Literature on the technical examination of printing ink in incunabula, with some additional references, in chronological order

A short bibliography for the Jikji to Gutenberg *Project.*

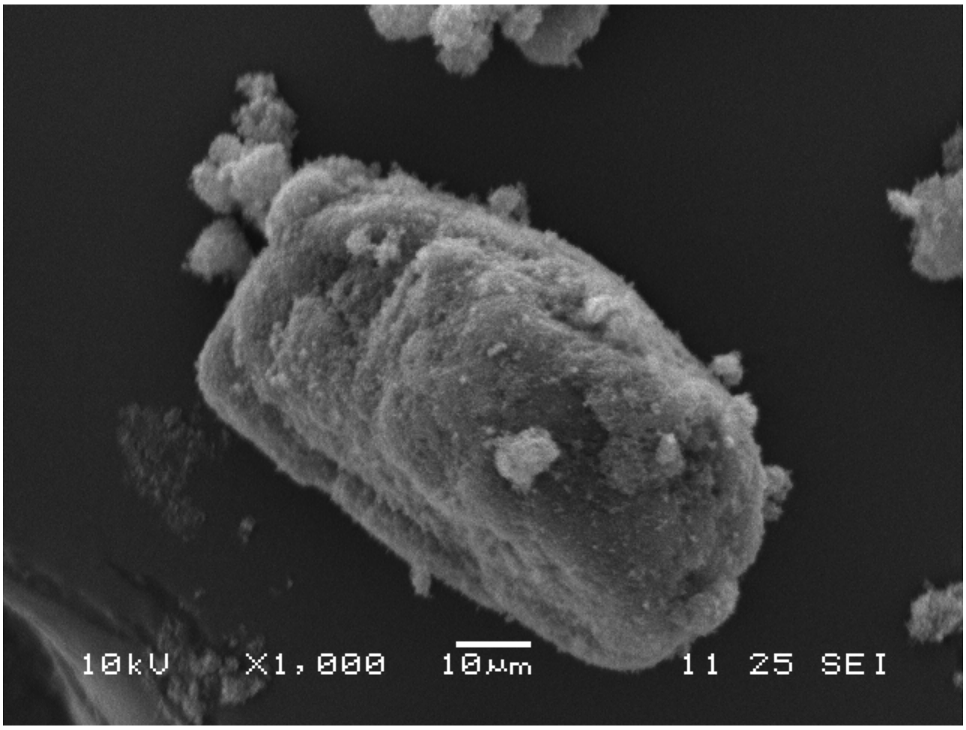
Ad Stijnman, 15 April 2022

Introduction

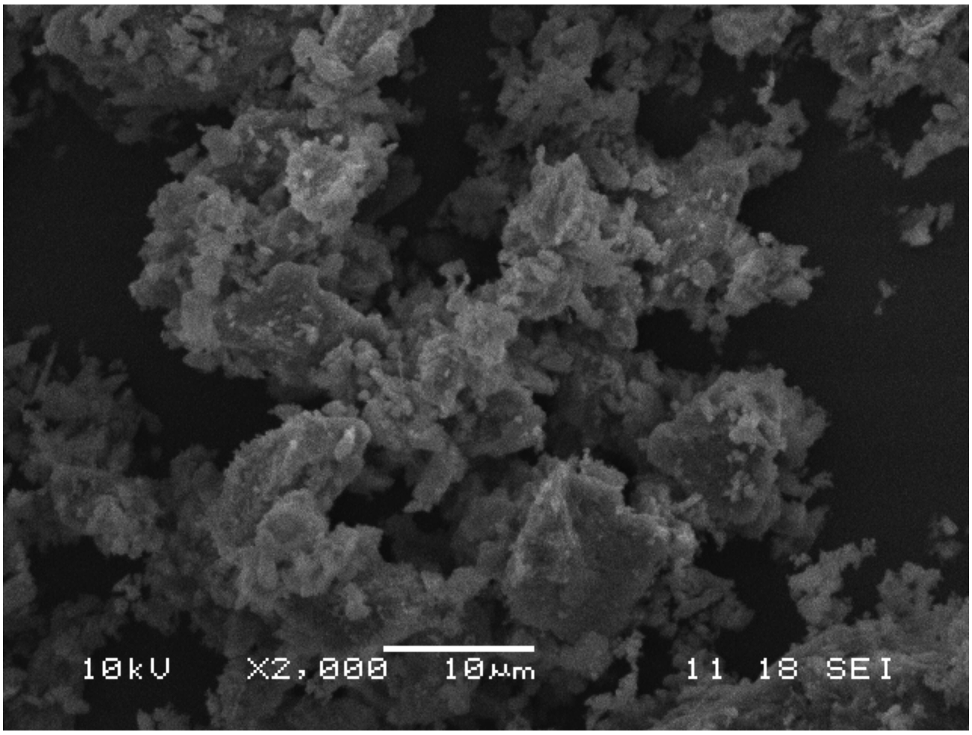
Oil-based printing ink as used by Johann Gutenberg (1395/1400–1468) and his followers consisted of a mixture of lampblack in oil-varnish with litharge (PbO) as a drying agent.

Lampblack was made by the charring of mineral asphaltum, vegetable oil, pine resin or beeswax, and the soot produced was collected. This soot contained a high percentage of pure carbon and was further refined by so called calcination. An earthenware pot was filled with soot, closed except for a tiny hole and the pot heated as long as gas escaped. The purity of lampblack could be increased by repeated calcination, which could be to up to six times in the 19th century. In the 19th century large deposits of natural gas were found, which were also used for the production of carbon, which pigment is now called 'carbonblack'.

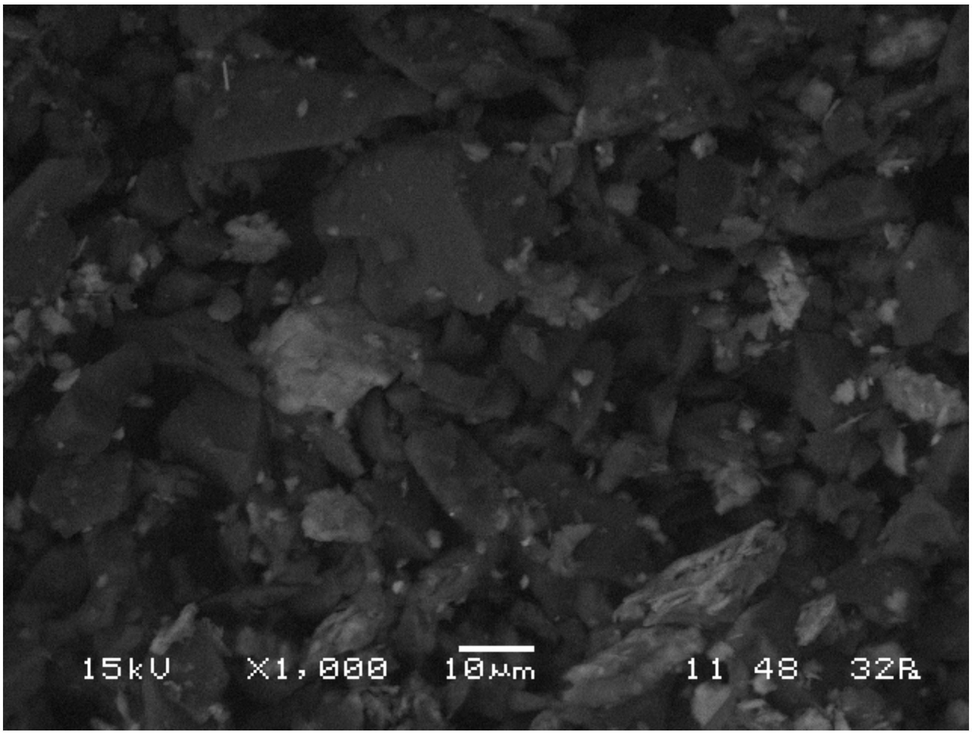
From the very beginning of letterpress printing lampblack was the chosen pigment for black printing ink, because it gave the most opaque and at the same time thinnest layer compared to all other black pigments. This was because of the very small particle size (0.2–0.5 micron in diameter) of lampblack pigment – the later carbonblack had even finer particles. With all other black pigments particle size starts at about 1 micron up to 50 micron in diameter, see images below. The other difference is that a lampblack particle is a conglomerate of a conglomerate of carbon atoms, the smallest particles appear like spheres or globules, while particles of all other black pigments are of irregular shape and size (see *Winter & West FitzHugh 2007*, p. 27, Figs. 16–21).



'Lump' showing a conglomerate of a conglomerate (etc.) of carbonblack pigment particles; photo Ineke Joosten, RCE, Amsterdam



Boneblack; photo Ineke Joosten, RCE, Amsterdam

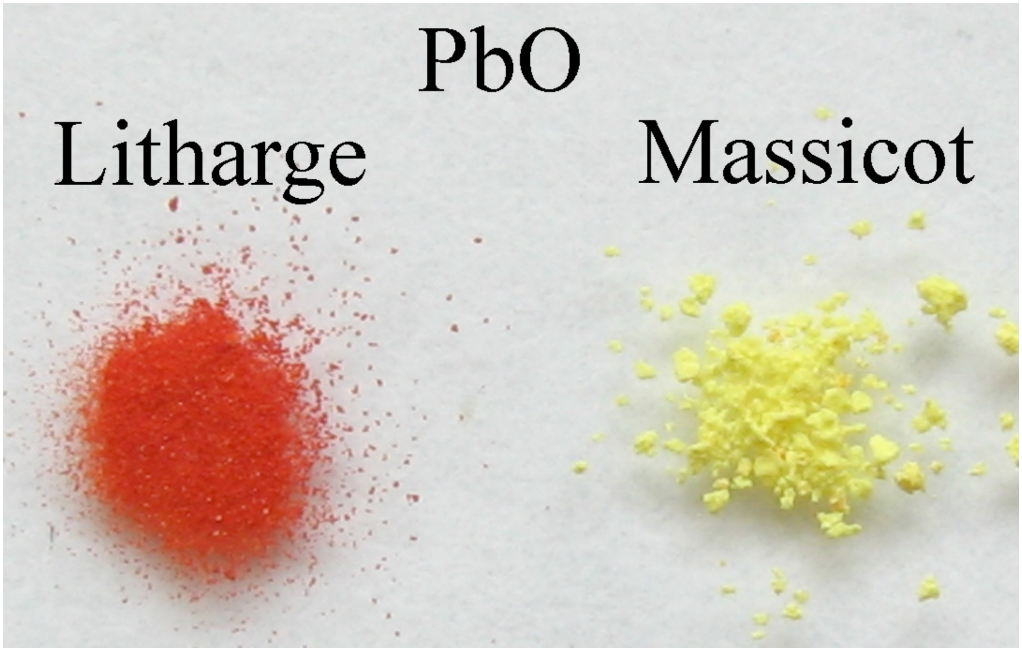


Charcoal black; photo Ineke Joosten, RCE, Amsterdam

Linseed oil, pressed from flax seed, was the commonly used vegetable oil for making oil varnish, the binding medium or vehicle for printing ink. Alternatively walnut oil could be used. Both oils contain a high percentage of unsaturated fatty acids (i.e. high iodine value), which makes them well suited for polymerisation. The oils were first stored for 2-4 years to start the polymerisation process, after which a batch of oil was heated above a fire at temperatures close to ignition point just over 300 °C. Usually it was lit before auto-ignition, a practice that changed only from later in the 18th century when oil was heated in closed crucibles. By longer or shorter boiling a more or a less viscous oil-varnish was produced. In inkmaking both viscosities were used in a particular ratio, depending on the required suppleness of the ink and the temperatures in the printshop.

Boiling and burning linseed oil in a cast iron pot on a charcoal fire

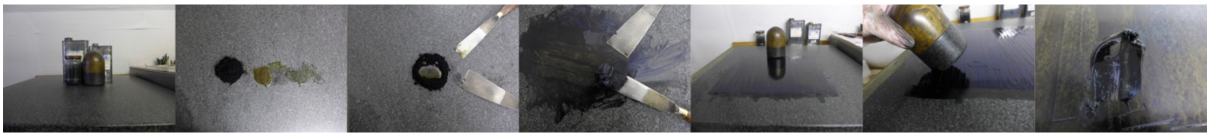
Lampblack retards the drying by oxidation (polymerisation) of the oil-varnish strongly (it may not dry for years), for which reason litharge (tetragonal PbO) was added to the oil in boiling as a drying agent. See also: https://de.wikipedia.org/wiki/Blei(II)-oxid.



red: tetragonal PbO   yellow: orthorhombic PbO

Oil was boiled in copper or iron vessles, other metals were unsuited or not available, yet, in Gutenberg's time. Boiling oil in copper vessles has the disadvantage that green copper compounds form during boiling, which turn the eventual oil-varnish green. Iron vessles may make the oil burn and thereby darken, but by itself does not discolour the oil.

Varnishes and pigment were mixed together to a stiff paste. The paste was further ground with a stone muller on a flat stone. The grinding broke up the pigment conglomerates into smaller particles and took care for encapsulating all particles in oil varnish. The final product, the ink, was of intense colour and very homogeneous in composition.



Reconstruction of the preparation of oil-based printing ink

The mixture of pigment and oil varnish became smoother and more fluid by grinding due to the so-called 'thixotropic effect'. Letting prepared ink stand for a while made it stiff again. The printer would therefore work the ink with a knife or muller to make it more fluid just in advance of printing. Also in printing, the moment pressure was exerted the ink became more fluid briefly, causing it to flow a little off the typeface. This shows as so called 'beaded edges' or 'squash' at the edges of the printed letter.

Any recipes for letterpress printing ink from Gutenberg's period are absent, only some administrative documents related to printshops referring to tools, interior and aquired materials. Ink used by Gutenberg and those of his followers may be compared with oil-based ink recipes for cloth printing during the 15th century.

Analyses

NB1: nearly all examinations concern the analysis of black ink for book printing (letterpress). Mentioning of red or blue ink is indicated.
NB2: the chronological order was chosen to indicate developments in research.

Klaetsch 1940
Hermann Klaetsch, *Die Druckfarbe in vergangenen Zeiten*, Mainz: Halle-Ammendorf, 1940.
§ Other imprint of the same text: Mainz: Gutenberg-Gesellschaft, 1940.
Perhaps the first technical examination of printing ink in incunabula: p. 9 (black ink is soot and oil varnish), p. 32 (red ink is made of vermilion).

Schwab 1983
Richard N. Schwab, (et al.). 'Cyclotron analysis of the ink in the 42-line Bible', *The Papers of the Bibliographical Society of America*, vol. 77 (1983) (Sep.), pp. 285–315.
§ Examination of the Cu/Pb ratios in the black printing ink; see especially p. 301. The authors are uncertain where these elements come from, but the copper (Cu) is presumably from the copper kettle in which the (linseed?) oil was boiled to make oil-varnish, the binding medium of the ink. The lead (Pb) will be from 'litharge' (red, tetragonal PbO), which was the drying agent commonly used in oil-based printing ink over the centuries until the introduction of cobalt driers.
Schwab et al. were working on an extended project analysing leaves with written and printed text 'from the Middle Ages through the incunabula period to the present'; p. 288, see details in note 6. On p. 285 the authors state they 'are at the University of California, Davis (Davis, CA 95616)', which suggests their research results might still be kept there.
Red ink or mercury (for vermilion) is mentioned on p. 293 nt. 9, p. 296 nt. 10, and on p. 302.
Comparisons with results of ink analyses of other incunables on pp. 310–315.

Kusko 1984
B.H. Kusko (et al.), 'Proton Milliprobe Analyses of the Gutenberg Bible', *Nuclear Instruments and Methods in Physics Research Section B: Beam Ineractions with Materials and Atoms*, vol. 3 (1984), nos 1–3 (April/May), pp. 689–694.
§ doi: https://doi.org/10.1016/0168-583X(84)90464-6
Abstract: 'The advent of printing with movable type is properly regarded as the most important technological event in modern cultural history, yet its earliest history is shrouded in mystery. The Davis proton milliprobe has enabled scientists and humanist scholars to collaborate in unlocking the secrets of earliest print, focusing on the contribution of Johannes Gutenberg. The 42-line Gutenberg Bible is not only the first book printed by movable type, it is considered by many to be the finest book every printed.

Unfortunately very little is known about the materials and techniques used in this first large scale printing operation. In October 1982 we had the unprecedented opportunity to examine page-by-page the inks, papers, illuminations and binding of volume I of the Doheny Gutenberg Bible. A similar study of the Lilly New Testament (most of volume II) was undertaken in March 1983. The results, some wholly unexpected and very exciting, add a large new body of information about this great work, and give us new enlightenment on the day-to-day production of this first and most important printed book. Moreover, the discovery of the uniqueness of the ink in Gutenberg's Bible, combined with our ability to taken minutely detailed and non-destructive elemental "fingerprints" with the milliprobe beam of all man-made papers and inks, gives us a weapon that has never been available before to investigate some of the controversial basic questions in the history of the origins of printing technology.'

Schwab 1985

Richard N. Schwab,(et al.), 'New Evidence on the Printing of the Gutenberg Bible: The Inks in the Doheny Copy', *The Papers of the Bibliographical Society of America*, vol. 79 (1985), pp. 375–-410.

§ P. 389: 'the red ink, although rich in mercury, had no lead and virtually no copper in it'.

Schwab 1986

Richard N. Schwab (et al.), 'Ink Patterns in the Gutenberg New Testament: The Proton Milliprobe Analysis of the Lilly Library Copy', *The Papers of the Bibliographical Society of America*, vol. 80 (1986) (third quarter), pp. 305–331.

§ Continued analysis of Cu/Pb ratios on another copy of the Gutenberg Bible confirmed earlier findings.

Schwab 1987a

Richard N. Schwab (et al.), 'The proton milliprobe ink analysis of the Harvard B42, volume II', *The Papers of the Bibliographical Society of America*, vol. 81 (1987) (Dec.), pp. 403–432.

§ Examination of one Gutenberg Bible showed that its printing ink was produced in small batches, with differences in recipe per batch. See the overview of Cu/Pb ratios per leaf in Figure 2.

Pp. 419–420: The agreement of deviation between analysis results of the same pages of two copies of the Gutenberg Bible is thought 'excellent' (but see the comment by *Teigen 1993*). Sometimes new ink of a slightly different recipe was produced during the printing of a single page, otherwise some ink seems to have been left over after the printing of one page and was used for another page. Mixtures of various ink batches seem to have been used occasionally.

Schwab 1987b

Richard N. Schwab, 'An Ersatz Leaf in the Doheny Gutenberg Bible, Volume I', *The Papers of the Bibliographical Society of America*, vol. 81 (1987) (Dec.), pp. 479–485.

§ Discusses a 'replacement setting' (different leaf replacing a removed leaf) of fol. I, 134 with different Cu/Pb ratio from its conjugate leaf fol. I, 133. This replacement is only found in the Doheny copy.

Zahn 1992

P. Zahn, 'Printer's Inks and Papers in Early Incunabula under Synchrotron Light (SYXRF): A Project in Progress', *Gazette du livre medieval*, vol. 21 (1992) (Autumn), pp. 18–29.

§ Description of the organisation of the project, without research results.

Teigen 1993

Philip M. Teigen, 'Concurrent Printing of the Gutenberg Bible and the Proton Milliprobe Analysis of Its Ink', *The Papers of the Bibliographical Society of America* , vol. 87 (1993), No. 4 (Dec.), pp. 437-451.

§ The author discusses the research by *Schwab et al.* (from Davis, CA) above and concludes that his findings 'cannot support the contention of the Davis team that single copies are a firm ground on which to base measurements of the elements in B42's ink. As a result, cautious bibliographers will take a wait-and-see attitude until multiple copies of pages I B42 are examined for copper/lead ratios.'

Mommsen 1996

H. Mommsen (et al.), 'X-ray Fluorescence Analysis with Synchrotron Radiation on the Inks and Papers of Incunabula', *Archaeometry*, vol. 38 (1996) no. 2 (Aug.), pp. 347–357.

§ Compares the compositions of black printing inks in 22 incunabula.

Rosenberg 1998

Achim Rosenberg (et al.), 'Röntgenfluoreszenzanalyse der Druckerschwärzen des Mainzer Catholicon und anderer Frühdrucke mit Synchrotronstrahlung', *Gutenberg Jahrbuch*, vol. 73 (1998), pp. 231–255.

§ Discusses XRF-analyses of the inks in copies of the four editions of the undated *Catholicon* and in ten other incunables, see the list on p. 237. Different Cu/Pb-ratios on different pages of the same volume were found, which made it impossible to say by which printshop(s) and thus when the editions of the *Catholicon* were printed.

Trace elements measured were: Ca, K, Sr, Fe, Cu, Pb, Zn, Mn, Ti, Ni.

Stanley 2018

Ted Stanley, 'Black and blue printing ink analysis by XRF, DRIFTS and Raman spectroscopy of recently discovered Gutenbergian *Ars minor* fragments', *Journal of the American Institute for Conservation*, vol. 57 (2018), issue 4, pp. 203-220 (selectie)

§ Discusses research of the inks of incunabula fragments kept in Princeton, University Library, Department of Rare Books and Special Collections. Results concern the Cu/Pb ratio of black printing ink, indigotin (said to be indigo, but more likely the more common woad produced in Germany) with

lead white in blue printing ink, mercury sulfide (vermilion) in red *drawing* ink, i.e. the fragments do not contain any printed red lettering, only hand-drawn red lettering..
This is the first time results of the analysis (with DRIFTS) of the oily binding medium of medieval printing ink are published, on pp. 9–10: the ink's binding medium is linseed oil with amber resin.

Further references

Livache 1899
Achile Livache, *The Manufacture of Varnishes, Oil Crushing, Refining and Boiling and Kindred Industries [etc.]*, transl. from the French, ext. by John Geddes McIntosh, London: Scott, Greenwood & Co, 1899.
§ Still close to production practices in earlier centuries, but also close enough to our time for us to better understand contemporaneous know-how.

Wiborg 1926
Frank B. Wiborg, *Printing Ink, a History, with a Treatise on Modern Methods of Manufacture and Use*, New York, London: Harper, 1926.
§ First study on historical printing inks.

Ellis 1940
Carleton Ellis, *Printing Inks, Their Chemistry and Technology*, New York: Reinhold, 1940.
§ Basic study on printing ink chemistry and technology.

Apps 1958
E.A. Apps, *Printing Ink Technology*, London: Hill, 1958.
§ 2nd ed.: 1961.
Basic study on printing ink chemistry and technology.

Bloy 1967
Colin H. Bloy, *A History of Printing Ink, Balls and Rollers, 1440–1850*, London: Adams & MacKay, 1967.
§ 2nd impr.: London: The Wynkyn the Worde Society, 1972.
Basic study on historical printing inks.

Winter 1983
John Winter, 'The characterization of pigments based on carbon', *Studies in Conservation*, vol. 28 (1983), pp. 49–66.
§ Figures show the shape of grains of black pigment.

For updated information see *Winter & West FitzHugh 2007*.

Stijnman 2001
Ad Stijnman, 'Oil-based Printing Ink on Paper: Bleeding, Browning, Blanching and Peroxides', *IADA Yearbook 2000*, Göttingen: IADA, 2001, pp. 61–68.
§ Discusses the influences of oil-based printing ink on paper.

Stijnman 2006
Ad Stijnman, 'Iron Gall Inks in History: Ingredients and Production', in *Iron Gall Inks: On Manufacture, Characterisation, Degradation and Stabilisation*, Jana Kolar, Matija Strlič (eds.), Ljubljana: National and University Library, 2006, pp. 25–68.
§ The volume contains the findings and results of the EU-supported InkCor project, concerning the degradation of paper, parchment and textile fabric due to the corrosive action of iron gall ink used in writing and drawing: https://cordis.europa.eu/project/id/EVK4-CT-2001-00049. Iron gall ink mixed with extra gum Arabic has been used to print single woodblocks and blockbooks in Europe during the 15th century, see *Stijnman 2013*.

Winter & West FitzHugh 2007
John Winter and Elizabeth West FitzHugh, 'Pigments Based on Carbon', in *Artists' Pigments: A Handbook of Their History and Characteristics, Volume 4*, Barbara H. Berrie (ed.), Washington: National Gallery of Art; London: Archetype, 2007, pp. 1–37.
§ Figures show the shape of grains of black pigment, cross sections and reflectance spectra.

Stijnman 2013
Ad Stijnman, 'The Colours of Black: Printing Inks for Blockbooks', in *Blockbücher des 15. Jahrhunderts, eine Experimentierphase im frühen Buchdruck: Beiträge der Fachtagung in der Bayerischen Staatsbibliothek München am 16. und 17. Februar 2012*, Bettina Wagner (ed.), Wiesbaden: Harrassowitz, 2013, (Bibliothek und Wissenschaft; 46), pp. 59–80.
§ Printing inks for blockbooks could be water-based mixtures of colourant and vegetable gum, iron gall inks with extra gum Arabic, or oil-based.

Oltrogge 2015
Doris Oltrogge, 'Colour Stamping in the Late Fifteenth and Sixteenth Centuries: Technical Sources and Workshop Practice', in *Printing Colour 1400–1700: History, Techniques, Functions and Receptions*, Ad Stijnman and Elizabeth Savage (eds.), Leiden: Brill, 2015, pp. 51–64.
§ Discusses recipes for black and coloured relief printing inks in 26 manuscripts from the 14th to the 16th century.