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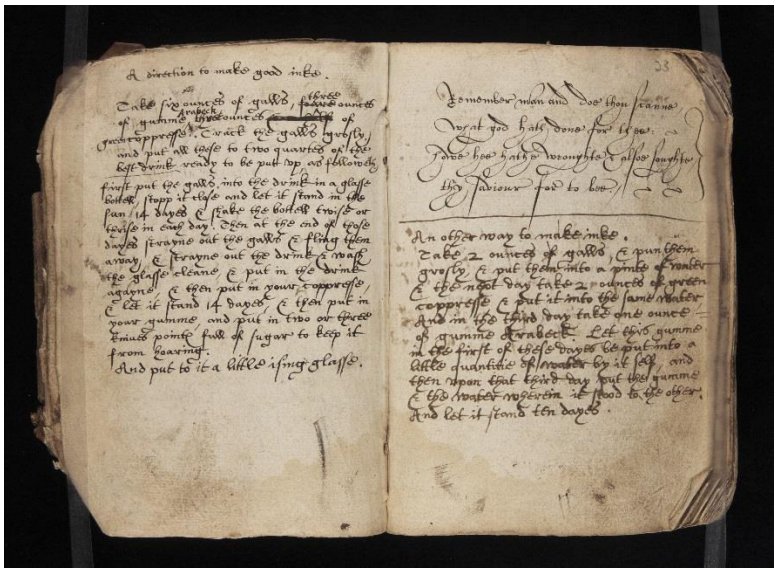
Have you ever wondered about the brown (or brownish-black) writing fluid that is found on so many of the pre-1900's documents in your collection? That fluid is known as "iron gall" or ferro-gallic ink. It was the standard ink used in Europe and European-colonized countries for fourteen hundred years, making it one of the most common inks to be found in the Center's manuscripts and records. Its ubiquity and unique chemical composition make it an important subject of study for collections care providers.

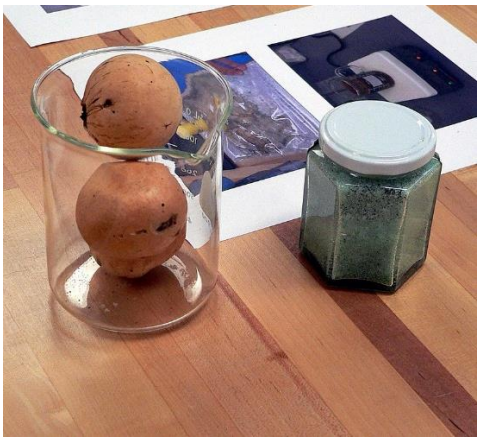


History

The history of iron gall ink dates back to an experiment recorded in the notes of Pliny the Elder in the first century CE, but the chemical interaction he noted when dropping iron salts onto a tannin-soaked scrap of papyrus was not used to make ink until the 5th century CE. The use of carbon-based inks made from burning resin, tar, or other substances and gathering the oily soot predated iron gall ink by an estimated 3,000 years, but by the late Middle Ages, iron gall ink was the preferred writing fluid of scribes. The particulates that make up carbon inks sit on the surface of the writing support; on a smooth, prepared surface such as parchment or vellum, carbon-based inks could simply be "erased" from the support using a pumice stone, creating what we call a palimpsest. The acidic bite of iron gall ink cuts into the skin, making it a relatively permanent ink. Iron gall also had the benefits of being waterproof, easier to manufacture, and less likely to clog a writing tool. Due to its short shelf life, iron gall ink was not readily commercially available throughout its heyday. Iron gall inks were made in-house at job sites and inside the private home; each site had its own recipe, sometime closely guarded and handed down through the generations. Ink-making was considered women's work and the wide variety of recipes and cooking methodologies resulted in the heterogeneity of the iron gall inks in your collections. Iron gall ink eventually fell out of favor in the 20th century when the discovery of cheap synthetic dyes made commercial inks more economically viable.

Preparation

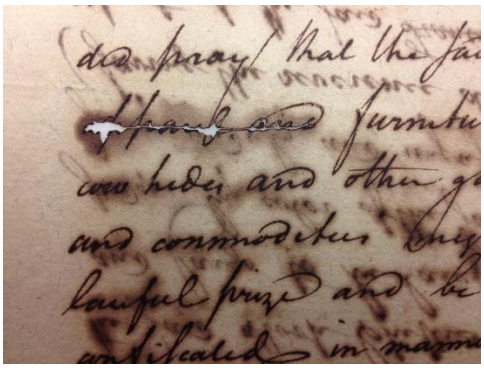
Oak galls (also known as “oak apples”) are knobby growths of plant matter that are created when wasps deposit eggs on the wooden branches and trunks. This material is high in tannic acids that can be released when the galls are crushed and soaked in water. These tannic acids are then aged a month, causing oxidation and hydration reactions that result in the creation of gallic acid. Iron gall ink recipes call for the mixture of both of these types of acids with iron sulfate (known historically as copperas or green vitriol and used in wool and leather dyeing), creating a water-soluble ferrous tannate complex that, upon exposure to air, is transformed into the dark pigmented ferric tannate that is resistant to water.



Other materials such as binders, anti-fungals, and acids to prevent sediment formation were also added to the recipe, as well as dyes and pigments that allow the ink to been seen easier as it was applied to the paper, before the chemical process that created the final dark gallotannic ink.

Preservation

Unfortunately, the same constituents that result in a dark, waterproof, permanent ink also act as agents of deterioration, especially when applied to paper. As mentioned earlier, iron gall ink was originally formulated as a permanent ink ideally suited for use on animal skins. The acidic proteins that make up skin were not readily affected by the acids in the ink, the thickness of the skin made it relatively resistant to structural weaknesses created by the acidic inks, and alkalinity of the chalk and pumice used to prepare skins for writing surfaces provided an additional protection. Nevertheless, we do see some of what we have come to characterize as iron gall ink deterioration on poorly prepared skins. Cellulose, on the other hand, is a very poor partner for iron gall ink. The cellulose molecule is most stable in a slightly alkaline environment and is destabilized in acidic environments. In addition, the oxidation of the iron salts in the ink from their Fe(II) to Fe(III) stage releases byproducts that catalyze oxidative deterioration of paper. Especially in the presence of excess humidity, these processes result in the types of deterioration most commonly associated with iron gall ink manuscripts on paper: haloing, sinking, losses and cracks, and color change.



While there are some treatments that can help slow or even counteract these processes (i.e., releasing water soluble acids via aqueous immersion, introduction of a metal chelator into the cellulostic matrix, brushing with a 3% solution of gelatin to bind the ink), these conservation interventions all result in some change to the ink, making them problematic for high value collections. The best way to prevent iron gall ink documents from becoming damaged beyond rescue is to store them in low temperature, low humidity conditions in pH neutral paper folders.

For more information and wonderful photos and tutorials about iron gall ink (including how to make your own!), please see the Cultural Heritage Agency of the Netherland's Iron Gall Ink Website.
Also see the work that the conservation department at the Cornell University Library did on the Gettysburg Address.

Please don't hesitate to reach out to us if you have any question about materials in your collections that have been affected by iron gall ink!

The Werner J. and Gisella Levi Cahnman Preservation Laboratory