Teacher and Technician Sheet

In this practical students will:

- Learn and use key terms, such as, **suspension, reaction, pigment, opacity** and **tack.**
- Create and use their own inks.
- Evaluate the effects of various factors on: the ease of use; opacity; drying time and pH of their inks.

Please note: this experiment will take at least 7 days to complete.

Introduction:

(The topic could start with a group discussion during which teachers introduce the following ideas, especially the words in bold. It is important to realise this practical takes at least 7 days to complete so might be worth considering as a demonstration or for use in a science club setting.)

We all use ink nowadays mostly in the form of a ballpoint pen. In times past, the user would dip a stick or feather with a nib cut or stuck on it into an ink and write. There are **medieval** (5^{th} to 15^{th} century) miniatures showing the Devil attempting to steal precious ink from St. John of Patmos. These demonstrate the importance of ink to the monks.

During the medieval period, two kinds of ink were used. The earliest ink, from around 2500 BCE, was black **carbon ink**. This was a **suspension** of carbon, water and gum. Later, from around 3^{rd} century CE, brown iron-gall ink was used. This was obtained from **oak galls**. Gum arabic is added to keep the **insoluble** solids in **suspension**.

The reaction that produced the ink was known about in Roman times. The Roman writer **Pliny the Elder** (23–79 CE) described in his *Naturalis Historia (Natural History)*, an experiment describing how to distinguish *verdigris,* copper(II) ethanoate $[Cu(CH_3COO)_2.2Cu(OH)_2]$, used to process leather, from the cheaper *copperas,* iron(II) sulfate ($FeSO_4.7H_2O$) with which it was often adulterated.

Pliny did not know the chemistry of the **reaction** but, he described the process so chemists can recognise the reaction. Chemists now know the reaction between the **iron(II) cation** (ferrous) and gallotannic acid found in iron-gall ink. **Analysis** of the Dead Sea Scrolls ink has shown evidence of iron-gall ink so although it was not a common ink until 200 CE the ink material had been used.

Modern ink is more complicated. It contains many ingredients. The coloured substance is the **pigment** and the liquid is known as the '**vehicle**'. These include substances that keep the **acidity** around neutral, known as pH modifiers. There are **humectants** that slow down the drying, resins to help binding and flow, defoamer/antifoaming agents to control the foaming of the ink, wetting agents to control surface properties, biocides to stop the growth of fungi and bacteria, and thickeners to control ink application.

The pigment is what gives the ink its colour and depth known as the **opacity**. However, when the inks are exposed to long periods of sunlight, especially bright sun, or strong heat the colour of the ink will change over time or fade this is known as the **permanence** of colour. Another important thing with an ink is the stickiness or flow known as **tack**. Too sticky and the ink will not flow with the nib onto the paper.

When carbon ink was used on the early **parchments** it would rub off because the surface is not absorbent, but the addition of gum arabic helped the ink to stick. The later iron-gall ink burnt into the surface by reacting with the **collagen** in the parchment. This however proved to be a problem because the ink was corrosive and over time burnt through the parchment. Nowadays many libraries have to carry out conservation to save the books.

Carbon ink worked well on **papyrus** because it is absorbed into the surface of papyrus where it dries and remains. Iron-gall ink when used on papyrus also reacts with the chemicals of the papyrus. This time it is reacting with the **cellulose** in the papyrus. However, again this reaction of the chemicals in iron-gall with the writing materials is also a problem since it burns the paper.

The iron-gall ink was used by people such as **Leonardo da Vinci**; Bach; Rembrandt and Van Gogh.

The recipe below is based upon one listed by **Pietro Canepario**, a Venetian, in his *De atramentis cuiuscumque generis* (***All Kinds of Ink*; 1619**).

(It is good to get the students to investigate the different types of galls that could be found on trees like the oak or cypress. It is advisable not to mix the different galls then they can investigate the different ink colours and the criteria for the best type of ink such as flow, rate and coverage.)

(This practical can be done with pupils working in groups of two. Groups of two allows for good discussion between the pupils. Teachers can use the questions set as the stimulus for discussion and the answers can be used as a group report, article, presentation, poster or talk.)

Curriculum range:

Suitable for middle and lower secondary schools and if the chemistry is considered upper secondary; it links with:

- asking questions and developing a line of enquiry based on observations of the real world, alongside prior knowledge and experience;
- using appropriate techniques, apparatus, and materials during fieldwork and laboratory work, paying attention to health and safety;
- making and recording observations and measurements using a range of methods for different investigations; and evaluating the reliability of methods and suggest possible improvements;

- presenting observations and data using appropriate methods, including tables and graphs;
- interpreting observations and data, including identifying patterns and using observations, measurements and data to draw conclusions;
- presenting reasoned explanations, including explaining data in relation to predictions and hypotheses;
- the concept of a pure substance; and
- mixtures, including dissolving.

Hazard warnings:

Iron(II) sulfate is harmful if swallowed (Acute toxin Cat 4, oral) and is a Skin/Eye Irritant (Cat 2)

Iron(II) sulphate solution is IRRITANT

Wear a mouth mask to prevent breathing in any of the dust of the galls since they can contain fungal spores

The water can be provided hand hot from the tap and should not present a hazard assuming the expected levels of behaviour.

Tannic acid is an eye irritant (Cat 2)

Gum Arabic is generally of low hazard but may be a skin/eye irritant (Cat 2). It may also be a skin/respiratory sensitizer. (Check with the safety data sheet.) This is still the case at the concentration found in the ink – so gloves are sensible.

Equipment:

Wear safety glasses. Wear disposable gloves.

For a group of 2 students:

- 90 g of dry oak galls
- 400 cm^3 of water
- 60 g of iron(II) sulfate
- 30 g of gum arabic
- 2 mouth masks
- 1 mortar and pestle
- 1 beaker (600 cm^3)
- 1 measuring cylinder (500 cm^3)
- 1 sheet of card to cover the 600 cm^3 beaker top
- 1 sheet of coarse filter paper
- 1 stirring rod

- 1 pen and pen nib
- 1 sheet of white paper

Alternatively, if using tealeaves instead of oak galls:

- Dry black tealeaves (could be labelled as 'Oak Galls substitute')
- Pestle and mortar
- 1 beaker (250 cm^3)
- 1 beaker (100 cm^3)
- Stirring rod
- 1 measuring cylinder (100 cm^3)
- Distilled water
- Iron(II) sulfate (HARMFUL and IRRITANT)
- Gum arabic (or craft glue)
- Plastic pipette
- Spatula
- Weighing boat
- Watch glass (or cover for the beaker)
- Filter paper
- Filter funnel
- 1 conical flask (100 cm^3) (if keeping, use a dark glass conical flask with a bung)
- Universal indicator paper and colour chart

Access to:

Straws

Scissors

A4 paper

Digital balance

Paper towelling

Disposable gloves

Blotting paper

Hot water

Technical notes:

Tealeaves can be substituted for oak galls for this practical.

Each group will need the equivalent amount of tealeaves that are contained in two teabags.

Iron(II) sulfate is HARMFUL at 0.9 M or above and .IRRITANT at 0.37 M and above

The solid is HARMFUL but the method above should produce an initial solution that is less than 0.5 M- however this will become more concentrated over the 3 days.

Tannic acid could be used instead of tealeaves, particularly for KS5.

Results:

The ink produced is easy to write with because of the added stabiliser.

The dark ink visibly deepens in colour within seconds of being on the paper.

It takes a short amount of time to dry, which could be decreased by using blotting paper, and has not faded in a week of exposure to bright light.

Testing the ink with universal indicator paper shows that it is strongly acidic (pH 2-3).

Students should be able to use the method above within the lesson time and achieve good results.

The hazards are minimal assuming the expected level of behaviour from students.

Going further

Keep your writing samples and examine them after several days. Did their appearances change? If so, what do you think caused the changes?

Find illustrations in art books showing drawings made by Leonardo da Vinci and describe the appearance of the lines he drew with iron–gall ink. How does iron(III) tannate pigment change over long periods? How would you explain this colour?