

The Chemistry of Historically Important Black Inks, Paints and Dyes

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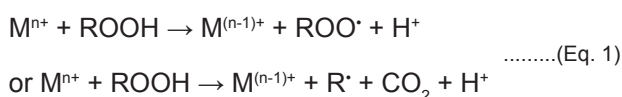
Before the advent of synthetic colourants, inks were based on two substances, carbon black and the iron-gall complex. The more ancient carbon black ink, sometimes known as “Indian ink”, was first used in China and Egypt 5000 years ago. The iron gall inks have been used, particularly in the west, for over 1000 years. These colourants were also extensively used as paints (in a suitable gum or fatty acid oil) and dyes (in aqueous solution).

Carbon Black Ink

This ink consists of finely divided carbon or soot particles suspended in a water-soluble binding agent such as a polysaccharide gum (Mitchell, 1937). As such, it can be classed as a water-colour paint. The carbon black was produced by burning resinous woods that contained large amounts of terpenes (saturated hydrocarbons). In a limited supply of oxygen, terpenes burn with a sooty flame, being reduced to carbon (charcoal) as well as some partly reduced, saturated and aromatic hydrocarbons such as retene (Mill & White, 1994) – (see structure 3, Fig. 1). The solid black material or soot produced, known as carbon black, was ground to a fine powder and suspended in a water-soluble natural polymer such as a gum or sometimes gelatin (collagen). These polymers gel and solidify, as the water evaporates (Mill & White, 1994) and this binds the carbon particles together on the substrate to which the ink is applied. Retenes and related aromatics present in the pigment are not chemically inert and can be expected to absorb ultraviolet light and become chemically active producing free radical species that can attack polysaccharide bindings and thereby compromise the adhesion of carbon black inks to the substrate surface. The ink is most satisfactorily applied with a brush and it is still used in the Far East in calligraphy. Carbon black ink often comes in the form of the solid cake containing the gum binder to which water is added and mixed with the brush. One of the disadvantages of carbon black ink is that it is unsuited to use with a quill or nib pen because the carbon deposits and quickly clogs these writing instruments. Also, the carbon particles settle out if the ink is in a liquid form and must be regularly stirred to re-suspend the particles. Because it is not physically or chemically bound to the surface of the substrate, a further disadvantage

of carbon black ink is that it is not water-fast and is prone to being rubbed off.

Carbon black pigment was also widely used as an oil paint, and much favoured in various schools of European art for its lustrous and translucent finish, e.g., Rubens and Van Dyck (Mill & White, 1994). The carbon black, that contains aromatics such as retene as a result of the way it was produced, was suspended in an unsaturated “drying” oil. These drying oils are polyunsaturated fatty acids of generic formula 2 (see Fig. 1) that polymerize to a solid by free radical chain reactions and still are the basis of Western easel painting. The best known and oldest of these is linseed oil, extracted from the seed of the linen plant, and it was used by the ancient Egyptians. Other drying oils that have been used were from the poppy seed and the walnut. However, the solidification (“drying”) of the paint is inhibited by the presence of the retene aromatics because they act as free radical scavengers that interfere with the polymerisation of the oil. To accelerate the drying of these paints small quantities of lead or other metal oxides were sometimes added to accelerate the polymerization of the oil vehicle by generating additional free radicals as shown in Eq.1. Such metal salts were known as siccatives.

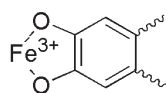


The pigments and paints used by Maori before European contact were similar to those used by other cultures. Their black paint, like that just described, was made from soot collected on the leaves of harakeke from burning resinous woods such as rimu and mixing with shark liver oil or weka oil (Beattie, 1918). This paint was used from the Archaic Maori period in rock art on the walls of limestone shelters in the South Island dating from as early as the 15th century.

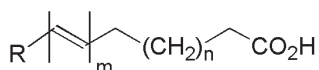
Iron-Gall Inks

The black colourant of iron gall ink is a ferric-tannate charge-transfer complex formed between iron(III) and catechol groups of tannins as shown in structure 1 (Fig. 1). The essential ingredients of this type of ink are iron, commonly in the form of ferrous

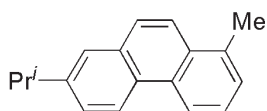
sulphate that is oxidised in air to the ferric valence state, and a tannin polyphenolic. Polyphenolics are found in many plants and their catecholic and/or gallic functional chemical groups bind strongly with ferric iron to form a dark black coloured complex as shown in structure 1 (Fig. 1). One of the richest sources of tannins that has been used in the production of these inks is gall nuts from various species of oak. These gall nuts are produced by the tree as a protective response to its invasion by certain insects such as the wasp of the *Cynipidae* family (Krekel, 1999). Alternatively, the barks of many trees are a useful source of tannins. There are many sources for the iron used in the manufacture of these inks the most common of which is ferrous sulfate, confusingly also called copperas in old recipes. Ferrous sulphate mineral deposits exist throughout the world and it is present dissolved in water that has trickled through such deposits (Krekel, 1999; Daniels, 2000). Iron gall inks also often contain some water-soluble polysaccharide binding agent to control the fluidity, the absorption of the liquid ink into the fibrous substrate and inhibit the deposition of solid iron-tannate material.



1, Irongall
black ink/dye



2, generic formula for
drying oils



3, retene

Fig. 1: Structural formulae

Freshly prepared ink, when first applied to paper, is very pale because the ferrous ion complex with tannin is a very weak absorber of light. The black colour of the ink slowly intensifies with time as the ferrous ions are oxidised to ferric ions in air with the consequent formation of the highly light-absorbing ferric ion-tannin complex. Once formed, the black complex is tightly bound to the fibre and is insoluble in water which confers the desirable waterproof and "permanent" properties to this ink.

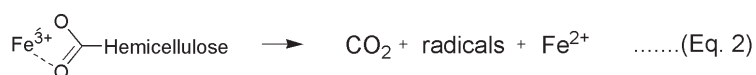
The same black iron-tannate colourant also has a very long history of use as a dye. A number of cultures have independently discovered the same type of black dyestuff based upon an iron-tannin complex, although the source of iron and tannin differed depending on the local materials. The ancient

Egyptians used it on papyrus and linen. It was used extensively both as a dye and as ink on wool, cotton, linen, paper and parchment in Europe for many centuries; it was used to write Magna Carta. It was used as a dye in Mali, in South America, by Maori and throughout Polynesia. However, when it has been applied to paper or textile fibres, it slowly degrades the underlying substrate eventually causing it to disintegrate. Not only is there a loss of mechanical strength and flexibility but the ink/dye also fades (Te Kanawa, Thomsen, & Smith, 2002). The mechanism of this degradation is not fully understood and there has been much research directed towards elucidating this chemistry in order to find ways of arresting it, or at least slowing it down. It has been established that the deterioration of the fibre involves water and oxygen, and it is accelerated by acid (Daniels, 1999a). As ageing and degradation proceed, the substrate evolves acetic acid and this further exacerbates degradation (Smith, Te Kanawa, Miller, & Fenton, 2005).

Gum Arabic is a widely used binder in iron gall inks. This gum is the polysaccharide, arabinose, which has a high content of carboxylic acid groups that are subject to hydrolysis and the formation of acidic products which will contribute to the degradation of the ink (Mills, 1994). It is interesting to note that when iron-tannate inks were used on parchment - animal skin that has been treated with lime - the substrate degradation and fading of the ink is significantly reduced, e.g., Magna Carta. Presumably, acids produced during degradation are neutralized by lime residues from the production of parchment process. Present day paper conservators have been experimenting with weak alkaline reagents such as magnesium bicarbonate and calcium carbonate to neutralise the acid formed during ageing of fibres containing hemicelluloses present in paper (Daniels, 1999b).

We have found that accelerated thermal ageing of black-dyed *Phormium tenax* fibres results in the evolution of carbon dioxide that is linked to the degradation of the fibre. We believe that excess iron(III) in the dyed material is complexed (or bound) to carboxylic acid groups associated with the hemicellulose component of the fibre and that these decarboxylate with the formation of CO₂ and reactive free radicals (Eq. 2). The radicals can cleave the cellulosic polymer backbone resulting in its fragmentation and a consequent loss of the mechanical integrity of the fibre (More, Smith, Te Kanawa, & Miller, 2003).

Some of the free radicals produced, such as peroxy radicals, are highly reactive and can abstract a hydrogen atom from a molecule to produce hydrogen



peroxide and more free radicals thereby propagating a chain reaction. One strategy to avoid this degradative chemistry has been to ensure there is an excess of tannin to scavenge surplus iron(III) that would otherwise bind to the carboxylic acid groups of the hemicellulose. This approach is very effective and slows the degradation of black fibres. Furthermore, it has the advantage that it does not involve the introduction of any materials that are foreign to the traditional ink (More, Smith, Te Kanawa, & Miller, 2003).

However, such careful adjustment of the amount of tannin relative to the ferric ion content is difficult to achieve in practise. A similar strategy to preserving iron-tannate inks has been employed by conservators at the Netherlands Institute for Cultural Heritage. They have used salts of phytic acid, polyphosphates, to complex and scavenge excess iron(III) that could otherwise initiate degradative decarboxylation reactions in the fibrous substrate (Neevel, 1995).

Another problem with the iron-gall ink alluded to above is the latent period associated with the aerial oxidation of ferrous to ferric ions during which the freshly applied ink has poor legibility. To overcome this deficiency, early in the 19th century, iron-gall inks were manufactured containing a 'provisional' natural dye to provide initial colour to the ink. The first such dyes used were logwood extracted from the tree *Haematoxylum campechianum* or from Brazilwood, *Caesalpinia echinata* (Karnes, retrieved 10 Feb 2009). However, these dyes have poor stability and fade when exposed to light. In mediaeval times, the problem of the degradation of textile fibres by black iron-tannin dye was well recognized and prompted the Doge of Venice to ban its use to dye wool (Cardon, 2007). However, it was later found that pretreatment of cloth with indigo provided some stabilization of the black-dyed fibres and an act of the English Parliament in 1581 required dyers to dye a *ground* of indigo on wool cloth before the application of iron-tannate dye (Francis & Griffith, 1846). In Germany, as far back as the late 18th century, mention is made of an iron-tannate ink containing indigo as a provisional colourant (Mitchell, 1937). The English poet, John Clare, wrote in 1832 that he had produced his own iron-tannate ink containing indigo (Grainger, 1983). Perhaps what prompted Clare to use this dyestuff was that it was produced from woad which was extensively grown as an alternative-to-food crop in his home county of Northamptonshire in England, (Thirsk, 1997). Parenthetically, Clare bit-

terly lamented woad's cultivation as a lucrative crop for producing indigo dye. It destroyed the fertility of the land and the extraction of indigo from the plant is one of the most nauseating of occupations¹. It was largely confined to the rural workhouses in England of the day, where the poor subsisted in makeshift buildings under miserable conditions.

The shattered workhouse of the parish poor
And towards the north wind opes the creaking door
A makeshift shed for misery no thought
Urged plans for comfort when the work was wrought
No garden spot was left dull to cheer
And make the calls for hunger less severe
With wholesome herbs that summers might supply
Twas not contrived to live but dye

The Parish (l. 1790 – 1797)
(Clare, 1985)

The inclusion of indigo in iron-gall ink improves the stability of the ink. Like the catechol and gallo moieties of tannin, indigo forms a strong complex with iron(II) and iron(III) (Larkworthy & Nyholm, 1959). It removes iron ions bound to the carboxylates associated with the hemicellulose component of the paper fibres and, consequently the degradation that would otherwise result from decarboxylation. There are also indications that indigo may be a good scavenger of damaging free radicals because oil paints containing this pigment are notoriously slow to dry (van Eikema Hommes, 2004) – a process that requires free radical-mediated polymerization of the oil vehicle. However, Clare used his indigo-containing ink to write on paper home-made from birch bark (Grainger, 1983). Although this paper is very white, it has an extremely high content of a pectic acid, 4-*O*-methylglucuronoxylan, a characteristic of trees of the *Betula* family (Mian & Timell, 1960), and is therefore subject to extensive hydrolytic deacetylation accompanied by the release of acetic acid that catalyses the degradation of the ink. Indeed, the smell of vinegar has been reported from Clare's manuscripts and the ink is badly degraded (Robinson, 1996). In this case the acetic acid produced by the degradation of the paper substrate appears to have negated the stabilizing activity of the indigo.

Stephens was granted a patent for *blue-black* ink in 1834, an ink containing an indigo additive and started manufacture of this ink in the mid 1830s (Carvalho,

1904; Nickell, 2005). Because of its “permanent” quality it was required by the British government for use in all legal documents and ships’ logbooks and it is even used today.

Recipes to make iron gall ink are given by Karnes (retrieved 2009).

Notes

¹ (www.youtube.com/watch?v=xznmDBG1S8&feature=related : go to 5 minute, 10 second point of the video clip and www.youtube.com/watch?v=ftH9k6htQPI&feature=related)

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