphite, rather than completely masking the image, like black opaque watercolor he used on the sky regions of his negatives.

However, it was not known if orange shellac applied to a paper negative would be sufficiently colored to absorb enough blue light to affect the density or contrast of the positive print. In addition, it was not clear whether the orange shellac would further transparentize the paper when applied over wax and sandarac, and if it did, whether that effect would outweigh any light-absorbing effects of the orange color. Therefore, an experimental test was designed to investigate whether local coatings of orange shellac on a negative would affect the density or contrast of the corresponding positive print.

Salted paper prints were made from coated facsimile negatives. The developed-out salted paper process was used to make facsimile negatives of a greyscale image (Figure 12).

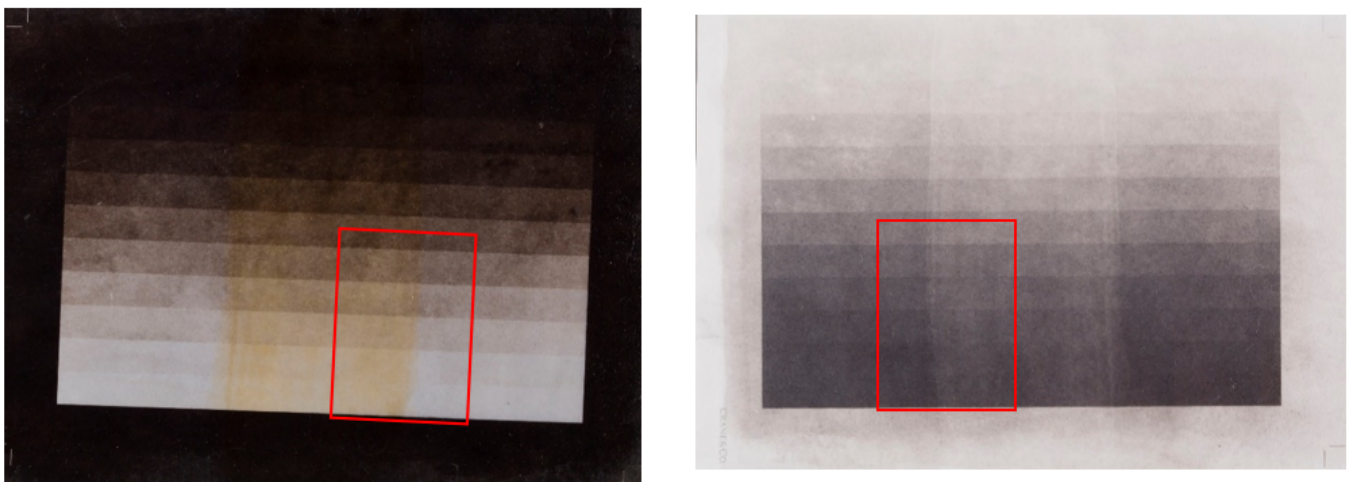


Figure 12. Left—Facsimile paper negative; Right—Corresponding positive salted paper print showing the effects of orange shellac on the negative. The red box highlights the border of the area that was coated with orange shellac on the negative and the corresponding area on the positive print.

In addition to facsimile negatives, the authors already possessed a waxed paper negative and waxed facsimile paper negative depicting landscape architecture, which had been locally coated with shellac (Figure 13).

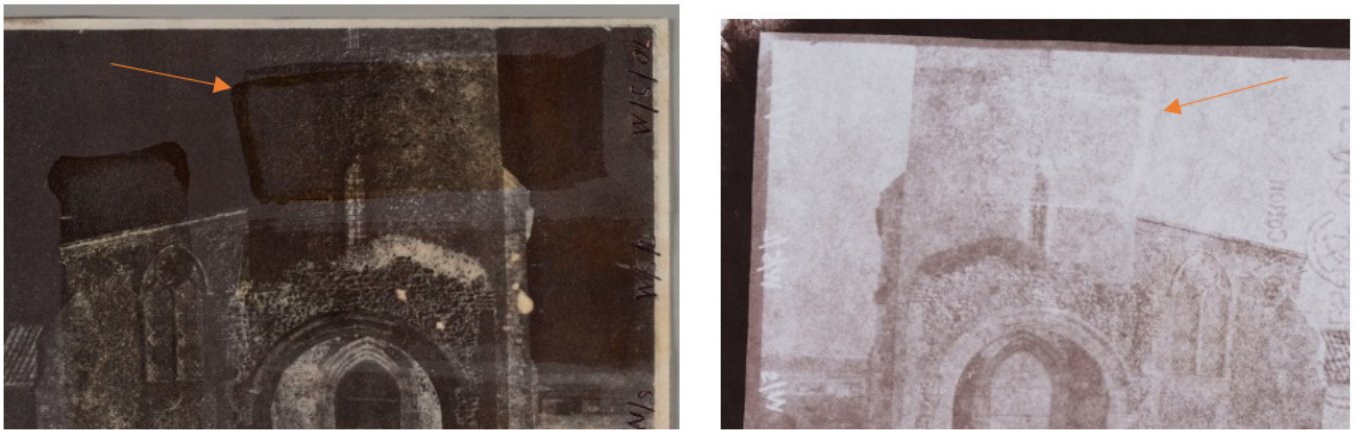


Figure 13. Left—Facsimile paper negative. Right—Corresponding positive print showing light-blocking effects of orange shellac on the negative. The red arrows indicate areas where shellac gathered at the edge of the brushstroke on the negative.

Flachéron's coatings were replicated by first coating the facsimile paper negatives with beeswax and sandarac. Parts of these facsimile negatives were then coated with a solution of orange shellac dissolved in ethanol. Salted paper prints were printed from the coated facsimile negatives, and from the locally coated waxed paper negative.

The facsimile negatives produced a greyscale image by exposing the sensitized DOP papers in contact with greyscale transparencies (Figure 12). These greyscale transparencies were similar in concept to the “digital negatives” often used by contemporary photographers working with alternative processes. They were printed using Digital Silver Imaging, Watertown, MA. The developed-out salt print process was chosen because the image material was found to be denser, and it penetrated the paper more deeply than the printed-out salted paper process, resulting in a better contrast with regard to the facsimile negative and resultant print [20]. True paper negatives were too cost-prohibitive for this study.

The procedure for making developed-out salted paper prints (facsimile paper negatives) was adapted from reference [20], in accordance with the advice of Mark Osterman. The procedure for the developed-out salted paper prints used in this research was as follows:

1. Milk whey acidified with 3% citric acid solution to achieve pH 5;
2. Acidified milk whey applied to Borden & Riley #125 Marker Paper with a cotton wad, and allowed to dry;
3. Paper sensitized using a 20% silver nitrate solution, applied with a cotton wad, and dried using a hairdryer;
4. Dry, sensitized paper placed in a printing frame against an inkjet-printed greyscale transparency (the “negative”), and exposed for 2 s in a UV light box, until a faint yellow-brown image was visible;
5. Print developed in a solution of 0.6% gallic acid acidified with glacial acetic acid (20 drops per 300 mL), which was developed for approximately 8 min on an angled glass surface, and continuously pressed with a cotton wad saturated with developing solution;
6. The print was rinsed;
7. Print fixed for five minutes in a solution of sodium thiosulfate (15% *w/v* sodium thiosulfate pentahydrate, 0.2% *w/v* sodium bicarbonate);
8. The print was rinsed, washed for 1 h, and dried between blotting;
9. Prints coated with beeswax, which was applied by rubbing gently into paper on a blotter, over a hot plate;
10. Prints coated with sandarac in turpentine;
11. Prints coated locally with shellac in ethanol.

Although Flachéron was not known to have made salted paper prints, and the appearance of a finished salted paper print can be very different from that of an albumen print, the salt print process relies on a similar chemistry to the albumen process. It was felt that the sensitivity of the silver halides in a salted paper print would be similar enough to that of an albumen print to demonstrate the effects of a shellac-coated negative on either an albumen or a salted paper positive print.

The procedure for making salted paper prints was adapted from reference [21]. The procedure for the salted paper prints used in this research was as follows:

1. Salted Crane & Co. 100% cotton rag paper was floated on a solution of 2% sodium chloride and 0.2% gelatin for 40 s, and then hung to dry;
2. Paper sensitized with a 20% silver nitrate solution, which was applied with a cotton wad, and dried using a hairdryer;
3. Dry, sensitized paper placed in a printing frame against a facsimile paper negative, and printed out in a UV light box until a clear image appeared, which took approximately 3–5 min;
4. The print was washed for 2 min;
5. The print was gold toned for 5 min in a gold chloride solution (20 mL of 0.65% gold chloride, diluted to 1 L with distilled water, sodium bicarbonate added to achieve pH 10);
6. Print fixed for five minutes in a solution of sodium thiosulfate (15% *w/v* sodium thiosulfate pentahydrate, 0.2% *w/v* sodium bicarbonate);
7. The print was rinsed;
8. The print was washed for 20–30 min, and it was dried between blotting.

Distilled water was used for mixing all chemical solutions described above. Tap water was used for all rinses and washing processes. All experimental samples were prepared at the Weissman Preservation Center, Harvard University.

The density and contrast produced by the coated and uncoated areas of each negative were visually compared. Unfortunately, the nature of the experimental samples limited the study of the results to qualitative observations. It was very difficult to precisely control the sensitization and exposure of the developed-out salted paper process, and the facsimile paper negatives were very mottled, such that the density in any given step of the greyscale was not consistent (Figure 12). This prevented a quantitative study of the experimental samples. For instance, it was impossible to compare spectrophotometer readings taken in areas of the final print that had been printed from coated areas of the negative, against those printed from uncoated areas of the negative. However, qualitative differences were pronounced.

Orange shellac applied to a paper negative reduced the density in the corresponding area of the positive print (Figure 13). Where shellac gathered at the edge of the brushstroke on the negative, it blocked some light passing through the negative, resulting in a white streak in the positive print. The salted paper prints made from the greyscale facsimile negatives showed an increase in contrast, in addition to a reduction in density (see the areas highlighted with a red box in Figure 12).

4. Discussion

The experimental tests showed that any transparentizing effect the orange shellac may have had was outweighed by the effect of its orange tint, which absorbed some blue light, and therefore, reduced density in the positive print. In nearly all applications of orange shellac, the orange shellac likely reduced density in the entire print, possibly to compensate for an over-exposed negative. In other negatives, Flachéron was targeting particular areas of the image. Daffner's original hypothesis concerning the purpose of local varnish remains plausible; these may have been the negatives that he printed most often, which were the most profitable, and therefore, which warranted additional steps with regard to retouching. However, the fact that the local coatings are orange shellac indicate that Flachéron was partially masking areas of the negative, not further transparentizing

them. In the hot and sunny environment in which Flachéron was working, it would have been even more difficult to ensure exposure was consistent. Orange shellac seems to have been one of several retouching materials that Flachéron used to ensure that he could use each of the negatives he worked so hard to produce.

The experimental samples showed that coating orange shellac onto a paper negative affected the positive print in three ways, as follows: (1) it slowed down the printing process; (2) it perfected the contrast; and (3) it improved the image detail in the positive print as a result of decreased density. Applying orange shellac to a negative would cause excessively dense areas in the positive image, such as those in shadow, to appear lighter and with more details as a result of the absorption of the blue light using the orange shellac.

The specular reflection FTIR method identified coatings of beeswax and sandarac on all the Flachéron negatives analyzed, in addition to local coatings of orange shellac. Both mathematically modeled mixtures and modern reproduction reference samples of mixtures that produced spectra, which were good matches with the spectra of the historic negatives, and which confirmed the presence of previously identified beeswax and sandarac, indicated its potential as a non-contact, non-sampling method for identifying multiple component coatings. In addition, specular reflection FTIR was able to identify an additional component of Flachéron's negatives, orange shellac, that had not been previously identified. The new identification of orange shellac allowed for a more precise understanding of the nature of Flachéron's retouching methods.

There is no evidence of chemical reactions between the different layers in the modern samples or in the spectra of the historic objects. A chemical reaction would be denoted in the spectrum as a loss of some peaks and an acquisition of new peaks, relative to the individual component spectra. There is also surprisingly little evidence of chemical changes due to the aging of the historic objects, given how well the spectra of the modern reference samples match the spectra of the historic samples.

5. Conclusions

This investigation of the effects of orange shellac indicated a purposeful manipulation of density and contrast in positive prints, which was achieved by slowing down the printing process in overexposed areas of the negatives. Although varnishes were historically considered to be a neutral protective finish on an artwork, recent research is recognizing the art historic and aesthetic value of these coatings [22]. The research presented here indicates that Flachéron's coatings of orange shellac served as an integral part of his image-altering technique. The color of orange shellac subtly alters the contrast and density, but it does not mask an area the way an opaque watercolor or highly pigmented paint might. The fine adjustments to the negatives with orange shellac were an attempt to perfect the contrast in the print, and better render depth and detail. These discoveries add to a growing body of recent research that points to the historic and art historic importance of negatives and coatings in photography, as well as to the importance of coatings and varnishes in other art forms. For instance, the analogous use of shellac for oil paintings has been proposed [19]. The specificity with which FTIR was able to identify the local coatings, and the areas in which they appeared, allowed for an understanding of his local coatings as a retouching method rather than a protective coating.

Interestingly, FTIR-ATR analysis, performed on French paper negatives that were contemporary to Flachéron's work at the Getty Museum and the Bibliothèque nationale de France, only indicated the presence of wax. No resins, neither sandarac nor shellac, were identified on the French paper negatives studied by Kaplan or Daher, respectively [23,24]. This suggests that Flachéron was experimenting with different processes on his paper negatives, given the addition of the layer of sandarac and localized orange shellac to his transparentizing media to adjust his prints.

The use of specular reflection FTIR for the identification of materials used in historic or artistic works has been around for approximately ten years. The specificity of the information that can be extracted from the reflection FTIR, even in objects with multiple

different coatings, as demonstrated here, can be surprising. As shown in Figure 9, even coatings as similar as blonde shellac and orange shellac provide distinct spectra. In the case of the paper negatives, the different layers did not chemically interact, therefore, the final composite spectrum was a linear combination of the individual components. By creating modern reproductions, it was determined that Flachéron's negatives were composed of layers of paper, beeswax, sandarac, and localized coatings of orange shellac, in that order.

The rarity and fragility of paper negatives, and the fragile surfaces of all paper-based photographic processes, requires non-contact methods of analysis to enable this kind of technical research. The specific identification of Flachéron's local coating as orange shellac, rather than as a general transparent varnish, provided new insight into his negatives and working process.

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