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Arsenic and Old Bookcloth: The Safe Handling, Treatment, and Storage of Victorian-Era Cloth Case Bindings

INTRODUCTION

The Winterthur Poison Book Project seeks to identify potentially toxic pigments used to color 19th-century bookcloth, and to provide recommendations for mitigating the risks associated with their handling and care. This article focuses on one toxic pigment in particular: arsenic-based emerald green (copper acetoarsenite).

Successful bookcloths were a closely guarded trade secret during the 19th century, and our current understanding of their materiality and manufacture is still incomplete. The Poison Book Project builds on William Tomlinson's work elucidating late-19-century bookcloth manufacturing techniques and Andrea Krupp's inventory of early-19th-century bookcloth patterns (Krupp 2008). Tomlinson's research demonstrates that late-19th-century bookcloths were colored by applying a surface treatment rather than dyeing cloth fibers directly. Bleached cloth was padded, meaning a colored starch slurry was scraped into the interstices of the weave, imparting color while also making the cloth more impervious to adhesive squeeze-through during the bookbinding process. Bookcloths were then backfilled with a material composed of colorant mixed with starch and other fillers (Tomlinson and Masters 1996). The backfill material sits on the surface of the cloth, and serves the function of both colorant and coating. This technique results in brilliantly hued bookcloths, but their surface can be vulnerable to mechanical abrasion.

The 19th-century craze for brilliantly hued arsenic-based greens is well documented (Whorton 2010). Arsenic-based pigments could be found in everything from apparel—such as gowns, hats, and shoes—to children's toys and wallpaper. This passion for emerald green required some degree of cognitive dissonance on the part of Victorian consumers, who also purchased and used arsenic-based green pigment as a rat poison and agricultural insecticide.

There are many common names for arsenic-based green pigments, and these were often used interchangeably by the contemporary public. Some historical sources also mistakenly conflate Scheele's green (copper arsenite) and Mitis green (copper arsenate) with the various other names for emerald green, such as Schweinfurt green, Paris green, Vienna green, and King's green; however, Scheele's green and Mitis green are distinct compounds. Paris green was a commercial name commonly used when emerald green was sold as a pesticide. *Emerald green* was the name used to describe the compound *copper acetoarsenite* by the German chemists who first synthesized it, and these two terms will be used interchangeably here.

Emerald green is a bright, brilliant green first synthesized around 1800, and commercially produced in Schweinfurt, Germany, in 1814 (CAMEO 2020). Its toxicity was realized soon after, but it continued to be sold as both a pigment and a pesticide. Its popularity as a green colorant in everyday consumer products persisted in Victorian England and the United States throughout the 19th century. Emerald green is more lightfast than the yellowish-hued Scheele's green, but is still susceptible to sulfurous air pollution, which causes the compound to oxidize and darken.

In early 2019, during the course of exhibit-related treatment of the volume *Rustic Adornments for Homes of Taste* (Hibberd 1857), the suspiciously bright green hue and friability of the colorant prompted pigment analysis in the Winterthur Scientific Research and Analysis Laboratory. The bookcloth colorant on *Rustic Adornments* was confirmed to be copper acetoarsenite, or emerald green. The presence of a friable toxic pigment on the exterior of a book in Winterthur Library's collection caused concern for the safety of library staff and patrons alike, the more so because many Victorian-era, cloth case bindings are housed in Winterthur's circulating collection. This concern prompted an analytical survey of the collections to better understand how many of the library's case bindings might be covered in potentially toxic bookcloth.

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METHODOLOGY AND RESULTS

The analytical survey was limited to English-language cloth case bindings published during the Victorian era (1837–1900), because by the turn of the 20th century, brightly colored, lightfast, coal tar dyes superseded many of the textile colorants that were popular in the 19th century. Using portable XRF (pXRF) for elemental identification, interns at Winterthur began by analyzing 200 books in a range of bright colors, including reds, yellows, greens, and blues. Where toxic elements were present, the elemental analysis was followed with Raman spectroscopy to confirm the molecular structure of the compound. The bookcloth covering the front board of each tested book was photographed for reference, and in anticipation of a future database. This initial survey revealed copper acetoarsenite to be the pigment of most immediate concern, so after the first 200 books, testing continued on books bound in green bookcloth only to work through the collection more efficiently. More detailed experimental parameters can be found in the appendix.

All green case bindings in both the circulating and rare book collections at Winterthur Library have been analyzed with pXRF and Raman spectroscopy. Thanks to special access provided by Head of Conservation Jennifer Rosner and her colleagues, green case bindings in the American and British publishers' binding collections at the Library Company of Philadelphia have also been analyzed with pXRF. In total, nearly 500 volumes have been tested across the two institutions, approximately 350 of which are covered in green cloth. Of those, 38 tested positive for the presence of arsenic and copper.

Arsenical cloth case bindings range in size from large quartos to petite duodecimos. The current data set is still too small to see any trend in publishers, but there are other helpful commonalities. The majority of emerald green bindings have publication dates in the 1850s (fig. 1). A few were published in the 1840s, but this does not necessarily indicate that emerald green bookcloth was being manufactured and used in the 1840s, because remaindered books may have been bound later. The latest publication date identified so far is 1860. A time-effective strategy for those considering searching for emerald green books in their own collections might therefore start in the 1850s and work out in either chronological direction.

Emerald green bindings tend to be highly decorated American or British imprints, with gold titling, gold and blind blocking, and often gilt edges. The bookcloth over the boards remains vividly green, with no sign of insect damage. The condition of emerald green spine cloth shows more variation in color, likely from exposure to oxidizing air pollution as the book sits on the shelf.

Winterthur's *Rustic Adornments for Homes of Taste* displays a binding ticket for Westley and Co., a prolific London bindery in the mid-19th century. According to a contemporary article in *Penny Magazine* (1845), "A Description of Westleys & Clark's Bookbinding Establishment" (the predecessor to Westley and Co.), bookcloth was purchased in rolls, and stored in a cloth warehouse, where it was cut down into pieces of several yards each before being handed over to the cloth case makers. Gas

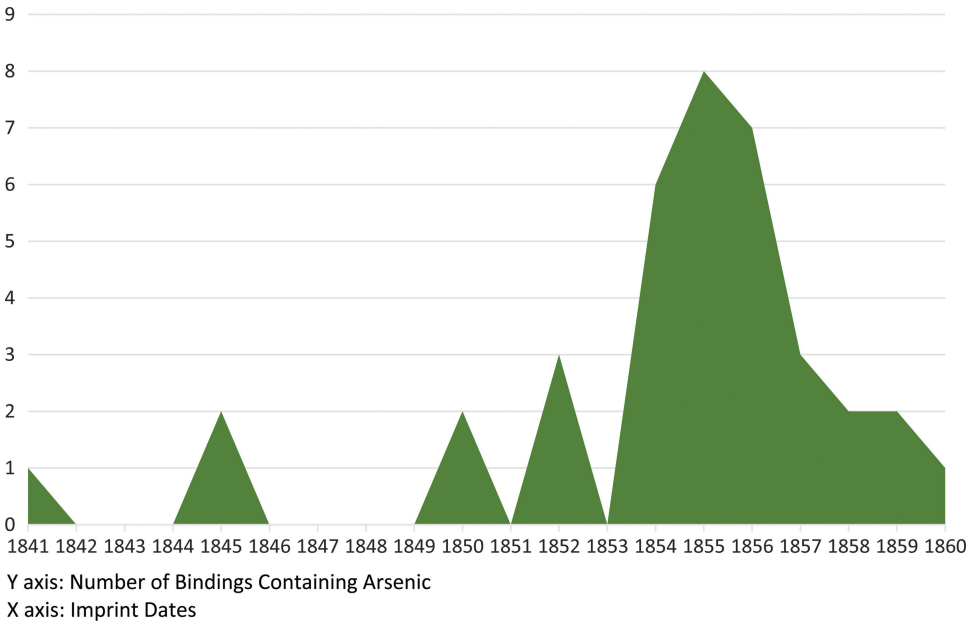

Fig. 1. Histogram showing number of arsenical green bindings (determined by XRF) by imprint date.

jet powered embossing machines impressed patterns on the precut pieces of bookcloth to hide the weave, raising questions about the effect of heat and steam on arsenic-pigmented cloth and the workers who used it. The article also notes that gilding was reserved for a "higher class of bound book," which speaks to the consumer demographic for these bindings (*Penny Magazine* 1845).

The qualitative survey results revealed that arsenical emerald green was not uncommon in mid-19th-century bookcloth, but quantitative analysis was needed to better understand the risks associated with emerald green bookcloth. A destructive sample, in triplicate, of 1-cm^2 bookcloth taken from underneath the pastedown was sent to the University of Delaware Soil Testing Laboratory for quantitative elemental analysis using the inductively coupled plasma–optical emission spectrometer (ICP-OES) (see the appendix for experimental details). The Soil Testing Laboratory also analyzed a "pick-up test" of dry cotton swabs rolled lightly across the surface of the bookcloth intended to simulate common handling.

The quantitative analysis indicated that the octavo-sized book *Rustic Adornments for Homes of Taste* contains several times the lethal toxic dose of arsenic for an average-sized adult, as little as 2 mg/kg of body weight (Gehle 2010). The cotton swab pick-up test resulted in a significant, measurable amount of arsenic offset from the dry bookcloth. A second pick-up test using nitrile gloves was also conducted, but the Soil Laboratory protocol was unable to digest the nitrile and therefore provided no results. There are limitations to the interpretation of these results. This singular binding may not be representative of all emerald green bookcloth. Not all emerald green bookcloth may be this friable. It is also impossible to determine how much pigment this binding may already have shed over its nearly 200-year history.

HEALTH AND SAFETY IMPLICATIONS

Conversations about this research with experts from various fields associated with health and safety have provided a broader context for interpreting the degree of risk present. Forensic toxicology, epidemiology, and industrial hygiene are related disciplines that consider risk from differing perspectives. According to forensic toxicologist Dr. Justin Brower (Skype call with the authors, March 22, 2020), there is no record of any person dying from exposure to arsenical bookcloth. From the perspective of pathology, he considers arsenical bindings to be low risk; however, he also acknowledged that institutions may need to act with an abundance of caution because of issues surrounding legal liability. Epidemiologist Dr. David Goldsmith (pers. comm., October 30, 2019) focused less on fatality as the primary risk factor, drawing attention instead to the potential for materials that people interact with in their daily lives to trigger serious, long-term health issues. Goldsmith suggested research into arsenical bookcloth should be communicated not only to conservators and librarians but also to epidemiologists, because potential problems from long-term, low-grade exposure to arsenic could be a public health concern. Safe handling and storage protocols for arsenical bindings at Winterthur Library are based on consultation with Industrial Hygienist and University of Delaware director of Environmental Health and Safety Michael Gladle. From Gladle's perspective (phone conversation with the authors, December 13, 2019), there are no safe exposure limits for copper acetoarsenite, so limiting direct contact, inhalation, and ingestion of bookcloth pigment insofar as possible is essential.

Emerald green bindings present a risk to library staff and users which should be taken seriously. Although every institution must work out its own logistics for meeting the goals of safe storage, handling, and treatment, the approaches being explored at Winterthur Library may provide a useful model. First, steps have been taken to restrict circulation of arsenical bindings. Users will not be allowed to check out emerald green books and bring them home. Whenever possible, researchers will be encouraged to use a digitized surrogate instead of the original. Researchers with a compelling reason to handle original emerald green bindings will do so in the controlled environment of the Winterthur Library Rare Book Reading Room, under the supervision of trained library staff. All library staff will be trained in safe handling practices, and a written policy will be posted for easy reference in staff areas of the library, including in the stacks at the location where the arsenical bindings will be stored.

Other precautions in place at Winterthur recommend that individuals wear nitrile gloves when handling arsenical bindings; take care to avoid ingestion or inhalation of pigment dust; and avoid touching the face, eating, or smoking until hands can be thoroughly washed, even if gloves have been worn to handle bindings. Arsenical bindings will be used only on hard surfaces that can be wiped down with a damp, disposable cloth. A nonpermeable "placemat" of polyethylene or polyester will be draped over book wedges, cushions, or futons during use. Additional guidelines for researcher use of arsenical bindings and the potential use of waivers are still under discussion among conservation, library staff, legal counsel, and other stakeholders at Winterthur.

The Covid-19 pandemic shutdown in 2020 interrupted practical conservation treatment of the emerald green binding *Rustic Adornments for Homes of Taste* at Winterthur. When treatment resumes, the treatment protocol will adhere to recommendations from University of Delaware Environmental Health and Safety. In addition to wearing nitrile gloves and observing the good hygiene practices already described, conservators should carefully consider the environment in which they plan to treat books bound in arsenical bookcloth. Moisture introduced by adhesives could cause the arsenic to

migrate and offset in greater concentration. Moisture could also trigger the release of highly toxic arsine gas. Therefore, best practice indicates working under a certified chemical fume hood. A second choice would be to work in a ductless particulate hood with a combination HEPA/charcoal filter. A respirator with organic solvent and particulate filters should be considered only as a last resort.

Conservation and library staff at Winterthur agreed that enclosures for arsenical bindings should be used to prevent casual touching and contain any pigment shedding. First, standard enclosures already in use were considered: the CoLibri book jacket system and corrugated clamshell boxes. CoLibri jackets are made of polyethylene, an effective choice of material as a barrier for emerald green pigment. However, CoLibri jackets have a large gap that exposes the head and tail of the spine, as well as a portion of the board edges, where colorant is most vulnerable. Paperboard boxes were also evaluated and rejected, as they could collect and then release shed pigment unpredictably during handling.

Ultimately, staff consensus settled on the humble, but perfectly serviceable, polyethylene zip-top baggie. The manual logistics of sliding materials in and out of the baggie encourages extra attention and care. The transparency of the polyethylene allows easy monitoring of pigment shedding, and the baggies are easy to label. Bagged books can continue to be shelved upright, and have a tight zip-top seal that keeps pigment in and water out in the case of a water disaster. The baggie differs enough from other standard enclosures at Winterthur Library to signal that something is notable about these contents; however, if desired, a bagged book could additionally be boxed.

Recommendations from University of Delaware Environmental Health and Safety suggest storing arsenical books together in one area with clear shelf signage, in addition to individual labels on each enclosed item. Winterthur Library already has a tradition of shelving certain collections items together based on physical attributes. For example, folia and miniatures collections are housed in designated shelving areas rather than being interspersed throughout the rest of the collection. A letter code at the end of the call number alerts library staff and users to the item's special location. Rehousing arsenical books together in one storage area easily fits into this pre-existing practice. A clearly labeled shelf in the Rare Book Vault has been designated for Winterthur's 10 arsenical case bindings, which further minimizes risk to salvage staff in case of a collection emergency.

NEXT STEPS

A primary goal of this project is to assist libraries and collectors without access to analytical equipment to identify potentially arsenical bookcloth in their own collections, a purpose which has led to the development of an emerald green color swatch bookmark freely available upon request. The bookmark is not a perfect tool; it can only give a visual indication that a book *might* be bound in arsenical bookcloth. However, all 38 bindings that have tested positive for arsenic have presented a remarkably consistent vivid green hue. Combined with other contextual clues, such as publication date, the bookmark may help narrow down the likelihood whether green case bindings are covered with arsenical bookcloth. Emerald green color swatch bookmarks are currently available from Winterthur Library.[1]

Ongoing analysis, archival research, and outreach to libraries, private book collectors, and book dealers continues for this project. Next steps include a peer-reviewed publication of the formal methodology and findings to date, and expansion of the arsenical bindings data set through local and international partnerships, beginning with University of Delaware Special Collections and the British Library. Expanding the data set in the UK is critically important, because England was the main manufacturing source of bookcloth used by 19th-century binderies in North America, as well as in the British Isles. The project also continues to collect data about other pigments of concern, including chromium-based, mercury-based, and lead-based pigments.

To share identification and safety tips broadly, Poison Book Project information will be maintained on the Winterthur Wiki.[2] Although a wiki page is gray literature, this format does allow nimble updates to public-facing information about the project as it evolves. At the time of this article's publication, the list of confirmed arsenical bindings has been posted as a static table, but plans are under way to create and grow a searchable, publicly accessible database of potentially toxic bookbindings.

Although this project focuses on the specific risks associated with arsenic-based pigment, generalized lessons can also be drawn from this work. First, allied disciplines related to health and safety have differing perspectives and risk tolerances, so consulting experts from multiple adjacent fields provides breadth of context for decision making. Second, a cookie-cutter approach to the logistics of storing, handling, and serving potentially toxic materials to library patrons will not work for every institution; involving stakeholders in a conversation about desired outcomes based on core safety guidelines can achieve a tailored solution that works. Finally, libraries need more materials research to identify hidden hazards in their collections. Research partnerships and inter-institutional knowledge sharing is vital for protecting library staff and users, as well as collection materials themselves.

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APPENDIX

1. Qualitative Testing

pXRF was used to collect elemental information from bookcloths. Analysis was performed with a handheld Bruker Tracer III-SD XRF spectrometer using a rhodium tube (40-kV high voltage, 9.6-μA anode current, 25-μm Ti/305-μm Al) for 30-second live time irradiation. A zero background plate (design courtesy of the Institute for the Preservation of Cultural Heritage, Yale University) was placed behind the cover to mask elements within the textblock. Spectra were interpreted using the PXRF1 software.

A total of 406 books from the Winterthur collection were analyzed. The Library Company of Philadelphia shelves its Americana collection chronologically according to imprint date. Volumes were selected for testing by a visual scan of the shelves in the appropriate date range (1830s–1900). Approximately 80 books bound in green bookcloth or with green paper onlays were tested using pXRF. Spectra and bibliographical data were saved for each volume.

When arsenic and copper were found together on Winterthur volumes, Raman spectroscopy was used to confirm copper acetoarsenite. The books were analyzed with a Renishaw Invia Raman spectrometer (785-nm diode laser) in conjunction with WiRE 3.4 software with extended scan from 200 to 2200 cm^{-1}, 50× objective lens, exposure time of 15 seconds/scan for three accumulations, and 1% laser power. Spectra were compared against an emerald green reference spectrum from the Raman Spectroscopic Library of Natural and Synthetic Pigments, University College London.

2. Quantitative Testing

The University of Delaware Soil Testing Lab performed destructive quantitative analysis on 1 cm^2 bookcloth samples from one Winterthur Library volume bound in emerald green bookcloth. A pick-up test was also performed on the cover of the same volume, by rolling dry cotton swabs across the surface with even pressure.

Triplicate samples were weighed and were placed in 10 mL of concentrated nitric acid. Samples were then digested by EPA Method 3051A using a CEM MARS5 microwave digestion system. The digest was then diluted to 50 mL using deionized water. Digests were analyzed for arsenic using a Thermo 7600 ICAP 7600 Duo View inductively coupled plasma–optical emission spectrometer (ICP-OES).

NOTES

1. Please email a postal address to reference@winterthur.org to request an emerald green color swatch bookmark; make sure to put "Emerald Green Bookmark" in the subject line.
2. The Poison Book Project site on the Winterthur Wiki can be found at http://wiki.winterthur.org/wiki/Poison_Book_Project.

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