Pre-Industrial Western Printing Inks, C.1450-1850

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Abstract

Key Words

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It is often assumed that all printing inks are the same: black, inert, and stable over centuries. However, the ingredients in their recipes (or, as measurements were standardised in the 18th century, the components in their formulation) have varied enormously since their invention in the mid-1400s. This chapter offers a starting point for understanding the kind of pre-industrial oil-based printing inks that were commonly used for printing texts, images, music, and other kinds of content, mainly on paper and parchment supports, in a printing press, first in Western Europe and Central and Eastern Europe, areas under European colonial control, and other areas as the printing press spread. (Block-printing in Europe and relief printing in Asia conventionally uses a water-based ink.) This study begins with the invention of printing ink c.1450, when Johannes Gutenberg (d. 1468) created black printing ink for his first publications, and red printing ink c.1455 for the Gutenberg Bible. It ends with transformation of its production due to industrialisation and the development of synthetic constituents around 1850. Relief, intaglio, and planographic (i.e. lithographic) printing inks had different pathways to industrialisation, but 1850 is a broadly indicative turning point because this timespan largely overlaps with the handpress period, c.1450–1830. Given the paucity of literature on this topic, it is believed that this chapter is the most substantial survey of the materiality of pre-industrial printing inks to date.

This study briefly touches on industrial printing inks, their rapid advances in chemistry, large scale invention of synthetic colourants, and development of industrial components and formulation processes after c.1850. It is relevant that the state of research on early industrial printing inks, 1850–1900, will be advanced by a PhD project by Ian Dooley, supervised by

Elizabeth Savage, from October 2022. In future, research would be valuable into the materiality and conservation of later industrial printing inks, printing inks c.1920–1950 (when their raw materials still tended to be manufactured primarily for other industries) (Clayton 1993, 140), printing inks for duplication methods in the 20th century, ink jet, and digital printing. This text does not address writing inks (see Chapter 11.11); inks and pastes for exclusively manual approaches to printing, such as block-printing on paper and textiles; workarounds for printing precious metals, for example applying gold leaf to a printed binder; or different media required for other approaches to printing on paper and parchment, for example pigmented liquid gelatine for Woodburytype.

The chapter begins with a survey of the remarkably brief literature, including early published references to the production of printing inks. As archival references to printing ink manufacture are even rarer, often vague by modern standards, and presumably indicative of information that circulated within a very limited audience, they are omitted here. It then lays out differences in the printing ink required for the three main categories of printing used in this period: relief, intaglio, and planographic. Much about the colourants and composition of printing inks has been based on assumption and comparison to continuing practice. This chapter supplies material evidence obtained from the instrumental analysis of printing inks to establish what is known to have been used in at least some printing inks within the scope of this study. Based on those data, it next summarises ways in which printing inks can change over time due to their colourants and binders, and cause associated change to their supports. Chapter 25.6 offers ways to address these changes with conservation treatment and guidance for storing and exhibiting objects with printing ink.

The Literature on Historical Printing Inks

Adrian Johns wrote in his study of early modern European inks that “ink is all but invisible in history” (Johns 2010, 103). Relatively little has been published on the history of ink in general, but much of that research focuses on water-based iron gall writing ink, not oil-based printing ink.

Archival Documentation

Early printers would have had an incentive to protect their trade secrets for this new media, and little archival documentation of printing ink has survived from the first centuries after its invention. It is not known how the inks were produced. Technical analysis has not been undertaken to determine how these ingredients map onto the inkfilms in publications by the printers or presses who noted information about their printing inks, and it cannot be assumed that those ingredients are representative of their, or others’, recipes.

For relief, the first known references are from the 1480s: a “shopping list” of ink-related materials bought by the Ripoli press in 1481 (Fineschi 1781, 49: linseed oil, turpentine, Greek pitch, black pitch, marcasite, vermilion, rosin, hard and liquid varnish, nutgalls, vitriol, shellac) and a note by the printer Peter Drach about vermilion c.1486 (Geldner 1964, 84). Ink manufacturers developed in the 1500s. In the 1560s, the Plantin press in Antwerp bought ready-made strong (*dur*) and weak (*faible*) black relief printing ink by the ton from local firms (“*ancriers*” or “*faiseurs dancre*”), for example 1,300 lb. from Giullaume van Esche (or IJsche) in 1563–66. The firm purchased vermilion pigment from other suppliers, to be made into ink as needed because it dried so quickly that it could not be stored for long (Voet 1969, vol 1, 48–50). Plantin was one of the largest presses in Europe at that time, so it is not necessarily representative; some commercial printers produced their own ink, or aspects of it, through the 20th century (Gaskell 1974, 126).

For intaglio, the earliest recipe is from the early 1500s (Stijnman 2012, 268, note 132). Recipes would have been highly variable, as intaglio ink production was a cottage industry at this time; at least, in Paris in 1566, engravers' wives produced their own ink (BimbenetPrivat and Le Bars 1994), and pre-made boiled oil for intaglio ink could be purchased only from the 18th century (Griffiths 2016, 33). Innovations in printing ink seem to have remained a closely guarded trade secret. Jacques Savary des Brûlons (1657–1716), Inspector General of the Manufactures for the King of France, wrote of intaglio ink-making in his (posthumous) dictionary of commerce that "there are not but two or three workers in Paris who know how to prepare this ink; they make a great mystery of their manner" (Savary des Bruslons 1726, vol. 2, col. 417).

Art technological source research has therefore focused on related materials. This includes "inks" for manually printing or stamping (Oltrogge 2015); some could have been used in recipes for oil-based printing inks for presswork. Also, research into contemporary oil paint can have relevance. It has been suggested at least since the late 19th century that Gutenberg adapted the newly refined media of oil paint (for example, De Vinne 1876, 533); a generation before the Gutenberg Bible, in the 1430s, Jan van Eyck had achieved renown for refining (not inventing) oil paint with a binder of heat-bodied linseed oil.

Published Sources

Much that is known about historical printing inks derives from continuing practice and a small number of well-known sources, especially the earliest publications on printing ink: Joseph Moxon (1627–1691) on relief printing inks (Moxon 1683, vol 1., 75–88: "Of Inck" and vol. 2, 328–331: "Of Printing Red, or other Colours with Black"), Abraham Bosse (c.1604–1676) on intaglio in 1645 (Bosse 1645, 66–69 (black), 71–72 (colours)), André-

François le Breton (1708–79) in Diderot's *Encyclopédie* (le Breton 1755, vol. 5, 633–34), and Jean Michel Papillon (1698–1776) on colour relief inks (Papillon 1766, esp. vol. 2, 346–50). Rare departures include advertisements or privilege or patent applications for innovations. They tend to represent exceptions rather than the rule, for example William Savage (1770–1843) promoted his novel replacement of boiled oil with copaiba balsam, an oleoresin from the trunk of *Copaifera langsdorffii* trees that were then found primarily in Brazilian rainforests (Savage 1832, 118–20).

Much research also relies on the sole dedicated study, Colin Bloy's history of relief printing inks to 1850 (Bloy 1967), and three brief historical surveys: the first dedicated published history of printing inks (Savage 1832), a historical introduction to manufacture in the 1920s (Wiborg 1926), and a 42-page pamphlet (Klaetsch 1940). Otherwise, the literature on the history of pre-industrial printing inks consists largely of well informed, brief texts that call for further research. Typical examples are Earl Fischer's 1947 address to the Bibliographical Society at Virginia, which is very brief (14 pages) and difficult to access (copies were distributed, but it was not published) and Steve Hoskin's historical chapter in his book on printmaking inks, which has room for brief discussions for the 13 kinds of techniques over the 500 years to its publication; each of the three techniques that fall during the scope of the current chapter are allocated about three paragraphs (Fischer 1947; Hoskins 2004, 13–29).

New Research and Technical Analysis

Their claims are largely unchallenged because few instrumental analyses of printing inks have been undertaken, despite the ground-breaking cyclotron and proton milliprobe analyses of the black and red printing inks of the Gutenberg Bible led by Richard Schwab in the 1980s (Schwab et al. 1983; Cahill et al. 1984; Schwab et al. 1985, 1986, 1987). In the last decade, Bloy's study has started to be supplanted in part by the first wave of instrumental analyses of colour printing inks (Walsh 2003; Price et al. 2015; Stiber Morenus et al. 2015; Lepape 2018a, 2018b). They build on recent historical research into the manufacture of black inks (Dachus-Hamm 1992); inks for relief (Stiber Morenus 2015; Stiber Morenus 2018; Stiber Morenus 2023); intaglio (Stijnman 2012, 267–87; see, for example, smaller studies such as Stijnman 2016, 84–85); lithography (Twyman 2013, 525–40); and methods of colour inking (Stijnman and Savage 2015). Research in *Printing Colour 1700–1830*, a forthcoming volume edited by Margaret Morgan Grasselli and Elizabeth Savage, will address approaches to inking (Savage 2023) and the results of instrumental analysis of 18th-century intaglio printing inks (Christoforou, van der Mullen, and Gonzalez 2023; Palandri 2023). Besides the text of the Gutenberg Bible, these analyses have focused on art-historically significant images that were printed in colour. The findings are believed to be applicable to other sites of colour printing in letterpress books, for example two-colour title pages in black and red, blue, or another colour; devotional imagery in certain liturgical texts; and printers' devices and colophons.

Kinds of Printing Inks

Three kinds of printing were in use before c.1850: relief, intaglio, and planographic (i.e. lithography). Each required ink with distinct characteristics. All involved three categories of ingredients or, later, components: (1) the binding medium or vehicle that "carries," (2) the colourant. The medium must be oil-based to form a film on metal printing surfaces, including metal type—water beads on metal—and sufficiently viscous for the pressure of the press. Linseed oil was common. It was boiled to yield varnish, so the terms "oil" and "varnish" can be used interchangeably in historical documents. Printing ink's properties can be adjusted with (3) additives, for example soap, rosin, or driers, also called siccatives (to expedite drying from days to seconds). Some pigments can also alter the characteristics or behaviour of the ink, so they can also serve as additives or reduce the need for other additives. Cost could be a factor: the longer the linseed oil is boiled, the "stiffer," "stronger," and better the ink, and the thinner the inkfilm on the printing surface—but boiling reduces the oil's volume. Less oil is required than for a "soft" or "weak" ink, which is easier to work and could be used with less colourant, but the impression might not be as clear and the oil could leach outwards into a "halo" around the inkfilm.

Technique-specific colourants are outlined below, but some pigments were used across all three. For example, Prussian blue, the first substantially stable blue that is suitable for a printing ink, became common (especially in translucent printing inks) soon after it was first synthesised in 1704. Chrome yellow (lead chromate) became common after its invention in 1797; the various tones result from differences in particle size.

Printing inks were often characterised by viscosity. More viscous inks, for example with oil that was boiled for longer or with an additive like rosin, were "strong" or "hard." "Soft" or "weak" inks were less viscous. The terms, or variants, are found throughout the historical record on printing inks for all three categories of printing. The earliest published reference is Moxon's clarification of their different functions for letterpress printing:

> But if no *Inck* were on the *Inck-block* before, then he lays new *Inck* on the *Inck-block*: Wherefore he considers what Work he Works on: whether it be small or great Letter: If it be small *Letter*, or curious Work, the *Inck* must be *Strong* he Works with: But if it be great *Letter* or slight Work, he makes *Soft Inck* serve, at least mingles but a little *Hard Inck* with it.//If the *Inck* be too *Hard*, as sometimes in very frosty Weather it will be, then, though his Work be curious, yet he must *Rub* a in a little

> *Soft Inck* to soften it; because it will not else *Destribute* well upon the *Balls* … [and] pull and tear the Grain off the Skin [of the inking balls].
>
> (*Moxon 1683, vol. 2, 314–15; emphasis original*)

Relief

In relief, the ink sits on top of the printing surface, often cast metal type or woodblocks, and a common press is used to evenly distribute pressure across a large, rectangular surface. The pigment is finely ground into the medium, with a dense concentration. Lamp black or carbon black were most common for black. Carbon black pigment is made by burning organic material, usually plants or animal bones. The absence of phosphorous, which would be present in ivory or bone black, indicates the carbon black is a result of burning plants or soot (also referred to as lamp black). They are slow drying, so additives including driers or siccatives are needed. Other pigments are detailed below.

The binding media is often boiled oil, unlike the heat-bodied oil used for oil paints. This is because the ink must be highly viscoelastic to achieve the necessary thixotropy. That is, it must be both so rigid and so plastic that it behaves like a solid under normal atmospheric pressure but a liquid under the pressure of the press. A heavily inked impression might be surrounded by a raised ridge of ink squash: the inkfilm should be even across the impression (behaving as a liquid where squeezed between the printing surface and the platen of the printing press), and squash can form when printing ink is squeezed out and surpasses the edge of the printing surface (behaving as a solid). If the ink were not sufficiently viscous, it might bleed or even squirt out and ruin the impression.

Intaglio

In intaglio, the ink is pushed into the grooves of the printing surface, often a heated copper plate. Plates could be worked in linear techniques such as etching and engraving (often with much deeper, larger grooves), tonal processes such as mezzotint (with much shallower, smaller grooves) or aquatint, or a combination. Excess ink is wiped off the surface of the plate, and a rolling press is used to concentrate a higher amount of pressure along the edge of a cylinder.

The ink must be less viscous than for relief so that it can be easily wiped into the grooves of the plate, and the excess then easily wiped off. Lamp black is so fine that it streaks when wiped. The standard black pigments for intaglio, vine and ivory blacks, had larger particle sizes and could be made by burning ivory, bone, woods, kernels, and wine lees (Stijnman 2012, 270–74). Frankfurt black was recommended as the best black for intaglio as early as 1645 by Bosse (Stijnman 2012, 272–74, Griffiths 2016, 32; Kern et al. 2020).

Common additives included toners (especially blue, which makes the ink appear darker; indigo was first recorded in 1699, Prussian blue slightly later) and conditioners (egg white to darken the ink and give more body is recorded in 1616) (Stijnman 2012, 274). Given the need for fluidity, dryers are not attested before 1800, although Prussian blue can have a siccative effect when used as a toner (Stijnman 2012, 274). In addition, the inkfilm should dry slightly more slowly than for relief, since applying and then wiping ink from the plate can take some time—especially if ink effects, such as plate tone, are used—and it should not dry on the heated plate during inking.

Tonal processes tend to have shallower grooves in the plate, so varnish could be added to thin the boiled oil to produce a less viscous ink. Varnish can migrate to the verso and darken over time, potentially creating a greenish or brownish appearance of the inkfilm—especially if lamp black or carbon black are used, as they are slow drying and therefore allow the varnish to migrate over a longer period (Stijnman 2012, 270–71). Excess oil, under-burned oil, or ink that is otherwise too "thin" (in the printers' term) can migrate outwards from the inkfilm, leading to an "aureole" or "halo" around the inkfilm that can itself discolour over time (Griffiths 2016, 33).

Planographic

In planographic printing, such as lithography, the ink is thin, paste-like, and intensely pigmented. Hand lithography requires a more viscous ink than modern offset lithography (Antreasian and Adams 1971, 302). The ink is applied to a flush printing surface (such as a lithographic stone), adhering to areas previously impregnated with grease, and various press structures were used during this period. The intensity of the inkfilm depends on the grease deposited on the stone or plate. Alois Senefelder, who invented lithography in 1798, wrote in 1818 that his first lithographic ink contained only "wax, soap, and lamp black", and his later ink

> rests still on the same principle: ink of wax, soap, etc., then gum, aqua fortis or another acid of which none has an advantage over the others, further oil varnish and lamp black,—these are, ever and in the same manner, the chief elements of stoneprinting as they were then. Not the slightest thing has been changed, improved, or invented in the fundamental principle.
>
> *(Senefelder 1818, 8, 21)*

As the stone was dampened before being inked for each impression, additives that repel damp, including wax and tallow, could be added to counter the water solubility of other ingredients or components in the printing ink (Twyman 2013, 525). Lithographic ink factories were established from the 1840s—the Parisian manufacturer Lorilleux & Cie advertised the first steam-powered grinding machines for pigments for lithographic inks in 1838 (Lorilleux & Cie 1838)—but printers largely still produced their own inks through the 1850s.

The binding medium was largely the same as that for relief printing, boiled linseed oil. The viscosity could vary according to need: greater viscosity was required for crayon work than pen-and-ink drawing or engraving designs on stone, as did projects printed in warmer weather and black (rather than colour) printing inks (Twyman 2013, 526). This "stronger varnish" could be produced by boiling the oil for longer or adding rosin.

Michael Twyman found that advertisements of the early manufactories list colourants by price (Twyman 2013, 525–27), which likely also gives insight into the colourants that were presumably used by individual producers. The following sources are reproduced in that landmark book on chromolithography. An early Parisian manufacturer, François Rohart, previously of Lemercier, Bénard & Cie, sold ground and non-ground colours advertised as carmine, vermilion carmine, vermilion, yellow, extra fine green, sky blue, dark blue, violet, ultramarine, lead white, extra fine lamp black (Rohart 1845). An advertisement for a Leipzig manufacturer, E. T. F. Gleitsmann, priced colours for lithographic inks as more expensive than those for letterpress, with a list for litho inks including "Parisian carmine," carmine lake, vermilion, vermilion-carmine (*Zinnobercarmin*), Cremnitz white (lead white), Paris blue (Prussian blue), light and dark mineral blue, ultramarine, light and dark chrome yellow, orange, red-brown, dark brown, gold-brown, gold ochre, and two grades of lamp black (*Russ* and *Lampenruss*), followed by three kinds of black, for lithographically printing engraving, penwork, and crayon work (Gleitsman 1849 reproduced in Twyman 2013, 526, no. 453).

Approaches to Inking

Printing inks can be applied to the type, block, plate, or stone in any number of ways. Monochrome is the most common. Relief printing inks were applied with ink balls until the early 1800s, when composition rollers (named after a mix, or composition, of materials—including molasses) were invented to provide a seamless construction. Another method involves applying many colours of ink to a single surface, so that all colours print at once, roughly like a monoprint today. It is often called selective inking or *á la poupée* ("with the rag-doll"; an anachronistic term that originally referred to the use of rolled rags in a style developed in the Netherlands at the turn of the 18th century, but which is often generalised to apply to this approach in other styles and time periods). Trichromatic printing involves optical mixing, creating the visual effect of many colours by layering three translucent inkfilms in the printing primaries, specifically developed hues of blue, red, and yellow, in a similar principle to today's CMYK. Dusting can involve sprinkling a material over a sticky printed surface, similar to flocking in wallpapers; it is notorious for the horrific health issues suffered by the printers who dusted imitation gold on the "golden" issue of *The Sun* to mark Victoria's inauguration as Queen of the United Kingdom in 1838.

Findings from Technical Examination and Instrumental Analysis

A vast range of pigments are attested in the printed historical record. They overlap with, but do not necessarily correspond exactly to, those that were named in contemporary documentation or that would be anticipated by researchers today. This section lays out the kinds of colourants that have been identified in printing inks. The groups that have been most subject to analysis have been very early black printing inks for letterpress, in the Gutenberg Bible of c.1455; multicolour woodcuts of the 16th and 17th centuries in Italy and Northern Europe (including chiaroscuro woodcuts, a style that often emulates wash drawing); trichomatic intaglios of the early 18th century, by and after Jacob Christoff Le Blon (1667–1741); and early chromolithography.

The 15th Century: Gutenberg's Printing Inks

The black printing inks in several copies of Gutenberg's 42-line Bible of c.1455 were subject to instrumental analysis in the early 1980s, using techniques including proton milliprobe analysis and particle-induced X-ray emission (PIXE). The results revealed high copper-tolead ratios uncharacteristic of other incunabula tested, including works printed by Sixtus Riessinger (Rome, 1468), Peter Schöffer (Mainz, 1471), and Anton Koberger (Nuremberg, 1478 and 1493) (Schwab et al. 1983, 310–12). The high levels of copper and lead might be responsible for the unique glittering effect of Gutenberg's black printing inks (Schwab et al. 1985, 389). These ratios changed with each new mixture of ink, sometimes "radically", enabling researchers to propose a complex chronology for the printing of folia of the Bible (Schwab et al. 1985, 189; see also Schwab et al. 1983; Cahill et al. 1984; Schwab et al. 1986, 1987). The findings corroborate the chronology of production as initially indicated by watermark and typographical analysis at the turn of the 20th century (Needham 1985a, 1985b; for example, see Schwenke 1900, pp. 51ff). The analysis also revealed high levels of calcium in the paper (Schwab et al. 1985, 392).

Five rubrics printed in red ink in the copy at the Doheny Library, University of Southern California, Los Angeles, were also analysed with the proton milliprobe technique (Schwab et al. 1985). Those specimens of Gutenberg's red printing ink contained mercury, consistent with vermilion pigment, but no lead and only traces of copper. The team therefore refined their hypothesis to suggest that high levels of copper and lead in the black ink were not part of Gutenberg's "oil base," but his black pigment(s): perhaps he did not use lamp black, but instead heated a copper oxide and a lead oxide until they turned black and deep purple, respectively (Schwab et al. 1985, 389).

Analysis of a larger group of 15th-century specimens might indicate whether Gutenberg's ink recipe was a well-guarded secret or also used or adapted by his "followers", that is, his former employee Peter Schöffer (c.1425–c.1503), who was engaged by his financier Johann Fust (c.1400–1466) soon after Fust sued Gutenberg, and seized his printing equipment ("*Werk der Bücher*", work of the book), and ended Gutenberg's printing career in November 1455 (Helmasperger 1455). This was just months after Gutenberg showed samples of the unfinished Bible at the Frankfurt book fair. The outcome is well known to historians through an archival document known as the Helmasperger Notarial Instrument, but it is also significant to ink historians because the "work of the book" presumably included the recipes, materials, and tools to produce printing ink. As the timing suggests that Fust rather than Gutenberg likely completed the run of the 42-line Bible, and as the black printing ink across copies of the 42-line Bible is characterised by that unique sparkle (even in folios printed at the end of the run), the printing inks described above might be more accurately described as both Gutenberg's and Fust's.

The 16th–17th Centuries: Colour Printing Inks for Chiaroscuro and Other Colour Woodcuts

The 16th to 17th-century Italian and northern European colour woodcuts (especially chiaroscuro woodcuts, which are in a style that uses multiple tone blocks to imitate wash drawing, and including those printed inside books) were printed in two to six different colour inks usually composed of pigment mixtures. Many of these pigments have been characterised through technical examination and instrumental analysis, including carbon black, calcium carbonate, lead white, ochers, vermilion, indigo, copper-based pigments, orpiment, organic red, yellow, and green colourants, hematite red, minium (red lead), and umber (Russell 2013; Stiber Morenus et al. 2015; Price et al. 2015; Lepape 2018a; Lepape 2018b). While the degree of pigment refinement varied from ink to ink, printmakers were using commonly available materials to produce chiaroscuro woodcuts. The majority of findings described below were first published in Stiber Morenus et al. 2015, unless otherwise stated.

Indigo is frequently identified, in keeping with artistic practices of the period. Indigo was popular with Renaissance oil painters because it could be ground into an extremely fine powder and easily dispersed in oil, and furthermore had strong tinting power. As such, it was considered an economical pigment. These properties also met the performance requirements for printing ink. However, because indigo blue printing inks can discolour to grey, they were problematic from their first attestation in 1457 (Ikeda 2015). Indigo is identified in blue inks as well as green, which are mixtures with yellow pigments determined to be ochers, orpiment, or organic yellow (unripe buckthorn berries or weld). Other green inks were found to contain green colourants such as copper-based pigments, ochers, or organic sap green, made from ripe buckthorn berries.

Violet inks were analysed in Italian chiaroscuro woodcuts that comprise hematite red, lead white, and organic red pigments, which Joanna Russell identified in an impression produced c.1540s by Niccolò Vicentino, after Perino del Vaga, *Christ Healing the Paralytic* (London, British Museum, 1860, 0414.84) (Russell 2013).

During the early 16th century, Italian painters used organic red lake pigments prepared from brazilwood and scale insects (kermes, cochineal, and lac) (Kirby and White 1996, 64–65; Berrie 2009); in Venice, pigments including brazilwood lake were employed (Hochmann 2016). In northern Europe, dyestuffs prepared from madder were often used instead (Kirby and White 1996). Consistent with this market trend, madder was identified in a chiaroscuro woodcut by the Flemish printmaker Frans Floris I (1519–1570) (Lepape 2018a; Lepape 2018b, see *Cérès*, 222).

The 18th Century: Trichomatic Intaglio Printing Inks

The introduction of three-colour printing by Jakob Christoff Le Blon in the 1720s relied on optical mixing, or the overprinting of translucent colourants to achieve a vast range of hues. He developed translucent colour printing inks, using innovative methods to prepare colourants, combing them in novel ways, and then preparing inks in specially adapted processes linked to each hue (Stijnman 2020, vol. 1, lxxvi–lxxxi: "Ink Recipes"). Technical examination and instrumental analysis of an impression of *Louis XV* by Le Blon revealed a primary triad of an organic red (probably cochineal, also referred to as carmine), an organic yellow (perhaps unripe buckthorn berries, also referred to as stil-de-grain), and Prussian blue, with white areas composed of lead white, extended with calcium (Walsh 2003, 24–25, notes 9–10). Le Blon also recommended the use of ochre and vermilion (Walsh 2003, note 11; de Montdorge 1756, 40, 116, 117). His student and later rival, Jacques Fabien Gautier, later Gautier-d'Agoty, proposed pigments including ochre, stil-de-grain yellow, vermilion, indigo, and transparent ivory black (Gautier 1749, 26). Recent, larger studies of 18th-century, "full-colour" intaglio prints confirm some of these colourants, in line with the different palettes that Le Blon and his followers proposed and/or used for specific purposes

(Christoforou, van der Mullen, and Gonzalez 2023).

The Early 19th Century: Printing inks for Lithography and Chromolithography

Soon after the invention of lithography, full-colour intaglio printmaking gave way to chromolithographic prints and posters. Like trichomatic mezzotints, they relied on optical mixing produced by the superimposition of translucent printing inks in a specific order. However, they could involve large numbers of colours. Up through the mid-19th century it was common for lithographic printers to mull their own colour inks from pigments purchased from colourmen. Ready-made colour inks seem to have been regarded as an exception until specialist suppliers began to offer colour inks in the 1860s (Twyman 2013, 525–27). Colourants identified in lithographs of this period include vermilion, red lead, chrome yellow, and Prussian blue (Centeno, Lladó Buisan, and Ropret 2006).

Since the discovery of the first aniline dyestuff *mauve* in 1856, many thousands of aniline and azo dyes were prepared into lake pigments. Printing ink formulations increasingly incorporated these synthetic, coal-tar derived pigments (Centeno, Lladó Buisan, and Ropret 2006). Coal tar colourants are made from the benzoid derivatives produced by the distillation of bituminous coal. Red and yellow azo dyes are identified in addition to chrome yellow, and Prussian blue on nine late 19thto early 20th-century lithographic posters (Centeno, Lladó Buisan, and Ropret 2006; Karnes 2009). Trade catalogues overwhelmingly cite azo inks due to their low cost, brilliance, tinting strength, translucency, and relative stability to light.

Change of Printing Inks over Time

Study of 16th- to 17th-century chiaroscuro woodcuts, 18th-century full-colour intaglio prints, and 19th- to 20th-century lithographic inks confirms a broad use of colourants that have a propensity to alter due to inherent instability or when exposed to light and/or pollutants. Lack of permanence can lead to misunderstandings about the palette, state, chronology of production, and even the authenticity of prints that contain them. This section describes some of the degradation that has been observed or may occur in printing inks as they age. It begins by highlighting the impermanence of pigments, which are the primary drivers of deterioration. The pigments are listed in a roughly historical chronology. Then, it addresses the degradation of the binder and paper. Parchment and textile are less common substrates, so they are not addressed here.

Carbon Black

Historically, lamp black was the preferred carbon-based pigment for letterpress printing (Bloy 1967, 42–47; Stijnman 2012, 271). In a chiaroscuro woodcut, the darkest block, which often holds the linear portion of the design, is typically printed in black or grey ink containing carbon-based black. As stated above, the carbon black found in the chiaroscuro woodcuts analysed is plant or soot based. If poorly processed, lamp black can contain traces of tar or added tannin constituents, which may migrate away from the inked areas and/or induce acid catalysed deterioration of the paper support. These compounds are likely to impart a brownish cast to an ink as well as discolour the paper support (Bloy 1967, 42; Van Eikema Hommes 1998, 115 and note 121). Bone or ivory black is made by charring bone or ivory in closed retorts. Its particles are coarser and more irregular in shape and size than lamp black (Gettens and Stout 1966, 99).

Lead White/Lead Carbonate

White printing ink was rare during the Renaissance and Baroque periods, given the difficulties of formulating a workable white ink (Griffiths 1991; Stijnman 1992). The French intaglio printmaker Louis-Marin Bonnet (1736–93) was the first to master reliable white ink, which he used to create the effect of white chalk on coloured paper in the chalk and pastel manners.

Lead white was more often added to alter the hue of other colours. Historical preparations of hand-manufactured lead white were a mixed product of basic and neutral lead carbonate, possibly some lead oxide—and if the product were improperly washed—basic lead acetate and finely divided lead metal (Tumosa and Mecklenburg 2005). Lead white is known to discolour to a grey or pinkish-brown hue by reacting with the air pollutant hydrogen sulfide or other sulfurous compounds, forming lead sulfide (Daniels and Thickett 1992; Smith, Derbyshire, and Clark 2002; Franceschi, Costa, and Franceschi 2011; Museum of Fine Arts 2020) as well as oxidising to plattnerite (Eastaugh et al. 2008, 307). Lead white-containing inks formulated with a low binder-to-pigment ratio are particularly vulnerable to discolouration.

In some 16th-century chiaroscuro woodcuts, the inks appear greyed around the perimeter of the sheets. This phenomenon also has been documented in oil paintings on paper by Joseph Mallord William Turner (1775–1851), most severely where the priming has a low proportion of oil binder (Norville-Day and Townsend 1992). This pattern of degradation can be explained by the fact that air-borne pollutants interact first with the perimeter of a paper object when it is stored in a stack, such as when it is housed on a page of a collector's album or in a window-mount within a box.

Vermilion/Cinnabar/Red Mercury Sulfide

The natural mercury sulfide mineral is called cinnabar, whilst vermilion is the synthetic form of the pigment. It blackens irreversibly to meta-cinnabar through light-induced, surface degradation that involves chlorine, chlorinated compounds, or other halogens (Grout and Burnstock 2000; Spring and Grout 2002; Keune and Boon 2005; Radepont et al. 2011; Radepont 2013). Chlorine ions may be present in native vermilion, but also can abound in dirt and other pollutants (Spring and Grout 2002). It has been demonstrated that the pigment changes more rapidly in linseed oil than watercolour and tempera because light penetrates most deeply into an oil-bound layer (Feller 1967, 107; Grout and Burnstock 2000, 17). The precise mechanism of deterioration and its by-products are not yet clearly understood. Because vermilion varies in colour from red/reddish-orange to darker varieties, it is difficult to ascertain, either optically or spectrophotometrically, whether a dark vermilion is in its original or darkened state (Feller 1967, 103–04). Moreover, if in the early stages of deterioration, it might be impossible to discern the darkening of vermilion visually. A conclusively discoloured pigment appears black or grey (Spring and Grout 2002, 59). Vermilion is understood to be the most common red for letterpress texts, followed by red lead. It is a rule of thumb that vermilion was used for higher-value texts, such as liturgical books, and red lead more for “cheaper” texts, for example ephemeral almanacks printed in the 16th and 17th centuries in northern Europe. However, they could be used in combination, and there are exceptions to every rule.

Minium/Red Lead

Red lead (lead tetroxide) has been synthetically prepared by roasting lead white (480o C) since before the 5th century BCE. Light exposure over time causes the formation of black or deep brown lead dioxide (plattnerite), sometimes with a silvery sheen. Acetic acid or nitric acid also reacts with red lead to form lead dioxide (Gettens and Stout 1966, 152–54).

Verdigris/Copper Acetate

Verdigris degrades over time, and advanced deterioration can be characterised by microfissures in the ink layer and yellow to brown discolouration. The discolouration is related to the pigment interaction with the oil and potentially resin-containing binder. Copper ions can complex with fatty and resinic acids in an oleoresinous medium, resulting in the formation of copper carboxylates and soaps (Groen 1975; Van Eikema Hommes 1998, 110–11; Gunn et al. 2002). The copper ion in verdigris can also catalyse the oxidative degradation of cellulose, which is accelerated in high humidity and light. Consequent deterioration of the paper is manifested as yellow-brown haloes around the printed ink edges or discolouration on the paper verso coincidental to the ink. In extreme instances, the mechanical strength of the paper is compromised, causing fine breaks in the sheet (Henniges et al. 2006).

Verdigris containing inks would have displayed a more bluish-green hue when freshly printed and the transition to brownish green significantly alters the aesthetic appearance (Woudhuysen-Keller 1995). This discolouration has caused misunderstandings. Multicolour figurative woodcuts that served as frontispieces in books printed by Erhard Ratdolt (1442–1528) in Augsburg in the 1490s are among the best known and most studied colour prints of the 15th century. What is often described as a brown ink was surely a copper green that has browned. This is indicated by the characteristic brown hue, damage to the paper visible on the verso, and contextual clues within the image: logically a bishop would be standing on green grass with emeralds on his mitre, not dead grass with brown gemstones. The mischaracterisation of discolouration for distinct palettes, or even states, could have significant implications for the attribution or dating of loose impressions (which might have removed from books or issued as single-sheet prints), as well as for a *catalogue raisonné* of the images or bibliography of the books in which they appeared.

Orpiment

Orpiment is a light-sensitive inorganic pigment that undergoes photo-oxidation to form translucent or white arsenic oxides (FitzHugh 2012, 51; Museum of Fine Arts 2020). Conversion of orpiment to white arsenic trioxide also can occur in the presence of ozone, a common atmospheric pollutant (Whitmore and Cass 1998). When mixed with another more lightstable colourant, as the orpiment degrades the other colourant will visually dominate, thereby changing the colour and tone of the inks. The behaviour of oil-bound orpiment under environmental conditions typical for the display and storage of works on paper warrants further study (Dubois et al. 2001).

Indigo

The fading of indigo to grey in oil paintings is thoroughly characterised by Margriet Van Eikema Hommes in *Changing Pictures: Discolouration in 15th–17th-Century Oil Paintings* (Van Eikema Hommes 2004; see also Van Eikema Hommes 2005). Through artificial light aging experiments on reconstructions of indigo paint films, Van Eikema Hommes demonstrates that during the drying of oil, aldehydes are formed by the oxidation of polyunsaturated fatty acids. These reaction products can then take part in the oxidation of indigo, which leads to fading. Moreover, Van Eikema Hommes' study shows that the fading of indigo paint reconstructions is accelerated when the paint is extended with lead white. The higher the ratio of lead white to indigo, the greater is indigo's susceptibility to fading. In Johannes Verspronck's Portrait of a *Girl Dressed in Blue* (1641), the colour has faded more in the lighter indigo passages than in the darker, as compared with paint protected by the frame; Van Eikema Hommes demonstrates experimentally that the light stability of indigo paint is determined by the pigment purity, or indigotin concentration (Van Eikema Hommes 2004, 91).

In addition to fading, colour change can also occur since indigo is a natural product that may contain widely different types and percentages of organic and inorganic impurities. At the time of manufacture, the colourant could be adulterated with various materials that might discolour over time, including ashes, soot, sand, blue wool and silk, starch, resin, and rust (Van Eikema Hommes 2004, 100). Thus, the degradation phenomena of blue ink containing indigo can alter the colour harmonies of a print to varying degrees.

Green and Yellow Organic Colourants

A possible source for green organic colourants used in the 16th to 18th centuries is sap green, produced from ripe buckthorn (*Rhamnus cathartica*) berry juice and an alkali. Buckthorn berries, also known as Persian berries, could produce a yellow colourant if extracted before ripening. Traditionally, these flavonoid-based green and yellow dyes were precipitated onto an inorganic substrate such as calcium carbonate (chalk), resulting in a lake pigment. Sap green has poor light-fastness. Similarly, research on the light-induced colour changes in yellow, flavonoid-based, lake pigments shows that unripe buckthorn berries and weld bound in linseed oil fade in artificial daylight; they fade slightly less if the light is filtered of ultraviolet radiation below 400 nm. The loss of yellowness is accompanied by an increase in redness. Moreover, light-fastness increases with colourant concentration (Saunders and Kirby 1994). Mixtures of yellow, flavonoid-based colourants with a more light-stable blue colourant (e.g. indigo) could result in a shift toward a bluer and/or perhaps redder hue. Gamboge yellow is a gum resin that is partially soluble in alcohol and some other organic solvents. It is alkali sensitive, discolouring to red upon contact over time. It also can be darkened by exposure to ammonia fumes and is faded by light exposure (Gettens and Stout 1966, 114–15; Book and Paper Group 2022).

Red Organic Colourants

In two chiaroscuro woodcut impressions of Niccolo Vicentino's (active c.1510–1550) *Christ Healing the Paralytic* that were printed in a palette of violet inks, (see British Museum, 1860, 0414.84 and Davison Art Center, Wesleyan University, 1992.26.1), in which the darkest block is printed in a very dark violet, not black), the medium and dark violets appear discoloured yellowbrown when compared to another, third impression (see Museum of Fine Arts, Boston, 64.1037), presumably because of the instability of the organic red pigments identified in the impressions (Russell 2013). These red lake pigments when bound in linseed oil, fade in daylight, and increase in yellowness during fading. Of the red lake pigments studied by David Saunders and Jo Kirby (kermes, cochineal, lac, brazilwood, madder), those derived from scale insect or brazilwood dyestuffs are more fugitive than those derived from madder (Saunders and Kirby 1994).

Prussian Blue/Ferri-ammonium-ferrocyanide

Prussian blue was first synthesised in Berlin in 1704. The preparation was kept secret until

John Woodward published it in 1724 (Woodward 1724), and the recipe became well known throughout Europe. The particles are so finely divided that it has almost the characteristic of a dye (Gettens and Stout 1966, 149–51). It is alkali sensitive and may turn brown upon contact over time. It fades in strong light, however the depth of blue will return after brief storage in the dark (Book and Paper Group 2022).

Chrome Yellow/Lead Chromate

As a pigment chrome yellow dates from the beginning of the 19th century. It is prevalent in chromolithography inks, especially for posters. The pigment acquires a green tone when mixed with colours of organic origin or exposed to alkalis, by reduction to chromic oxide. The pigment has excellent light fastness (Gettens and Stout 1966, 106–07). Chrome yellow darkens to dark brown or grey on reaction with hydrogen sulfide in polluted air. In the 19th century it was often mixed with Prussian blue to produce a green (Book and Paper Group 2022).

Coal-tar Colours/Aniline and Azo

Many aniline and azo dyes prepared into lake pigments lack permanence (Gettens and Stout 1966, 108). Analysis of three early 20th-century red lithographic inks identified Hansa Red, a monoazo-toluidine red pigment, and barium lithol red. Fibre optic micro-scale spectroscopy indicated that the toluidine reds are fairly lightfast, while the lithol red demonstrated fading behaviour (Karnes 2009, 134).

Chemically Interactive Colourants

Discolouration of chiaroscuro woodcut inks can be caused by chemical interaction between certain colourants that are admixed within one ink or between colourants in adjacent or superimposed ink layers. Pigments containing sulfur such as vermilion, ultramarine, orpiment or realgar can react with those containing copper including verdigris and azurite, or those containing lead, such as lead white and lead-tin yellow (Van Eikema Hommes 1998, 114–15). As early as the 14th century, verdigris had a bad reputation for contaminating other colours (Woudhuysen-Keller 1995).

Binder

Linseed oil, walnut oil, and resins share a tendency to become brittle and yellowed with age. Storage in darkness and humidity increase discolouration (Gettens and Stout 1966, 46). In a British Museum study, sample papers prepared with coatings of linseed and poppy seed oil, and the oils mixed with Venice turpentine or mastic resin, had discoloured more under conditions of dark-humid oven ageing (50% RH; 55° C), as compared to dark-dry oven aging (70° C) and light ageing (in a Microscal light fastness tester). Though the light aged samples appeared brighter they were the most brittle (Kosek and Green 1992). The major aging processes are polymerisation, hydrolysis, oxidation, and soap formation if reactive metal ions are present (such as lead white or red lead pigment) (Erhardt, Tumosa, and Mecklenburg 2005; van den Berg 2002). Degradation leads to the formation of carboxylic acids. The associated increase of acidity is confirmed by titration studies (van der Weerd, van Loon, and Boon 2005).

Breakdown of coloured ink can lead to blanching caused by the swelling of the oil binder in water or water vapour. This kind of blanching results in a dull whitish, foggy appearance. Water may take days to diffuse through pure oil medium, but it can channel along poorly bound, flocculated pigment particles within a film in minutes (Michalski 1990). Other potential mechanisms, such as free fatty acid migration to the ink surface and subsequent oxidation, or the formation of lead soaps in oil, remain incompletely understood (Koller and Burmester 1990; Higgitt, Spring, and Saunders 2003; Cotte et al. 2007).

Paper Support

Oxidised and acidic oil/resin binder in ink may interact with the paper support, causing discolouration and embrittlement of the sheet. The aforementioned British Museum study also monitored the evolution of peroxides which drive cellulose oxidation. In the study's sample papers, peroxides continued to be generated after 85 days of ageing, though at a diminishing rate as ageing advanced (Kosek and Green 1992, 101). After 52 days of ageing, the samples were tested for organic acid content. Due to their volatility, organic acids had been lost from the heat aged samples but not entirely from those that were light aged. Should the paper support be discoloured by the synergistic action of peroxides and organic acids, the optical appearance of the inks will be altered by the colour of the underlying sheet. The thicker and more uniform the ink film, the less paper discolouration is a factor in the perceived hue of a given ink.

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Endnotes

Antreasian, G.Z. and Clinton Adams. *The Tamarind Book of Lithography: Art & Techniques*. Los Angeles, CA: Tamarind Lithography Workshop, 1971.

Berrie, Barbara H. "An Improved Method for Identifying Red Lakes on Art and Historical Artifacts." *Proceedings of the National Academy of Sciences of the United States of America* 106, no. 36 (2009): 15095–96.

Bimbenet-Privat, Michèle, and Florence Le Bars. "New Documents on Sixteenth-Century Printmaking in Paris." *Print Quarterly* 11, no. 2 (1994): 151–55.

Bloy, Colin H. 1967. *A History of Printing Ink, Balls and Rollers 1440–1850*. London: Evelyn Adams & Mackay, 1967.

Book and Paper Group. "Media Problems." *Book and Paper Group Wiki*. American Institute for Conservation, 2022.

Bosse, Abraham. *Traicté des manières de graver en taille douce sur l'airain*. Paris: chez ledit Bosse, en l'Isle du Palais, à la Roze rogue, devant la Megisserie, 1645.

Cahill, T.A., B.H. Kusko, R.A. Eldred, and R.N. Schab. "Gutenberg's Inks and Papers: Non-Destructive Compositional Analyses by Proton Milliprobe." *Archaeometry* 26, no. 1 (1984): 3–14.

CAMEO Chemicals. "Stoddard Solvent." Version 2.8.0 rev 1. https://cameochemicals.noaa.gov/chemical/8871. Accessed 27 June 2022.

Centeno, Silvia A., Virginia Lladó Buisan, and Polonca Ropret. "Raman Study of Synthetic Organic Pigments and Dyes in Early Lithographic Inks (1890–1920)." *Journal of Raman Spectroscopy* 37, no. 10 (2006): 1111–18.

Christoforou, Dionysia, Manon van der Mullen, and Victor Gonzalez. "From Colour Theory to Colour Practice: Printmakers in Pursuit of the Ideal Pigments in 18th-Century Europe." In *Printing Colour 1700–1830: Histories, Techniques, Functions, and Receptions*, edited by Margaret Morgan Grasselli, and Elizabeth Savage. Publications of the British Academy. Oxford: Oxford University Press, 2023.

Clayton, M. "Raw Materials." In *The Printing Ink Manual*, edited by R.H. Leach, and R.J. Pierce, 140–323. Dordrecht: Springer Netherlands, 1993.

Cotte, Marine, Emilie Checroun, Jean Susini, and Philippe Walter. "Micro-analytical Study of Interactions between Oil and Lead Compounds in Paintings." *Applied Physics A* 89, no. 4 (2007): 841–48.

Dachus-Hamm, Patricia. "A History of the Manufacture of Printing Ink from 1500–1900 with Notes for the Conservator." In *The Institute of Paper Conservation: Conference Papers Manchester 1992*, edited by Shiela Fairbrass, 30–34, 1992.

Daniels, Vincent, and David Thickett. "The Reversion of Blackened Lead White on Paper: Analytical Appendix by T. Baird and N.H. Tennent." Edited by Shiela Fairbrass, 109–15.

London: Institute of Paper Conservation, 1992.

de Montdorge, Antoine Gautier. *L'Art d'imprimer les tableaux traité d'après les ecrits, les opérations et les instructions verbales, de J. C. Le Blon*. Paris: P. G. le Mercier, Jean-Luc Nyon, Michel Lambert, 1756.

De Vinne, Theodore Low. *The Invention of Printing: A Collection of Facts and Opinions, Descriptive of Early Prints and Playing Cards, the Block-Books of the Fifteenth Century, the Legend of Lourens Janszoon Coster, of Haarlem, and the Work of John Gutenberg and His Associates*. New York: Francis Hart, 1876.

Dubois, Hilhne, Sabrina Meloni, Erika Metz, Barbara Schoonhoven, and Arie Wallert. "Breakdown Processes of Orpiment- and Realgar-Based Sixteenth-century Paints." In *Deterioration of Artists' Paints: A Joint Meeting of ICOM-CC Working Groups Paintings 1 & 2 and the Paintings Section, UKIC, British Museum London, 10th and 11th September 2001*, 75–97. London; Paris: United Kingdom Institute for Conservation of Historic and Artistic Works; International Council of Musuems, 2001.

Eastaugh, Nicholas, Valentine Walsh, Tracey Chaplin, and Ruth Siddall. *Pigment Compendium. A Dictionary and Optical Microscopy of Historical Pigments*. New York: Taylor & Francis, 2008.

Erhardt, David, Charles S. Tumosa, and Marion F. Mecklenburg. "Long-Term Chemical and Physical Processes in Oil Paint Films." *Studies in Conservation* 50, no.2 (2005): 143–50.

Feller, Robert L. "Studies on the Darkening of Vermilion by Light." *Report and Studies in the History of Art* 1 (1967): 99–111.

Fineschi, Vincenzio. *Notizie storiche sopra la stamperia di Ripoli le quali possono servire all'illustrazione della storia tipografica fiorentina*. Florence: Francesco Moücke, 1781.

Fischer, Earl Knudt. *Printing Ink: An Address before the Bibliographical Society of the University of Virginia, November 17, 1947*. Charlottesville, VA: University of Virginia, 1947.

FitzHugh, Elizabeth West. *Artists' Pigments: A Handbook of their History and Characteristics*. Washington DC: National Gallery of Art, 2012.

Franceschi, Chiara M., Giorgio A. Costa, and Enrico Franceschi. "Aging of the Paint Palette of Valerio Castello (1624–1659) in Different Paintings of the Same Age (1650–1655)." *Journal of Thermal Analysis and Calorimetry* 103, no. 1 (2011): 69–73.

Gaskell, Phillip. *New Introduction to Bibliography*. Oxford: Clarendon Press, 1974.

Gautier, Jacques Fabien. *Lettres concernent le nouvel art de gravur et imprimer les tableaux*. Paris, 1749.

Geldner, Ferdinand. "Das Rechungsbuch des Speyrer Druckherrn, Verlegers und Großbuchhändlers Peter Drach mit Einleitung, Erläuterungen und Identifizierungslisten." *Archiv für Geschichte des Buchwesens* 5 (1964): 1–196.

Gettens, Rutherford John, and George Leslie Stout. *Painting Materials: A Short*

Encyclopedia. New York: Dover Publications, 1966.

Gleitsman, E.T.F. “Advertisment: Preis-Courant bunter und schwarzer Buch-& Steindruck-Farben von E. T. F. Gleitsmann in Leipzig.” *Journal für Buchdruckerkunst* 11 (1849).

Grasselli, Margaret Morgan. “Multiple-Plate Colour Prints and the Problems of Variant Impressions, Missing Plates, and Disappearing Inks.” In *Printing Colour 1700–1830: Histories, Techniques, Functions, and Receptions*, edited by Margaret Morgan Grasselli, and Elizabeth Savage. Publications of the British Academy. Oxford: Oxford University Press, 2023.

Griffiths, Antony. “White Ink.” *Print Quarterly* 8, no. 3 (1991): 286–90.

———. *The Print Before Photography: An Introduction to European Printmaking 1550–1820*. London: British Museum Press, 2016.

Groen, C.M. “Towards Identification of Brown Discoloration on Green Paint.” In *Icom Committee for Conservation. 4th Triennial Meeting, Venice, 13–18 October 1975. Preprints*, 91–130. 75213-1–75213-8. Paris: ICOM, 1975.

Grout, Rachel, and Aviva Burnstock. 2000. “A Study of the Blackening of Vermilion.” *Zeitschrift für Kunsttechnologie und Konservierung* 14, no. 1 (2000): 15–22.

Gunn, Michèle, Geneviève Chottard, Eric Rivière, Jean-Jacques Girerd, and Jean-Claude Chottard. “Chemical Reactions Between Copper Pigments and Oleoresinous Media.” *Studies in Conservation* 47, no. 1 (2002): 12–23.

Helmasperger, Ulrich. Outcome of the lawsuit Johann Fust vs Johann Gutenberg, Mainz, 6 November 1455, Mainz (Helmasperger Notarial Instrument). Ink on parchment. Niedersächische Staatsund-Universitätsbibliothek Göttingen, 2i Cod. Ms. hist. lit. 123 Cim., 1455. Digitised at www.gutenbergdigital.de/notar.html, 2001. Accessed 28 June 20225.

Henniges, Ute, Ulrike Bürger, Gerhard Banik, Thomas Rosenau, and A. Potthast. “Copper Corrosion: Comparison Between Naturally Aged Papers and Artificially Aged Model Papers.” *Macromolecular Symposia* 244, no. 1 (2006): 194–203.

Higgitt, Catherine, Marika Spring, and David Saunders. “Pigment-Medium Interactions in Oil Paint Films containing Red Lead or Lead-tin Yellow.” *National Gallery Technical Bulletin* 24 (2003): 75–95.

Hochmann, Michel. “A Visit to Titian’s Studio.” *Burlington Magazine* 158, no. 1362 (2016): 692–701.

Hoskins, Steve *Inks*. London: A & C Black, 2004.

Ikeda, Mayumi. “The Fust and Schöffer Office and the Printing of the Two-Colour Initials in the 1457 Mainz Psalter.” In *Printing Colour 1400–1700: History, Techniques, Functions and Receptions*, edited by Ad Stijnman and Elizabeth Savage, 65–76. Leiden: Brill, 2015.

Johns, Adrian. “Ink.” In *Materials and Expertise in Early Modern Europe: Between Market and Laboratory*, edited by Ursula Klein and E.C. Spary, 101–24. Chicago, IL: University of Chicago Press, 2010.

Karnes, Cyntia. “Lithography in the Age of Silent Cinema.” In *Printed on Paper: The Techniques, History and Conservation of Printed Media*, edited by Jane Colbourne, and Reba Fishman Synder, 124–36. Newcastle upon Tyne: Northumbria University, 2009.

Kern, Marie, Ad Sitjnman, Jana Müller, Yvonne Wiegand, and Irene Brückle. “From Wine to Print: Reconstruction of Frankfurt Black Pigment and Intaglio Printing Ink.” *Journal of Paper Conservation* 21, no. 2 (2020): 42–56.

Keune, K., and J.J. Boon. “Analytical Imaging Studies Clarifying the Process of the Darkening of Vermilion in Paintings.” *Analytical Chemistry* 77, no. 15 (2005): 4742–50.

Kirby, Jo, and Raymond White. “The Identification of Red Lake Pigment Dyestuffs and a Discussion of their Use.” *National Gallery Technical Bulletin* 17 (1996): 56–80.

Klaetsch, Hermann. *Die Druckfarbe in vergangenen Zeiten*. Halle-Ammendorf: Hartmann, 1940.

Koller, Johann, and Andreas Burmester. “Blanching of Unvarnished Modern Paintings: A Case Study on a Painting by Serge Poliakoff.” In *Cleaning, Retouching and Coatings: Technology and Practice for Easel Paintings and Polychrome Sculpture: Preprints of the Contributions to the Brussels Congress, 3–7 September 1990*, edited by John S Mills, and Perry Smith, 138–43. London: International Institute for Conservation of Historic and Artistic Works, 1990.

Kosek, Joanna, and Lorna R Green. “A Survey of Oil Paintings and Sketches on Paper in the Collection in the British Museum: An Assessment of Stability.” In *The Institute of Paper Conservation: Conference Papers Manchester 1992*, edited by Shiela Fairbrass, 96–102. London: Institute of Paper Conservation, 1992.

Le Breton, André-François. “Encre noir.” In *Encyclopédie*, edited by Denis Diderot, and Jean Le Rond d’Alembert, 632–42. Paris: Briasson, David, Le Breton, and Durand, 1755.

Lepape, Séverine. “Les matériaux colorants dans les encres.” In *La Gravure en clair-obscur. Cranach, Raphaël, Rubens*, edited by Séverine Lepape, 34–37. Paris: Liénart; Musée du Louvre, 2018a.

Lepape, Séverine. “Résultats des analyses scientifiques des encres des estampes nordiques en couleurs (Projet Claro).” In *La Gravure en Clair-obscur. Cranach, Raphaël, Rubens*, edited by Séverine Lepape, 220–23. Paris: Liénart; Musée du Louvre, 2018b.

Lorilleux & Cie. “Advertisement.” *Annales de la typographie française et étranger* 1, no. 1938.

Michalski, Stefan. “A Physical Model of the Cleaning of Oil Paint.” In *Cleaning, Retouching and Coatings: Technology and Practice for Easel Paintings and Polychrome Sculpture: Preprints of the Contributions to the Brussels Congress, 3–7 September 1990*, edited by John S. Mills and Perry Smith, 85–92. London: International Institute for Conservation of Historic and Artistic Works, 1990.

Moxon, Joseph. “Mechanick Exercises: Or, the Doctrine of handy-works: Applied to the Art of Printing.” 1683.

Museum of Fine Arts, Boston. "Orpiment." *CAMEO: Conservation & Art Material Encyclopedia* Online, 2020. https://cameo.mfa.org/wiki/Orpiment

Needham, Paul. "The Paper Supply of the Gutenberg Bible." *Papers of the Bibliographical Society of America* 79, no. 3 (1985a): 303–74.

———. "Division of Copy in the Gutenberg Bible: Three Glosses on the Ink Evidence." *Papers of the Bibliographical Society of America* 79, no. 3 (1985b): 411–26.

Norville-Day, Heather, and Joyce H. Townsend. "Turner's Oil Paintings on Paper: Treatment and Display," edited by Shiela Fairbrass, 103–8. London: Institute of Paper Conservation, 1992.

Oltrogge, Doris. "Colour Stamping in the Late Fifteenth and Sixteenth Centuries: Technical Sources and Workshop Practice." In *Printing Colour 1400–1700: Histories, Techniques, Functions, Receptions*, 51–64. Leiden: Brill, 2015.

Palandri, Chiara. "A *Voyage pittoresque* in Norway through Colour Prints, 1789–c.1815." In *Printing Colour 1700–1830: Histories, Techniques, Functions, and Receptions*, edited by Margaret Morgan Grasselli, and Elizabeth Savage. Publications of the British Academy. Oxford: Oxford University Press, 2023.

Papillon, Jean Michel. *Traité historique et pratique de la gravure en bois*. Paris: Pierre Guillaume Simon, 1766.

Price, Beth, Nancy Ash, Haddon A. Dine, Shelley R. Langdale, Ken Sutherland, Lucia Burgio, and Jo-Fan Huang. 'A Technical Study of Sixteenth-Century Italian Chiaroscuro Woodcuts.' In *Printing Colour 1400–1700: Histories, Techniques, Functions, Receptions*, 140–50. Leiden: Brill, 2015.

Radepont, Marie. "Understanding of Chemical Reactions Involved in Pigment Discoloration, in Particular in Mercury Sulfide (HgS) Blackening." *diss., Université Pierre et Marie Curie*, Paris VI: Universiteit Antwerpen, 2013.

Radepont, Marie, Wout de Nolf, Koen Janssens, Geert Van der Snickt, Yvan Coquinot, Lizet Klaassen, and Marine Cotte. "The Use of Microscopic X-Ray Diffraction for the Study of HgS and its Degradation Products Corderoite (α -Hg3S2Cl2), Kenhsuite (γ -Hg3S2Cl2) and Calomel (Hg2Cl2) in Historical Paintings." *Journal of Analytical Atomic Spectrometry* 26, no. 5 (2011): 959.

Rohart, François. "Advertisement: François Rohart, ancien imprimeur de la Maison Lemercier, Bérnard et Cie, fabricant de noirs et de couleurs pour la lithographie, Rue de Grenelle-Saint-German, 59, Mainson de la Fontaine, Paris." *Le Lithographe* 4, 1845.

Russell, Joanna. "The Analysis of Inks on Seven Italian Chiaroscuro Woodcut Prints." *CSR Analytical Request No. AR2013-21* London, British Museum, Department of Conservation and Scientific Research; unpublished and cited with permission, 2013.

Saunders, David, and Jo Kirby. "Light-induced Colour Changes in Red and Yellow Lake Pigments." *National Gallery Technical Bulletin* 15 (1994): 79–97.

———, and Jo Kirby. "The Effect of Relative Humidity on Artists' Pigments." *National*

Gallery Technical Bulletin 25 (2004): 62–72.

Savage, Elizabeth. "Colour Printing Inks and Colour Inking in 18th-Century Europe." In *Printing Colour 1700–1830: Histories, Techniques, Functions, and Receptions*, edited by Margaret Morgan Grasselli, and Elizabeth Savage. Publications of the British Academy. Oxford: Oxford University Press, 2023.

Savage, William. *On the Preparation of Printing Ink, both Black and Coloured*. Printed for the author, and sold by Longman, Rees, Orme, Brown, Green, and Longman, 1832.

Savary des Bruslons, Jacques. *Dictionnaire universel de commerce. Contenant tout ce qui concerne le commerce qui se fait dans les quatre parties du monde*. Amsterdam: Janssonius van Waesbergen, 1726.

Schwenke, Paul. *Untersuchungen zur Geschichte des ersten Buchdrucks*. Burg. a. M.: A. Hopfer, 1900.

Schwab, Richard N., Thomas A. Cahill, Bruce H. Kusko, and Daniel L. Wick. "Cyclotron Analysis of the Ink in the 42-Line Bible." *Papers of the Bibliographical Society of America* 77, no. 3 (1983): 285–315.

———, Thomas A. Cahill, Robert A. Eldred, Bruce H. Kusko, and Daniel L. Wick. "New Evidence on the Printing of the Gutenberg Bible: The Inks in the Doheny Copy." *Papers of the Bibliographical Society of America* 79 (1985): 375–410.

———, Thomas A. Cahill, Bruce H. Kusko, Robert A. Eldred, and Daniel L. Wick. "Ink Patterns in the Gutenberg New Testament: The Proton Milliprobe Analysis of the Lilly Library Copy." *Papers of the Bibliographical Society of America* 80, no. 3 (1986): 305–31.

———, Thomas A. Cahill, Bruce H. Kusko, Robert A. Eldred, and Daniel L. Wick. "The Proton Milliprobe Ink Analysis of the Harvard B42." *Papers of the Bibliographical Society of America* 81, no. 4 (1987): 403–32.

Senefelder, Alois. *The Invention of Lithography*. New York: Fuchs & Lang Manufacturing, 1818.

Smith, Gregory D., Alan Derbyshire, and Robin J.H. Clark. "In Situ Spectroscopic Detection of Lead Sulphide on a Blackened Manuscript Illumination by Raman Microscopy." *Studies in Conservation* 47, no. 4 (2002): 250–56.

Spring, Marika, and Rachel Grout. "The Blackening of Vermilion: An Analytical Study of the Process in Paintings." *National Gallery Technical Bulletin* 23 (2002): 50–61.

Stiber Morenus, Linda. "The Chiaroscuro Woodcut Printmaking of Ugo da Carpi, Antonio da Trento and Niccolò Vicentino: Technique in Relation to Artistic Style." In *Printing Colour 1400–1700: Histories, Techniques, Functions, Receptions*, edited by Ad Stijnman, and Elizabeth Savage, 123–39. Leiden: Brill, 2015.

———. "Recreating the Italian Chiaroscuro Woodcut." In *The Chiaroscuro Woodcut in Renaissance Italy*, edited by Naoko Takahatake, 256–75. Los Angeles, CA and New York: Los Angeles County Museum of Art/Prestel, 2018.

———. “Masking the Matrix: Technical Comparison of Lifetime and Posthumous Impressions of Niccolò Vicentino’s Chiaroscuro Woodcuts to Posthumous Impressions, Including Andrea Andreani’s Restrikes.” In *Printing Things: Blocks, Plates, and Other Objects that Printed, 1400–1900*, edited by Elizabeth Savage, and Femke Speelberg. Publications of the British Academy. Oxford: Oxford University Press, 2023.

———, Charlotte W. Eng, Naoko Takahatake, and Diana C. Rambaldi. “16–17th Century Italian Chiaroscuro Woodcuts: Instrumental Analysis, Degradation and Conservation.” *Journal of the American Institute for Conservation* 54, no. 4 (2015): 238–71.

Stijnman, Ad. “White Ink.” *Print Quarterly* 9, no. 2 (1992): 181–83.

———. *Engraving and Etching 1400–2000: Historical Developments of Manual Intaglio Printmaking Processes*. London: Archetype, 2012.

———. “Hercules Seger’s Printmaking Techniques.” In *Hercules Segers: Painter Etcher*, edited by Huigen Leeflang, and Pieter Roelofs, 75–90. Amsterdam: Nai Publishers, in association with the Rijksmuseum, 2016.

———. *Jacob Christoff Le Blon and Trichromatic Printing.* Ouderkerk aan den IJssel: Sound & Vision Publishers in cooperation with the Rijksmuseum, 2020.

———, and Elizabeth Savage, eds. *Printing Colour 1400–1700: History, Techniques, Functions and Receptions*. Leiden: Brill, 2015.

Tumosa, Charles S., and Marion F. Mecklenburg. “The Influence of Lead Ions on the Drying of Oils.” *Studies in Conservation* 50, Supplement I (2005): 39–47.

Twyman, Michael. *A History of Chromolithography: Printed Colour for All*. New Castle, DE and London: Oak Knoll Press and The British Library, 2013.

van den Berg, J.D.J. “Analytical Chemical Studies on Traditional Linseed Oil Paints.” diss., University of Amsterdam, 2002.

van der Weerd, Jaap, Annelies van Loon, and Jaap J. Boon. “FTIR Studies of the Effects of Pigments on the Aging of Oil.” *Studies in Conservation* 50, no. 1 (2005): 3–22.

Van Eikema Hommes, Margriet. “Painters’ Methods to Prevent Colour Changes Described in Sixteenth to Early Eighteenth-Century Sources on Oil Painting Techniques.” In *Looking through Paintings: The Study of Painting Techniques and Materials in Support of Art Historical Research*, edited by Erma

Hermens, Annemiek Ouwerkerk, and Nicola Costaras, 91–131. London; Baarn: Archetype; De Prom, 1998.

Van Eikema Hommes, Margriet. *Changing Pictures: Discolouration in 15th–17th Century Oil Paintings*. London: Archetype, 2004.

———. “Interpreting Historical Sources on Painting Materials and Techniques: The Myth of ‘Copper Resinate’ And the Reconstruction of Indigo Oil Paints.” In *Art of the Past: Sources and Reconstructions, Proceedings of the First Symposium of the Art Technological Source Research Study Group*, edited by Mark Clarke, Joyce Townsend, and Ad Stijnman, 16–23. London: Archetype Publications with the participation of ICN Amsterdam, 2005.

Voet, Leon. *The Golden Compasses: A History and Evaluation of the Printing and Publishing Activities of the Offlcina Plantiniana at Antwerp*. Amsterdam; New York: Van Gendt; Abner Schram, 1969.

Walsh, Judith. “Ink and Inspiration.” In *Colorful Impressions: The Printmaking Revolution in Eighteenth-Century France*, edited by Margaret Morgan Grasselli, 22–33. Washington, DC: National Gallery of Art, 2003.

Whitmore, Paul M., and Glen R. Cass. “The Ozone Fading of Traditional Japanese Colorants.” *Studies in Conservation* 33, no. 1 (1998): 29–40.

Wiborg, Frank B. *Printing Ink: A History, with a Treatise on Modern Methods of Manufacture and Use*. New York: Harper & Brothers, 1926.

Woodward, John. “Praeparatio coerulei Prussiaci es Germanica missa.” *Philosophical Transactions of the Royal Society of London* 33, no. 381 (1724): 15–17.

Woudhuysen-Keller, Renate. “Aspects of Painting Technique in the Use of Verdigris and Copper Resinate.” In *Historical Painting Techniques, Materials, and Studio Practice: Preprints of a Symposium, University of Leiden, the Netherlands, 26–29 June 1995*, edited by Arie Wallert, Erma Hermens, and Marja Peek, 65–69. Los Angeles: Getty Conservation Institute, 1995.