RADIOCARBON MEASUREMENTS ON EARLY PHOTOGRAPHS: METHODS DEVELOPMENT FOR TESTING WAXED PAPER NEGATIVES

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ABSTRACT. The earliest years of photography were full of experimentation and innovation; many photographers from this era carefully documented their experimental procedures. Consequently, it is possible to reproduce historically accurate photographs and negatives today. One of the oldest forms of photographic technology is the waxed paper negative, popular during the mid-19th century. It consists of a photosensitive sheet of writing paper coated with a layer of wax to render it transparent. Modern waxed paper negatives made using 19th century paper can potentially pass for historically significant 19th century negatives. This poses problems to museums and others interested in studying or collecting authentic 19th century photographic images. We have developed methods for separating the organic components of waxed paper negatives and measuring their radiocarbon content as a means of distinguishing between modern and historic waxed paper negatives. By detecting the presence or lack of bomb carbon in a given negative, this process can act as a tool for authentication. We have mainly focused on the extraction and ^{14}C measurement of the wax component, reasoning that modern photographers might have easy access to 19th century paper, but would less likely use 19th century beeswax.

INTRODUCTION

Determining the age of complex objects, such as photographs, by radiocarbon analysis is a complicated but feasible process. Photographs are unconventional objects to date using carbon isotopes because of their composition and young history. Materials vary greatly from photograph to photograph and can include mixtures of cellulose, wax, gelatin, albumen, and resins to name a few possibilities (Reilly 1986). Each component may have been collected or fabricated at different times. This potential mixture of ages makes photographic materials difficult to interpret. Therefore, protocols must be established to separate and individually date each component. This project focuses on the earliest form of photographic negatives. Often referred to as waxed paper negatives, these early photographic materials were fabricated on paper. Patented in 1838 by William Henry Fox Talbot, they were created by exposing a plain piece of writing paper imbibed with a photosensitive emulsion through a camera obscura (Lavédrine 2007). The paper could be coated with a layer of wax either prior to or after light exposure. This wax layer provided the paper sheet with transparency so that it could be later used to create a positive print. Therefore, the 2 major components of these negatives are wax and paper. A number of early photographers emulated Talbot's method by creating and perfecting their own version of the waxed paper negative, making mid-19th century photography an incredibly experimental and innovative field (Brettell et al. 1984). Because the chemistry, materials, and techniques of these historic photographic processes were often recorded in detail, modern replications of historic waxed paper negatives are not uncommon. These modern replicas may be taken for historic negatives, a possibility that presents difficulties for collectors interested in the historic medium.

In this study, procedures are established to separate the 2 main components of waxed paper negatives by melting and by dissolving the coating. These protocols are determined through preliminary experiments using modern waxed paper made to emulate the thickness and consistency of a waxed

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paper negative. A single negative of unknown age was provided on which to test the procedures and analyze using ^{14}C. Because the purpose of this project is to create a method for determining the presence of either modern or 19th century materials, bomb carbon detection is of importance. Pre- and post-bomb known-age samples of both paper and beeswax were obtained to observe their ability to reflect atmospheric ^{14}C levels, and to compare to the negative components of unknown age. Particular attention was given to post-bomb natural wax because it is believed that a modern photographer will have greater difficulty obtaining 19th century wax than 19th century paper.

MATERIALS AND METHODS

Sample Waxed Paper Negative

The sample waxed paper negative obtained for study is of French origin and unknown age. It was on this negative that established protocols for component separation were tested. All ^{14}C measurements for the negative and any known-age materials were performed at the NSF-Arizona Accelerator Mass Spectrometry (AMS) Laboratory. Chemical composition of the negative was investigated by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). Analysis was performed using a Thermo Scientific Nicolet Avatar 360 FTIR and OMNIC FTIR Thermo Electric software at the Arizona State Museum. The presence of a natural wax as the coating material was confirmed by spectral matching with a known spectrum of beeswax, available through the Infrared and Raman Users Group (IRUG) database. Over the course of this study, the negative was sampled twice at the Arizona AMS Lab. The first removal was used to date the negative as a whole, with both wax and paper intact. No wax extraction, pretreatment, or any other modifying procedures were performed on this sample before combustion. The second removal was performed to study the ^{14}C content of the wax and the paper separately.

Known-Age Materials

The most common coating material for historic waxed paper negatives was beeswax (Daffner 2005). Therefore, samples of beeswax with known ages were obtained from the Carl Hayden Bee Research Center in Tucson, Arizona, and from the collection of Kim Flottum, editor of *Bee Culture* magazine. Beeswax pieces obtained from the Carl Hayden Research Center were collected in the early 1970s, 1991, and 2011. Samples from the collection of Kim Flottum date to the early 1980s and 1921. All known-age beeswax samples were combusted and graphitized without pretreatment.

Two samples of mid-19th century paper were obtained from the Art Conservation Department at the University of Delaware. They were fabricated in 1839 and 1846. During pretreatment, pieces from the 19th century papers were run through 4 Soxhlet extractions using hexane, ethanol, methanol, and water as solvents. The paper samples were then subjected to a standard acid-base-acid (ABA) treatment, and their ^{14}C content measured using standard AMS techniques.

Preliminary Extraction Method

Prior to testing the provided paper negative, a number of preliminary experiments were performed on mock samples of waxed paper to determine the optimum extraction conditions. Conditions were derived for both physical wax removal by melting and chemical removal by dissolution. The mock waxed paper samples were created by coating strips of modern paper with a thin layer of modern beeswax to emulate the sample size and composition of a paper negative.

Physical extraction involved folding a strip of waxed paper, placing it in the bottom of a combustion tube, and surrounding the paper with a porous particulate silica absorbent, Chromosorb® W (Fluka

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Chemicals). The Chromosorb W had been prebaked at 500 °C for several hours before use. After adding the absorbent, the combustion vial was tightly covered with aluminum foil and heated to 80 °C in a dry oven so that the wax melted and was drawn into the surrounding Chromosorb by capillary action. After 1 hr, the vial was removed from heat and the paper removed with a glass hook. What remained in the tube was mixed with CuO and directly combusted on an evacuated combustion line. The mass of each paper sample was recorded before and after extraction to estimate the amount of wax absorbed into the silica particles. Preliminary physical extraction removed up to 15.2 wt% of the total waxed paper mass, equal to approximately 46 wt% of the available wax. The other half of the wax remained on the paper.

Preliminary chemical extractions involved placing a waxed paper strip into a combustion vial, surrounding the paper with HPLC-grade hexane (Fisher Scientific), and periodically agitating it using a vortex mixer. The paper was then removed from the vial by a glass hook and allowed to dry on a clean glass surface. The vial was placed in a heating block under a hood and heated at approximately 35 °C until the hexane completely evaporated, leaving behind a visible wax residue. The mock paper samples were weighed before and after extraction. From the data, it was concluded that chemical extraction was more efficient than physical extraction, removing 30 wt% of the total mass and 63 wt% of the wax layer. A 10-min extraction time was found to be sufficient. To determine if hexane contaminates the remaining wax residue after extraction and evaporation, comparisons were made between the fraction modern (Fm) values of 2 samples from the same block of 1980 beeswax. One sample was analyzed by AMS without any prior treatment; the other was dissolved in hexane and then recovered again by evaporating off the hexane. The untreated beeswax measured 1.2601 ± 0.0050 Fm, while the beeswax dissolved in and then recovered from hexane was 1.2528 ± 0.0050 Fm. These 2 measurements are the same within experimental error. Hexane interference would be recognized by a significant decrease in the Fm of the hexane-dissolved beeswax sample.

Waxed Paper Negative Extraction Method

Using a 10.5 × 0.3 cm sample from the top edge of the provided paper negative, physical and chemical extraction procedures were performed sequentially. The sample was first heated in a dry oven, surrounded by 0.5 mL of Chromosorb using the same procedure provided by the preliminary tests. During physical extraction, 34% of the total sample mass was extracted into the absorbent. After physical wax extraction, the same negative sample was agitated in hexane for 10 min using the chemical extraction procedure. During chemical extraction, 16.4% of the remaining sample mass was removed. The ^{14}C content of the residues from each extraction was measured separately. The paper recovered from the wax extraction protocols was subjected to Soxhlet extraction using the solvent series of hexane, methanol, ethanol, and water. It was then carried through standard acid-base-acid extractions and combusted and graphitized for ^{14}C measurement.

RESULTS

Known-Age Material AMS Data

Table 1 provides AMS data for all samples analyzed in this study. Beeswax samples from the early 1970s, the early 1980s, 1991, and 2011 were used to create a general curve following the atmospheric bomb ^{14}C spike. Using the Fm values of each known-age beeswax sample, a graphical comparison between the atmospheric bomb curve and each known-age sample is shown in Figure 1 (Levin and Kromer 1997).

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Table 1 AMS results for all samples, of known age and unknown age. Data provided by the NSF-Arizona AMS Laboratory.

Sample description	$\delta^{13}C$ (‰)	Fraction modern (Fm)	Uncalibrated age (yr BP)
Beeswax, 1991	–29	1.1487 ± 0.0048	N/A
Beeswax, 1970s	–28.1	1.5495 ± 0.0062	N/A
Beeswax, 1921	–27.9	0.9852 ± 0.0042	120 ± 34
Beeswax, modern	–23.5	1.0398 ± 0.0043	N/A
Beeswax, 1980s	–27	1.2601 ± 0.0050	N/A
Paper, 1839	–25.5	0.9819 ± 0.0042	147 ± 34
Paper, 1846	–24.9	0.9806 ± 0.0042	157 ± 34
Negative wax + paper, combined	–26.5	0.9825 ± 0.0055	142 ± 45
Negative wax, Chromosorb extraction	–27.2	0.9251 ± 0.0079	626 ± 69
Negative wax, hexane extraction	–27.7	0.9491 ± 0.0057	419 ± 48
Negative paper 1	–25.3	0.9800 ± 0.0041	162 ± 34
Negative paper 2	–25.2	0.9841 ± 0.0041	129 ± 34

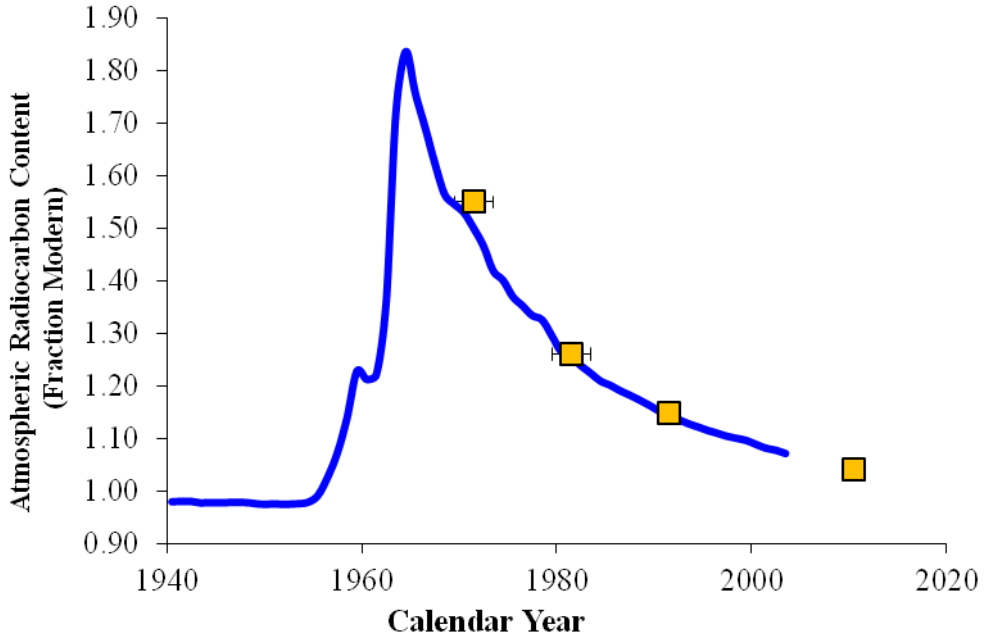


Figure 1 Bomb carbon curve with the fraction modern of beeswax samples plotted in their respective locations, annotated by the yellow squares. The progression of the curve must be extrapolated beyond the early 2000s.

The *x* axis intercept of each data point represents the average timeframe of when the beeswax sample was known to have been collected, while the *y* axis intercept represents the measured mean Fm value. Visually speaking, the Fm for each post-bomb known-age beeswax sample corresponds well with the atmospheric bomb carbon curve. The pre-bomb known-age materials, such as the 1921 beeswax and paper samples from 1839 and 1846, were calibrated using OxCal v 4.1.7 software (Bronk Ramsey 2009) and IntCal09 calibration data (Reimer et al. 2009) with a 95.5% confidence interval. The resulting calibrations are shown in Figure 2.

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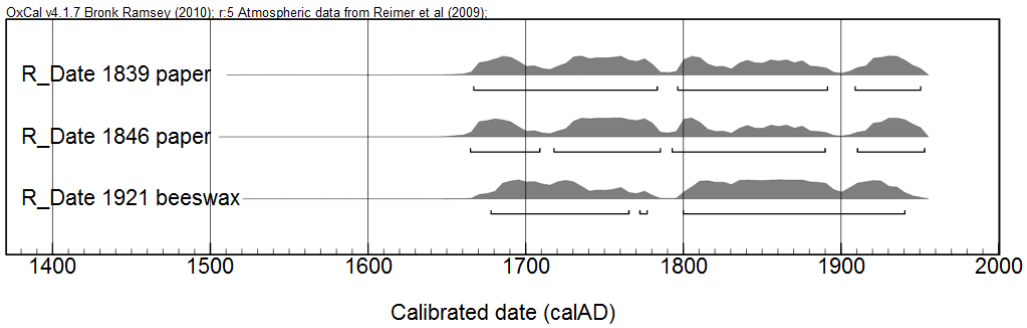


Figure 2 OxCal calibration multiplot for pre-bomb known-age materials: 1839 paper; 1846 paper; and 1921 beeswax

These samples are intended to provide a pre-bomb means of comparison for the unknown negative coating and paper ages. Since the atmospheric ^{14}C content between the 19th century and early 20th century does not change significantly, a beeswax sample from any year in that particular timeframe would act as a good representation for a negative coating comprised of only mid-19th century materials. The bare paper substrate of the separated negative was divided into 2 separate samples and measured twice by AMS. The OxCal calibration graphs for Negative paper 1 and Negative paper 2 are shown in Figure 3, also with a 95.5% confidence interval.

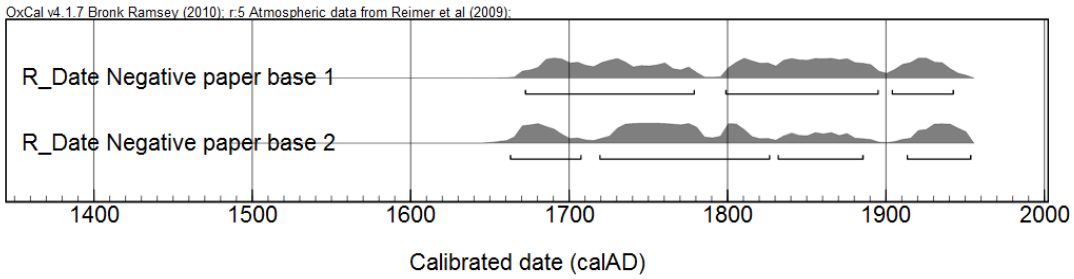


Figure 3 OxCal calibration multiplot for 2 separate samples removed from the paper negative

Both calibrations indicate that the paper is consistent with 19th century data, and the presence of bomb carbon cannot be detected. The extracted coatings did not provide results indicative of bomb carbon, nor did they provide results indicative of 19th century carbon, surprisingly. The OxCal calibrations for both extractions are shown in Figure 4.

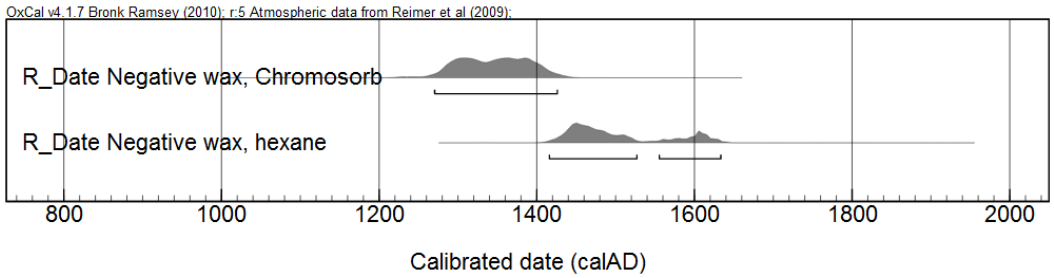


Figure 4 OxCal calibration multiplot for the Chromosorb and hexane extracted wax from the paper negative

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DISCUSSION

The ^{14}C content of the coating measurements are clearly not consistent with 19th century expected atmospheric ^{14}C levels (Figure 4). While the ^{14}C results from the extracted negative coating were unexpected, a few possibilities might explain the data. Although we assumed the coating material to be beeswax, its true composition is unknown. It was identified as a natural wax by its FTIR spectrum, based on its similarity to FTIR reference library spectra of other beeswaxes. Thus, the identification as beeswax could be artificially precise. In addition to beeswax, the coating might include traces of paraffin, a petroleum-based wax that is free of ^{14}C. Traces of paraffin are unlikely to be noted spectroscopically. Its presence would explain the depressed ^{14}C content of the wax mixture and its apparent older age.

If the negative is of 19th century origin, the use of paraffin wax by the photographer is possible. Paraffin was discovered in 1830, and became commercially popular by 1850 (Nature 1935). It was commonly used in the candle industry, much like beeswax, by the mid-19th century. Therefore, it is possible that paraffin wax was mixed into the coating during the negative fabrication process. Paraffin has also been used as a conservation material for waxed negatives as a means to smooth uneven or irregular coatings, although this practice is uncommon (Jennings et al. 2005). It may be possible that the negative was treated, and that a thin surface layer of paraffin was added to particular areas or across the entire negative.

A second line of evidence supports this hypothesis. The sequential extraction protocol that was adopted as an expedient to limit sample size, generated wax fractions with different ^{14}C contents (Figure 4). Whether due to an initial mixing of bee and paraffin waxes when the negative was first produced, or a layering of them at different times in its history, one would expect that sequential wax extraction would generate 2 samples of slightly different compositions. It could either be due to a last-on-first-off effect if the waxes were layered, or due to a different partitioning of the bee and paraffin waxes between solid and liquid phases during partial melting or partial solvent dissolution. The Chromosorb extraction protocol left more than half the wax behind, so even a slight difference in the melting temperature of beeswax versus paraffin would tend to create different proportions of each in the Chromosorb and paper-bound fractions. A similar partitioning would be expected during solvent extraction, if solvation did not go to completion. The presence of a mixture of paraffin and beeswax might be revealed by GC-MS, based upon differences in molecular compositions.

While the results can be explained in terms of a mixture of beeswax and paraffin, the possibility of contamination by other materials should not be entirely overlooked. It is possible that genuinely old wax was used as a coating material, either by a 19th century photographer or a modern photographer. Because of its chemical structure, beeswax is a very stable material. It is also highly resistant to bacterial attack and therefore does not significantly deteriorate over time (Nelson et al. 1995). ^{14}C measurement alone could not resolve such a scenario.

CONCLUSIONS

Noticeable mass removal from negative samples indicates that part of the coating was transferred to its respective combustion vial. The formation of carbon dioxide gas during combustion of each extracted sample confirmed the presence of organic material that had been removed from the paper. The original intent of this project was to completely separate the coating from the paper fibers, in order to minimize the sample size and maximize the result. Complete separation was not achieved through Chromosorb or hexane but may be through the use of other solvents. After extraction, complete wax removal was necessary so that residual carbon from the coating would not contaminate AMS results of the paper base. Further research could involve testing a number of solvents for

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extraction efficiency. Much like hexane, the ideal solvent will have a fairly high volatility so that it evaporates at a reasonable rate. It will also leave no carbon residue so as to not affect the $^{14}C/^{12}C$ or C^{14}/C^{13} ratio of the extracted coating.

The extraction results indicate that there is no evidence of bomb carbon or post-mid-19th century carbon in the wax layer. There is no proof to say that the negative is modern, but it still cannot be determined with certainty that it is of 19th century origin. Research using GC-MS may provide some further evidence towards the coating composition and origin.

While this study focused on analysis of 1 particular paper negative, the question remains as to whether the proposed protocol is applicable to any waxed paper negative. Because of the wide variety of materials used during early photography, such a question is difficult to answer. A large quantity of the paper negatives still in existence did in fact use beeswax or some form of low-melting wax to coat the paper and create the illusion of translucency. Therefore, the object used in this study acts as a good representation of the materials commonly found in historic paper negatives. One must also be aware of the potential for additives. Overall, the extraction protocol devised for ^{14}C analysis of this particular paper negative is applicable to a majority of historic paper negatives. The presence of additives and other materials should be considered on a case-by-case basis if necessary. The most important factor for a collection or institution to consider is the destructive, lengthy, and expensive nature of carbon isotope analysis. Nevertheless, carbon dating can be an incredibly useful tool for authentication when other methods of analysis cannot provide significant evidence.

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