Oil-based printing ink on paper

Bleeding, browning, blanching and peroxides

Printing with oil-based ink is known in Europe from the 11th century, when it was used for decorating textile. Printing on paper is done here by the end of the 14th century. Although oil-based inks are usually considered stable, there are phenomena such as bleeding, browning or blanching which are typically related to printing ink on paper. To facilitate a better understanding of the presented phenomena the different printing techniques and their history, the inks, their properties and ingredients are outlined.

Reading this text is possible because the black ink contrasts with the white paper it is printed upon. One can print a text or image upon other materials but not without ink, because this is what makes them visible due to the contrast with their carriers. Other ways to create such a contrast have been sought, such as cutting out letters or blind embossment. With the latter raking light causes the relief to throw a shadow which makes text or image visible. This is occasionally used in printmaking and for visiting cards. Braille lettering enables the blind to read the raised dots.

There are the idiosyncrasies of the several graphic techniques that require certain properties of their inks needed for printing successfully on a carrier. Oil-based printing ink on paper is the subject of this essay, their interrelation giving rise to a number of possible phenomena – like bleeding of the ink or browning of the paper – after printing. The emphasis will be on the printing ink, while the properties of paper are not under discussion here. This essay is limited to books and prints, images and texts on paper printed with an oil-based ink. It is likely that similar phenomena will be visible with other carriers and different kinds of objects.

The little research done regarding printing ink on paper will be sketched first. Thereafter a brief survey of the principal graphic techniques and their history will be given, followed by a description of the properties and ingredients of printing inks. This is to create a better understanding of the phenomena described.

Before continuing, a word on etymology. “Encre” (French), “ink” (English) and “inkt” (Dutch) can mean both the paste-like material used in printing as well as the watery material for writing: they are homonyms. In the context of the present article, the term “ink” is used for the paste-like, oil-based material. “Printing”, in English, means pressing an inked block, stone or plate (a printing form) and a carrier against each other. The more specific meaning of the term is “printing text”, such as a printing press is a press for printing books. The term “printmaking” in English means making prints, i.e. printing images. More specifically it is used for printing works of art, thus not diagrams or reproductions.

Research

Oil-based printing inks have long been thought to be inert. Although discoloration of the pigments is often visible, inks usually are not thought to degrade paper. There are, however, phenomena which should be taken into consideration when studying printing ink on paper (Fig. 1).

Research on browning in prints and printed books was initiated by the Royal Library in The Hague. Thereafter the Central Research Laboratory (merged into the Instituut Collectie Nederland in 1997) in Amsterdam asked the present author to do a literature search on the materials and techniques for printing books with an eye on the possible causes of browning. Several other research projects have been carried out thereafter, such as on bleeding dyes in lithographic inks, the photocatalyst zinc white in printing ink and blanching on woodcuts (Ligterink, Porck, Smit 1989-1; Stijnman 1992; Townsend, Perry 1992; Brown 1994; Hallebeek, Reiland, Stijnman 1998; Schmutzler 1999).

History

Cutting an image, symbol, text into or out of a surface is known from prehistoric times. One step further is to press this matrix into a soft surface, such as Assyrian seals pressed into

1 Browning in printed books related to the text.
clay. However this is not printing in the sense of transporting a colourant in a vehicle from one surface to another, i.e. from plate to carrier. Early, primitive forms of printing can be seen in prehistoric cave paintings. A hand was dipped into paint and pressed against the wall, or an unpainted hand was pressed against the wall and paint sprayed over it making its outline visible, meaning: “I was here, I state that it is as I want it.”

Printing in relief, as we define it, started more or less simultaneously in Central America, China and Egypt about two thousand years ago. Small ceramic, stone or wooden stamps were inked and pressed against textile to decorate it. It was in China that the first images from woodcuts were printed on paper from the 7th century onwards. Western and Southern Europe started printing decoration on textile in the 11th century, when China was already printing text with separate loose ceramic characters. Korea followed in the 14th century with the invention of metal type.

In contrast to Europe, technical developments in Asia did not continue, let alone mechanisation. In Europe the printing of woodcuts on paper started late in the 14th century and engravings in copper plates were printed from about 1430. Printing was done by hand, machines were not yet in use. With the invention of typographic printing from metal type around 1440 came the printing press, followed in 1460 by the roller press for intaglio printing. Both were invented and used in the Rhine area north of Basel. The use of the printing press spread rapidly in the second half of the century, the roller press was slow to follow.

Techniques refined, presses improved and shortly before 1800 new developments started taking place. Metal printing presses came on the market, experiments started with new plate materials like glass and steel, and a totally new printing technique was invented: lithography. The 19th century was full of new inventions. Experiments were made with maybe a thousand new printmaking techniques, mainly incited by the introduction of photography, many of which never came to fruition. Steam power allowed the mechanisation of the printing and lithographic presses. Roller presses were still operated manually due to the properties of the engravings and engravings. Only when new plate making techniques were developed by the turn of the century, it became possible to mechanise their printing also. In 1907 the modern screenprinting technique was patented. This allowed the printing of any kind of subject on any kind of surface.

**Graphic techniques**

Up until the invention of photocopying in the 1930s, and following its wide-spread use (and thereafter of inkjetprinting, laserprinting and the like), four fundamental graphic techniques were in use. These were, in chronological order of usage: stencil, relief, intaglio and planographic printing. With all these methods both texts and images may be printed.

All methods for creating a printing form were manual or mechanical before 1840. In the preceding decades several photographic techniques had been invented and in 1839 the patent for the Daguerreotype made public. From then on many attempts were made to incorporate photography into printmaking, the so-called photomechanical techniques. Success came after 1850. Printing methods, nevertheless, basically remained the same.

With stencil printing, either an object is laid onto a surface and ink spread around it, leaving the surface underneath the object blank, or else, an image is cut out of sheet material and the ink squeezed through, leaving the surrounding area blank. Techniques used are: stencilling, pochoir, screenprinting. Any kind of medium may be and has been used for stencil printing, but usually they were and are water-based. Water-based inks will not be dealt with here, nor the resin-based inks which have been used widely for screenprinting.

When an image is drawn on a block or plate, and the areas around the image are cut out, the resulting relief can be inked, leaving the cut out parts white. This inked relief and a carrier are pressed against each other and thereby the print is created. Techniques used are: woodcut, typographic printing, woodengraving, autotype.

Cutting or etching an image into a plate is called in English an intaglio technique (derived from the Italian “intagliare”). The plate is inked and the ink removed from the surface in such a way that the ink is left in the grooves. Plate and carrier are pressed against each other, the paper is pressed into the grooves against the ink and thereby the print created. Techniques used are: engraving, etching, mezzotint, dry point, helio-engraving (Fig. 2).

Treating a stone or metal plate chemically without creating a relief of some sort, causes the image to be on the same level as its surrounding whites. Therefore it is called planographic printing. The inked surface and a carrier are pressed against each other and thereby the print is created. Techniques used are: lithography, photolithography, offset printing.

Each printing technique requires its own type of press and its own manner of printing. The inks for the different techniques are alike only in the sense that they are usually oil-based. They cannot be interchanged just like that. On the
contrary, specific inks are manufactured for every different plate or block as will be seen below.

**Printing ink**

Oil-based printing ink consists of a binder, the varnish, ground with a colourant. Varnish is vegetable oil, usually linseed oil, heated for a certain time to make it more viscous. Resin, soap, extender, drier and toner may be added to modify the ink. The essential properties of the printing ink itself are determined by the mixture of several varnishes with dry pigments in certain ratios. Driers, extenders and toners — added in the preparation of the varnish or the ink — refine the ink’s properties. All these will be dealt with below in more detail.

**Essential properties**

The oldest varnish recipe we know is in Theophilus’ manuscript from the first quarter of the 12th century. This varnish is meant as a transparent lacquer to cover paint layers on wood (Theophilus 1979: 28–29; Theophilus 1999: 20–21, 66–67). Theophilus heats linseed oil until boiling and adds resin. It was during this time that textile printing from woodblocks began in Europe, but only in the late 14th century Cennino Cennini describes its production technique, giving the oldest known recipes for printing ink (Cennini 1954: 58–59, 115–118). Both authors give basic recipes from which the inks for the different kinds of printing techniques have been developed.

Ink for printing from metal type on paper, for instance, has higher demands than ink for printing woodcuts on textile. It is important that the ink adheres to the metal in a smooth and thin — while at the same time as opaque — as possible layer which offsets easily again onto the paper. In printing the ink may not pick, the matter may not be filled with ink and the ink should not dry on the surface of the type. It should dry on the paper directly after the sheet comes from the press. Therefore it always contains driers which accelerate oxidation of the varnish. When drying the ink should harden completely without starting to powder, offset or bleed giving rise to halos around the text.

Different requirements are needed for intaglio printing ink. Its viscosity is lower than for relief printing. The ink should be opaque, should dry but not too fast, should offset easily from the grooves of the plate onto the paper. Wiping the ink from the plate should be fairly easy, but without drying onto the plate, the pigment particles scratching the surface, or the ink being wiped from the grooves. When the ink is dry, it should harden completely without the ink starting to powder, offset or bleed giving halos around the imagery. Black intaglio inks contain no or just a little drier, coloured inks do.

For lithographic ink the most viscous varnish is used compared to other printing techniques. Also the ink has a high pigment : varnish ratio. This allows for printing extremely thin but still opaque layers of ink on the paper. The blacks contain no drier, coloured inks do. The black inks harden only slowly, but also should not bleed, offset or powder. More important is that lithographic ink should not contain a constituent that could dissolve in water, since the printing is done from dampened stones of plates.

**Preparation**

Formerly, in preparing his ink the printer considered the structure of the image or text he had to print and accordingly chose his varnishes, pigments and extenders. He mixed the dry and the fluid materials separately and added the varnish to the pigment in a certain ratio. The materials were mixed together and then thoroughly ground until all the dry particles were encapsulated in the medium. This is printing ink. Nowadays mixing and grinding is done by machines and the printer buys his ink ready-made, although he might admix some varnish or extender.

**Oil & varnish**

Varnish is a drying vegetable oil boiled and burned at temperatures starting at 250 °C to 400 °C for periods ranging from a few minutes to several hours. In the process unsaturated fatty acids oxidize and polymerise, making longer chains together with crosslinks. The temperatures at which the oil is boiled, together with the time of boiling, determine the viscosity of the final product. Additives like resins or soap modify this. A varnish with a lower viscosity gives an easier flow to the ink whereas a varnish with a higher viscosity dries faster, to mention only a couple of characteristics.

Linseed oil has always been and still is the common oil for varnish. Other vegetable oils have been used too, like walnut-oil (expensive, but discolours less than linseed-oil) and rape-oil (cheap, but with bad drying properties). Trane-oil, from whales, is mentioned in the 17th century. It was cheap, but since it does not dry it will create halos in the paper. Mineral oil came into use late in the 19th century and had preference after 1950. Nowadays the properties of vegetable oils are appreciated again.

**Resin & soap**

For relief printing colophony resin, or sometimes other kinds of resin, is always added to increase viscosity and adherence to the type metal. For some kinds of lithographic ink varnishes with resin added are used. Their increased viscosity prevents emulsifying of the ink in the printing process.

Soap was boiled with the oil from the late 18th century onwards, starting in England. It reduces the viscosity of the relief printing ink and thereby its tack, which prevents picking. Cleaning the form after printing is easier.

**Driers & extenders**

Driers are needed in relief printing ink because lampblack, the only suitable pigment for this type of ink, acts as a retarder. In colour printing several layers of ink are printed next to each other. Driers are added here, because usually there is not enough drying time available. Driers catalyse oxidation of the unsaturated fatty acids in the varnish. Before 1800 recipes...
always mention to boil lead oxides with the varnish, which oxides form chemical compounds with the oil and the resin when boiled together. These compounds are the catalysts, the actual driers. In the course of the 19th century other driers were found, such as cobalt and manganese compounds. From then on driers are not boiled with the varnish anymore, but added in the preparation of the ink.

In recipes for black intaglio ink no driers are mentioned before 1900. For colours they may be needed, depending on the colour printing technique and the colourants used, as some pigments have a drying effect. Black lithographic ink needs no drier, even though it is occasionally mentioned. The layers of ink on the paper are extremely thin and most of the varnish bleeds into the paper, which prevents offsetting. Driers are used in coloured inks.

Extenders are white inorganic solids, which are (semi-) transparent. This means they can be added to the ink without influencing its actual colour. They can have such properties as giving body to the ink, reducing the colour strength, facilitating wiping or preventing bleeding.

**Blacks & toners**

Only lamp-black – the finer variation of carbon black is called “gas-black” – is suited for relief and lithographic ink. It was used already by Johann Gutenberg for his typographic experiments. Lamp-black has the highest opacity of all pigments, while its particle size is very small. It therefore allows very thin layers of ink. The earliest reference to the use of lamp-black only for printing ink is found in 1555 (Alessio 1555: 189): “L’inchiostro poi da stampar lettere si fa di solo fume di ragia” [= The ink for printing letters should be made with smoke from resin only]. There follows a short description on the preparation of the varnish and the ink. In the 20th century a number of other fine grained black pigments came on the market, but carbon blacks are still most used. A small quantity of blue pigment may be added in grinding the ink. It acts as a toner, making the black optically blacker or neutralising a certain brownish hue caused by the varnish.

Concerning intaglio printing a somewhat coarser-grained pigment is needed. Before printing the plate is completely covered with ink and then wiped. With very fine pigments, such as lamp-black, the surface cannot be cleaned without constantly dragging ink from the grooves. A coarser grain prevents this. The classical pigment for intaglio ink is Frankfurt black, commonly made by combustion of lees of white wine. Mentioned frequently from 1600 onwards it disappears from the market around 1900. Other suitable blacks are made from charred vine tendrils, kernels, bones and other organic matter. All black pigments of organic origin should be calcinated or washed with lye to remove bituminous matter, which may bleed from the ink after printing and thereby stain the paper.

Toners may be added to the black inks. Toners are colourants that give the black a blueish or brownish hue. They give the ink a warmer or cooler appearance depending on the kind of image wanted and the habits of the printer. Blue is usually mentioned, sometimes green and in the 19th century brown, red and even orange. Lamp-black may be added to intaglio ink for an intenser black and a greater opacity.

**Colours**

In principle all colourants used in oil painting may be used for coloured printing inks. The pigments should have a fairly small particle size to prevent damaging the printing plate or metal type in inking. Precipitated dyes or lakes may also be used. The pigments with the finest grains should be used for relief and planographic printing, and somewhat coarser grained pigments for intaglio printing. Colourants for lithographic ink should not dissolve in water.

**Suppliers**

Making an ink proper to its purpose is a difficult and slow task. Professional inkmakers are already known from the 16th century onwards in France and England and the oldest printing ink company was founded by William Blackwell in London in 1754. Most printshops, however, had a specialised inkmaker or they bought their ink from another printer. An example is the Haarlem printer Isaac van Wesbusch, who advertised his printing ink on 17 February 1671 (Wesbusch 1671: verso): “Men laet by desen allen Boeck-drucke- ren weten, dat Isaac van Wesbusch, Boeckdrucker te Haerlem in de korte Zijl-straat, maect en verkoop extraordinaire har- den en weeken Druck-Inct, welcke heeft eenen schoonen glants, en is seer wel droogende, oock ongemeen gesuyvert van de vettighyte der Olye; soo dat deselve, natuerlijk getem- pert, en het Swartsel daer wel in gewreven zijnde, gants geen noot heeft van oversetten of geel deurslaen.” “Have a can brought and you can buy as much as you like.” [= One hereby notifies all book printers, that Isaac van Wesbusch, book printer at Haarlem in the Korte Zijl-straat, makes and sells extraordinary strong and weak printing ink, which has a beautiful shine, and dries very good, is also exceptionally well purified from the greasiness of the oil; because it is heated properly, and the blacking is ground well into it, it does not offset nor bleed yellowish.]
needed. It partly takes care of the “drying” of the ink and causes a better adherence to the paper. “Drying” means that the layer of ink only feels drier, because it contains less medium, but in fact the varnish has oxidized and polymerised only a little. Ball-point ink also dries in the same way.

Bleeding shows through halos around the ink deposit. The shape of the halos may tell something about the viscosity of the binding medium and its components, for example, a low viscous oil will seep faster and deeper into the paper and spreads wider than a thick oil varnish. Shortly after printing halos are colourless but when seen against the light the paper around the ink is transparent. In time the halo will turn yellowish or greenish to a golden tinge and finally becomes dark brown. Book printers added driers to their varnish to accelerate drying. Nowadays extenders are added to prevent halos.

It is calculated that in printing with a handpress, before 1800, 200 to 220 sheets per hour could be printed on one side (Pollak 1972: 218-264; Stijnman 1992: 23-24). This means that it took printers 18 seconds or less to print a sheet of paper on one side. These printed sheets were piled up and not interleaved. After printing one side of all the sheets, the other side was printed. It was not intended that the text on the recto side should offset on the verso side of the next sheet, this should stay blank. This means that the surface of the first printed sheet should dry in the 18 seconds it took for printing the second sheet, and so on.

In intaglio printing an interleaving with Seidenpapier to prevent offsetting is first described in 1805 (Schwarz 1805: 94-95). Before that, as in typographic printing the sheets were piled up after printing. Driers were not used, or at least not commonly in intaglio ink. Printing an etching or engraving takes one minute or longer, depending on the size of the plate, the quality of the impression required (portraits were printed with the utmost care), the qualities of the ink (particle size, viscosity of the ink), and the kind of wiping. In general, it is dependent on the care a printer takes with the plates. Again, driers are not mentioned before the 20th century and therefore offsetting is not an uncommon phenomenon in intaglio printing. So too is bleeding of the ink, especially because intaglio ink is less viscous than typographic ink. The amount of bleeding is also related to the amount of surface sizing on the paper and the depth of the etched or engraved grooves. The deeper they are, the more ink they will contain and the higher the chances are for varnish running into the paper due to the thick ink deposit. This is contrary to stencil, relief and planographic printing where the layer of ink is always of the same thickness.

With lithography bleeding is hardly or not at all observed. This is probably due to the extreme stiffness of the ink because of the high viscosity of the varnish and the high amount of pigment. Other reasons are that lithographs are preferably printed on a thicker kind of paper and the layers of ink are extremely thin.

Up to the 1970s screenprinting was done with oil-based inks. The thick, continuous layers of ink cause similar problems as in oil painting on paper (Townsend, Perry 1992: 129-132).

Degrading, powdering, bleeding & discolouring pigments

Some pigments in the inks may have a degrading effect on the ink and on the paper (causing browning), even though not much is reported on this matter. While the blacks have no effect, some colours may, such as copper acetate (verdigris) or zinc oxide (zinc white). The former because of the corrosive effect copper has on paper, the latter because of its photocatalytic properties. Photochemical effects may include deterioration of the binder, whereby the ink is degraded by the zinc oxide itself. It may also promote the composition of peroxides from the varnish, which in turn may degrade the paper of the prints and/or the cardboard onto which the print is mounted (Daniels 1990: 236-243; Hallebeek, Reißland, Stijnman 1998; Whitmore, Bailie 1990: 144-149).

The whole idea behind printing ink is that all pigment particles are completely encapsulated in the varnish and will stay there. Excessive bleeding might remove too much
medium from the ink, laying bare a certain amount of pigment. This causes powdering of the ink, a phenomenon known to printers, and prevented by thorough grinding and the use of more viscous varnishes. Sometimes, as in printing helio-engravings, thin varnishes must be used for best results. These varnishes are so thin that most of it will seep into the paper. In the course of time the dried ink layers will start to powder.

Pigments used in planographic inks should not dissolve in water, because in the printing process the stone or plate is dampened. The bleeding of pigments is observed though (Brown 1994).

A number of pigments – and most dyes – discolor due to light or chemical effects. The varnish itself yellows. These reactions do not seem to affect the paper.

**Anastatic impressions**

A phenomenon which should be taken into serious consideration is the degradation of paper at the wet/dry interface between the ink, or its halo of varnish, and the paper. This process takes place both laterally and vertically. “Laterally” is within the sheet at the sides of the ink deposit. “Vertically” is underneath the ink deposit, and to the sheets touching above and below. This is visible in books with printed texts and images, in books in which prints have been mounted on blank sheets, and in cardboard onto which prints are mounted.

Fig. 4 a shows what may be called an anastatic impression of the back of the print which was mounted on this board. A print, an impression of an engraving of the portrait of Paulus de Vos after Antony van Dyck (Fig. 4 b), was mounted on the cardboard. There was no mat and the print was kept in a stack of similar mounts. Over the course of time the cardboard started to discolor (it turned brown) where there was ink in the adhering print above. Similarly browning must have taken place in the next mount touching this van Dyck print. Comparable kinds of degradation are visible in printed books (see fig. 1).

The possible explanation behind this phenomenon is that there is a constant transport of water vapour through the sheet itself and through the pile or book. Ink may be considered as a kind of plastic: it is hydrophobic and no water gets through it. This causes three dimensional accumulations of minute amounts of water around the ink deposit, where migration is halted, with the possibility of local condensation and as a consequence degradation in the longterm at the wet/dry interface (Ligterink, Porck, Smit 1989: 225-233; Hofenk de Graaff 1994: 21-42; Dupont 1996: 1-21; see also the following).

**Drying oil films, water & peroxides**

After printing it takes several hours to a few days before the ink is dry enough for the printed sheets to leave the printshop. It may take two years or longer before the ink is completely oxidized and polymerised. Fatty acids dry through oxidative polymerisation. In chemical terms the reaction progresses as described here: “Oxygen adds at a double bond in an unconjugated chain to form a biradical. This reacts with another unsaturated chain to give a conjugated chain. Farmer and Sutton isolated an olate hydroperoxide from partially oxidized oleic esters. Conjugation increases with rise in peroxide content. These hydroperoxides are unstable and readily undergo dehydration. These steps correspond to the taking up of appreciable [amounts of] oxygen by the film followed by some water being evolved; one to two moles of water are liberated per mole of oil ester during drying.” (Apps 1958: 293; compare with Townshend, Perry 1992: 130). In conclusion it can be stated that during the drying process of the oil film water as well as peroxides are formed. The amount of water released in the drying process depends on the amount of oil.
present on the paper - but in general only minute amounts are formed.

Apps (1958: 29) further states that "It is known that printed pamphlets can cause fogging of photographic plates, and this has been traced to peroxides present to some extent in dry vegetable-oil films.". This shows that peroxides are not only formed during the drying process, but can also be formed later on as a result of oxidative degradation of the dried oil film.

Some of these peroxides are volatile and can migrate and react promoting oxidation on any organic material (e.g. mounting papers, contact leaves) in the immediate surroundings of the oil film.

Blanching deposits & white mould

A phenomenon observed by Ruth Schmutzler with prints is blanching, also known as blooming: the (black) ink is covered with a white veil of fine crystals (Fig. 5). This is caused by the bleeding and following crystallization of free fatty acids from ink layers; blanching is better studied with oil-paintings. It is observed on thick deposits of ink, the ink being manufactured with excessive amounts of varnish of low viscosity or maybe even unboiled oil. It should go together with halos (Schmutzler 1999; Skaliks 2000). Blanching should not be confused with white mould growing on the size in the paper or on size used in chine collé; the difference between crystals and moulds is easily seen under high magnification.

Discussion

The second part of this essay merely mentions phenomena related to printed images and texts and their interaction. It is difficult to give causes for them let alone remedies. More will be found and hopefully more research will be carried out to gain a better understanding of these phenomena.

Acknowledgements

Thanks to Agnes Gräfin Ballestrem and Judith Hofenk de Graaff for stimulating and supporting my research in historical printing inks and their effects over the past twelve years. Thanks to Frank Ligterink, Jaap Mosk, Luiz Pedersoli and Birgit Reißland for editing the text and giving comment on the chemical backgrounds of the different phenomena. Thanks to Fiona McKinnon for correction of the English spelling.

Literature


---

5 Detail of a woodcut showing blanchin,. Photo courtesy by Ruth Schmutzler.

Author

Ad Stijnman, trained as an artist and librarian, afterwards studying codicology and paleography, professional printmaker and printhistorian, employed at the Instituut Collectie Nederland where he does research into art technological sources related to conservation research. Ad Stijnman, Instituut Collectie Nederland, Postbox 76709, 1070 KA Amsterdam, The Netherlands. Tel. +31-20-3054738, ad.stijnman@icn.nl
Even Johan Gutenberg’s printing inks have been blends of air-drying oils and natural resins. With the development of the chemical industry parallel the diversification of printing technologies, more and more synthetic, petro-chemical products have been used in the formulation of printing inks. Organic pigments petro-chemical resins and petrochemical solvents have been developed to satisfy the demands of modern inks and progressive printing technologies.