Article: Carbon Isotope Analysis of Waxed Paper Negatives
Author(s): Elyse Canosa, Gregory W. L. Hodgins, and Gawain Weaver
Topics in Photographic Preservation, Volume 15.
Pages: 264-268
Compiler: Jessica Keister

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

Carbon Isotope Analysis of Waxed Paper Negatives

Elyse Canosa, Gregory W.L. Hodgins, and Gawain Weaver

Presented as a poster at the 2013 AIC & ICOM-CC Photographs Conservation Joint Meeting in Wellington, New Zealand.

Abstract:
Early photographic technology was well documented; because of this it is possible for modern photographers to replicate historic processes, such as the waxed paper negative process. It may be difficult to visually discern if a paper negative is modern or historic, making analytical tools useful in such endeavors. We hypothesized that radiocarbon isotope analysis acts as a means to distinguish paper negatives made with modern materials from those made with genuine nineteenth century materials. Photographs are unconventional objects to date using radiocarbon isotopes. The dating process is inherently complicated due to the multi-component nature of photographic materials. In order to achieve a complete interpretation of radiocarbon results from a given waxed paper negative, its major components (paper and wax) must be separated and dated individually. Preliminary experiments were performed on samples of modern paper coated with modern wax to devise a protocol for separating the wax layer from the paper layer. Such experiments allowed us to determine the efficiency of the protocol and the amount of sample necessary for analysis. After establishing two successful wax extraction methods, both protocols were applied to a waxed paper negative sample of unknown age. Radiocarbon measurements were then individually performed on the wax and paper components. Analysis of a negative sample prior to extraction, and analysis of the bare paper support did not show radiocarbon levels indicative of modern (post-1955) material. Radiocarbon measurements of the extracted wax component were unexpectedly low, suggesting that it is either composed of old (14^{th} – 16^{th} century) wax, or is a mixture of beeswax and a material containing no traceable radioactive carbon isotopes, such as paraffin wax. While the established protocols were performed on a single negative, it is the intent of this project to apply them to any waxed paper negative.

Introduction:
Radiocarbon analysis of organic materials is a useful tool to determine a range of dates for a sample of unknown age. These materials are generally plant or animal remains older than a few hundred years. Photographs, while they are composed of both plant- and animal- based materials, are very young on the radiocarbon spectrum, and are very complex due to their layered structure. Each photograph component (paper, binder, etc.) may have been collected or fabricated at a different time, providing a potential mixture of ages and thus complicating radiocarbon data analysis. Due to this unique structure, each photographic layer must be separated and dated individually. It should be noted that the process of radiocarbon dating is destructive, only requiring a small sample, but can provide useful age authentication information about objects that other methods of analysis cannot. This project focuses on waxed paper negatives, which generally only consist of paper and a thin layer of wax. Popular during the mid nineteenth century, waxed paper negative production was not part of a commercial industry and therefore varied slightly in terms of composition depending on the photographer. The chemistry, materials, and techniques of these historic photographic processes were often recorded in detail, thus

modern replications of historic waxed paper negatives are not uncommon. These modern replicas may be taken for historic negatives, a possibility which presents difficulties for collectors interested in the historic medium. In this study, procedures are established to separate the two main components of waxed paper negatives, using modern materials to emulate the thickness and consistency of historic negatives. A single negative of unknown age was provided on which to test the procedures and analyze using radiocarbon isotopes. Unnaturally high levels of radiocarbon detectable in plants and animals living after 1955 (known as bomb carbon), acted as a means to differentiate between a photograph made of modern (post-1955) materials and a photograph made of historic materials. This article presents a summary of work from a previously published article. To access the full data and analysis, please refer to Canosa et al. 2013.

Bomb Carbon

Around the 1950's, the natural content of atmospheric radioactive carbon was offset by the detonation of thermonuclear devices. Nuclear weapons testing began in the mid 1940's, peaked during 1961 – 1962, and reduced since 1964 due to a weapons testing ban. Such detonation greatly increased the amount of radiocarbon in the atmosphere in a short period of time, which then tapered off after testing ceased. This spike and the subsequent characteristic decline was (and still is) recorded to produce what is known as the "bomb curve". Any object made of materials after 1950 will have noticeably different radiocarbon content than an object made from nineteenth century materials.

Experimental:

Preliminary Extraction Method

Preliminary extraction involved paper and wax layer separation using samples of modern paper coated with modern beeswax. These tests were used to determine the optimum conditions for component separation. The first test involved separating the wax layer from the paper layer by melting the wax and absorbing it into a carbon-free silica absorbent. The presence of the absorbent does not affect radiocarbon analysis of the extracted wax. It was calculated that approximately 46% of the wax was transferred into the absorbent during the melting process. The second test involved separating the wax layer from the paper layer by dissolving the wax in hexane. Hexane is a petroleum-based solvent with no noticeable remaining radioactive carbon, and was found to not affect radiocarbon analysis of the extracted wax. It was found that hexane extraction was more efficient than melting, removing approximately 63 wt% of the wax layer.

Waxed Paper Negative Extraction Method

A section was removed from the corner of the actual waxed paper negative measuring 10.5 cm by 0.3 cm. The removed section was subjected to two separate wax extractions to create two separate wax samples for radiocarbon dating. The first extraction was performed by melting, and the second was performed by hexane dissolution. The remaining paper base was subjected to several Soxhlet extractions to remove any residual wax, eliminating the possibility of wax contamination. It should be noted that this sample size provided enough extracted wax for proper radiocarbon analysis, and could probably be reduced depending on the thickness of the wax layer on a given negative.

Results and Discussion:

The bare paper substrate of the separated negative was divided into two separate samples and measured twice for radiocarbon content. The radiocarbon age ranges resulting from both paper measurements were consistent with nineteenth century radiocarbon data. It can therefore be said with certainty that the paper base of the negative was not fabricated after 1950, due to the lack of bomb carbon. The extracted coatings did not provide results indicative of bomb carbon, nor did they provide results indicative of nineteenth century carbon, surprisingly. Figure 1 shows the multi-plot for the wax coating extracted from the negative of unknown age (Bronk Ramsey 2012; Reimer et al. 2009).

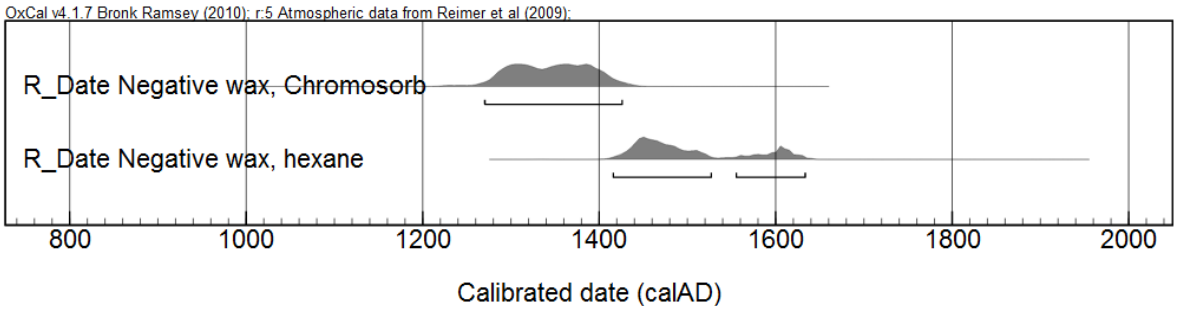

Fig. 1. Multi-plot for two samples of the extracted negative coating. Both indicate ages much older than the expected 19th century values. This could be due to the presence of petroleum-based materials.

While the radiocarbon results from the extracted negative coating were far older in age than expected, a few possibilities might explain the data. Analysis of the negative by FTIR indicated the presence of a natural wax coating. It is possible that a petroleum-based wax such as paraffin wax was also present in the coating. Traces of paraffin are unlikely to be noted on an FTIR spectrum if a natural wax such as beeswax is also present. If a radiocarbon-free material (such as paraffin) is mixed with a material containing radiocarbon (such as beeswax), a noticeable depression in the overall radiocarbon content of the mixture will occur, giving it an apparent older age. Introduced to the public in the mid-nineteenth century, petroleum-based waxes could either have been incorporated into the wax layer during negative production, or during a later conservation treatment.

The presence of paraffin or some other petroleum-based wax is currently a theory, which could potentially be proven or disproven through the use of gas chromatography - mass spectrometry on the extracted negative wax. Also, 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 nineteenth 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). Radiocarbon measurement alone could not resolve such a scenario.

Conclusions:

This study showed that radiocarbon analysis of waxed paper negatives is possible by extraction of the wax layer through melting or dissolution. Further research could involve testing a number of solvents for extraction efficiency, and thus reduction of necessary sample size. The extraction

results indicate that there is no evidence of bomb carbon in the wax or paper layer of the sample negative. There is no proof to say that the negative is modern, but it still cannot be determined with certainty that it is of nineteenth century origin due to potential interference from petroleum-based materials. Research using GC-MS may provide some further evidence towards the coating composition and origin. The modern materials used in this study acted as good representations of common materials used in waxed paper negatives, and the actual negative was of a common thickness and wax distribution. One must also be aware of the potential for additives, which should be addressed on a case-by-case basis. Overall, the extraction protocol devised for radiocarbon isotope analysis of this particular paper negative is applicable to a majority of historic paper negatives. 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.

Acknowledgements:
We would like to acknowledge the NSF-Arizona AMS Laboratory, and the Arizona State Museum Conservation Laboratory for use of their facilities throughout the extent of this project. Also a large thank you to Dr. Nancy Odegaard, Dr. Pamela Vandiver, the University Spectroscopy and Imaging Facilities (USIF) at the University of Arizona for providing SEM images, Diana Sammataro and the Carl Hayden Bee Research Center for beeswax samples, Kim Flottum for beeswax samples, and Jae Gutierrez and the University of Delaware Art Conservation Department for nineteenth century paper samples.

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Elyse Canosa
Heritage Conservation Science Program
Department of Materials Science and Engineering
University of Arizona
Tuscon, Arizona, USA

Gregory Hodgins
Arizona Accelerator Mass Spectrometry Laboratory
University of Arizona
Tuscon, Arizona, USA

Gawain Weaver
Gawain Weaver Art Conservation
San Anselmo, California, USA

Papers presented in *Topics in Photographic Preservation, Volume Fifteen* have not undergone a formal process of peer review.