Teacher and Technician Sheet

In this practical students will:

- Write messages with a variety of substances which can be used as invisible inks.
- Change the conditions of the invisible inks to see if messages become visible.
- Use their scientific knowledge to explain how changing the conditions the inks are under affects their visibility.

Introduction for teachers:

(This topic could start with a group discussion or a short story woven around the facts given below, during which the teacher introduces the ideas especially the words in bold. This is a fun activity but does have some real chemistry behind it. However, for younger children probably the best are the heat-stimulated inks.)

Invisible ink is any substance that you can use to write a message that is invisible until the ink is revealed. Anyone can write an invisible message, assuming you have paper, because body fluids can be used as invisible ink.

Invisible ink has a history that goes back in time. Ovid (43 BCE-17/18 CE), a Roman poet wrote in his *Ars Amatoria* in 18BCE:

> "Characters written in fresh milk are a well-known means of secret communication. Touch them with a little powdered charcoal and you will read them."

At the other extreme, Mary, Queen of Scots (1542-1587), used invisible ink and ciphers to communicate with Catholic supporters. Her supporters wrote to her using two common substances: alum (hydrated potassium aluminium sulfate) or gall ink (tannic acid from parasitic wasps in oak trees galls). The alum letters would be developed by soaking the letter in water, and the gall ink would be developed by soaking the letter in iron sulfate solution.

During times of secret love, war or in the world of spies in the cold war, **high security** is important and there is often the need for invisible ink with which a message can be written, be invisible, and when it reaches the recipient be brought back so it can be seen.

During **World War II** the **Special Operations Executive** (SOE) were a group of secret agents operating behind enemy lines. This meant they had to operate without being detected. Hence, messages were often passed using invisible ink. In their training manual the following **properties** of an 'ideal' invisible ink were identified.

1. It needs to **mix with water** so it can be widely used.
2. **Non-volatile**, i.e. no pronounced smell to the ink.
3. Must not **deposit crystals** on the writing paper, i.e. not easily seen in glancing light.
4. Be invisible under **ultraviolet light**.

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5. Does not **decompose** or **discolour** the paper, as with photo paper using silver nitrate.
6. **Non-reactive** with iodine, or with any of the other usual developers.
7. Potential **developer**s for the ink should be as few as possible.
8. Should not develop under **heat**.
9. Easily obtainable and has at least one plausible innocent use by the holder.
10. Not a compound of several chemicals.

SOE agents were trained not to risk their lives so they used invisible inks as a back-up method of **communication** when other, more secure communication techniques were unavailable. The agency supplied special inks to its field agents. When agents were forced to improvise, they were advised to **dilute** their invisible ink as much as possible to reduce chances of detection.

The properties identified by the SOE could be discussed by students as to why they are important criteria for an invisible ink.

The students will enjoy the practical activity and the explanation is best given after they have results they can talk about. If they work in groups using different inks to write questions they can pass those messages to another group who can develop the message and send the answer to the question back.

A good way of recording this work is to get the pupils to write a story involving the ink they have used for their experiment.

Curriculum range:

All ages can take part in this activity but at different levels since the aim is to gain some understanding of the thinking of the scientist and artist with regard to the properties of materials. It links with:

- setting up simple practical enquiries, comparative and fair tests;
- reporting on findings from enquiries and observations, including oral and written explanations, displays or presentations of results and conclusions;
- using straightforward scientific evidence to answer questions or to support their findings;
- comparing and grouping together everyday materials on the basis of their properties such as solubility and transparency;
- knowing that some materials will react to produce a visible product;

- building a more systematic understanding of those types of materials by exploring and comparing the properties of a broad range of materials;
- asking questions and develop a line of enquiry based on observations of the real world, alongside prior knowledge and experience;
- using appropriate techniques, apparatus, and materials during laboratory work, paying attention to health and safety;
- making and recording observations and evaluate the reliability of methods and suggest possible improvements;
- presenting observations using appropriate methods;
- interpret observations, identifying patterns to draw conclusions;
- presenting reasoned explanations, including explaining data in relation to predictions and hypotheses;
- the concept of a chemical change, oxidation, pH and decomposition; and
- knowing about the idea of a chemical change, mixture and solution, including dissolving.

Hazard warnings:

Students should wear eye protection and disposable gloves.

Supervision may be necessary when the students are using the heating equipment.

Ammonia is TOXIC

Concentrated ammonia is CORROSIVE & DANGEROUS FOR THE ENVIRONMENT

Suggest not using. Ammonia gas is TOXIC. Ammonia concentrate is CORROSIVE & DANGEROUS FOR THE ENVIRONMENT. This would need a very well ventilated room and student behaviour assessment also CLEAPSS advises a maximum of 2M for Year 7.

Sodium carbonate (solid) is IRRITANT

Phenolphthalein is HIGHLY FLAMMABLE & HARMFUL

Thymolphthalein is HIGHLY FLAMMABLE & HARMFUL

Copper (II) sulphate (solid) is HARMFUL & DANGEROUS FOR THE ENVIRONMENT

Lead (II) nitrate is TOXIC & DANGEROUS FOR THE ENVIRONMENT.

Iron sulphate (solid) is HARMFUL

Sodium sulphide is CORROSIVE & DANGEROUS FOR THE ENVIRONMENT

Cobalt chloride is TOXIC & DANGEROUS FOR THE ENVIRONMENT

Iodine is HARMFUL (will stain skin but is low hazard at 0.1M)

Iodine solution should not be present with Ammonia solution. An explosive mixture can be formed.

Potassium ferricyanide should not be present with Ammonia because an explosive mixture can be formed. It should also not be present where concentrated acid could be added because it would produce TOXIC gases.

Potassium ferricyanide & phenolphthalein should not be used where there are naked flames (do not use Bunsen burners).

Some of the metal compounds such as copper, cobalt, and lead can be toxic in varying quantities and can be an irritant if the liquid is spilt or put on the skin.

Ultra-violet light can be harmful to eyes so pupils should be supervised when handling the lamp or they can observe as an adult uses the lamp. Portable counterfeit money detectors can be used for this and are easily sourced and reasonably priced.

Use one of the methods below to write a question on a piece of white paper. Pass the message to another group who will develop your message and then write an answer to the question and pass it back to you to develop. It would be good to use different types of ink as advised by your teacher.

Heat-Activated Invisible Inks:

These inks are best for younger children since most of the chemicals are household and generally less hazardous. They can be developed by heat generally ironing them with a hot iron or placing them in an oven or (on a white tile) on a hotplate.

Equipment:

Any of the following:

- Any acidic fruit juice (e.g. lemon, apple or orange juice)
- Onion juice
- Baking soda (sodium bicarbonate) solution or 1 M sodium hydrogen carbonate
- Vinegar or 1 M ethanoic acid
- Dilute cola
- Diluted honey
- Milk
- Soapy water or 0.1 M sodium carbonate hydrated

- Sucrose (table sugar) solution (1 tsp in 10 cm^3 water)
- Iron or oven at 230 °C or hotplate
- Hairdryer
- A4 paper or filter paper
- Paintbrushes (and/or straws, cotton buds, spills)
- White tiles (For using on the hotplate. The tiles heat up but protect the paper from burning)

Inks Developed by Chemical Reactions:

These are best used with secondary students and most could be used comfortably with lower secondary students. Many of them work as pH indicators, so paint or spray a suspected message with a base (e.g. sodium carbonate solution) or an acid (e.g. lemon juice). Some of these inks will also reveal their message when heated (e.g. vinegar). The substances in milk weaken the paper and may be more susceptible to heat than the paper, so although the message dries clear, the paper weakens and darkens where the milk was applied.

Equipment:

Any of the following:

- Phenolphthalein (pH indicator) HIGHLY FLAMMABLE & HARMFUL, developed by sodium carbonate (Solid is IRRITANT – solution is LOW HAZARD) (or another base). Suggest not using. Ammonia gas is TOXIC. Ammonia concentrate is CORROSIVE & DANGEROUS FOR THE ENVIRONMENT. This would need a very well ventilated room and student behaviour assessment also CLEAPSS advises a maximum of 2M for Year 7.
- thymolphthalein HIGHLY FLAMMABLE & HARMFUL, developed by sodium carbonate (Solid is IRRITANT – solution is LOW HAZARD) (or another base)
- vinegar or 1 M (ethanoic) acetic acid, developed by red cabbage water
- ammonia (1 M ammonium hydroxide) , developed by red cabbage water
- 1 M sodium hydrogen carbonate, sodium bicarbonate (baking soda), developed by grape juice
- 1 M sodium chloride (table salt), developed by 0.1 M silver nitrate
- 1 M copper sulfate, developed by sodium iodide, sodium carbonate, or 1 M ammonium hydroxide
- 0.005 M lead (II) nitrate, developed by 1 M sodium iodide (Lead (II) nitrate is TOXIC at = > 0.01M and HARMFUL in solutions less than this.)

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- 1 M iron sulfate IRRITANT, developed by 0.1 M sodium carbonate
- 1% starch solution (e.g. corn starch or potato starch), developed by 0.1 M iodine solution
- Lemon juice, developed by 0.1 M iodine solution
- Hairdryer
- A4 paper or filter paper
- Paintbrushes (and/or straws, cotton buds)

Inks Developed by Ultraviolet Light (Black Light):

These can be used with younger children but the chemistry is more complex so the theory is best left to secondary age students. Most of the inks that become visible when you shine an ultra violet light on them also would become visible if you heat the paper.

Equipment:

Any of the following:

- dilute laundry detergent (the bluing agent glows) or 1 M sodium carbonate hydrated (Lead (II) nitrate is TOXIC at => 0.0 M and HARMFUL in solutions less than this.)
- tonic water (quinine glows)
- vitamin B-12 dissolved in vinegar
- Hairdryer
- A4 paper or filter paper
- Paintbrushes (and/or straws, cotton buds)

Technical notes:

Because of the wide range of materials, teachers should select either a few of the materials or group students to allow a wider range of materials to be investigated. If using groups then sufficient time needs to be allowed for whole class reporting on the results and evaluation of the materials being used.

Provide solutions of solids if preferred. Solutions made of one spatula measure or teaspoon mixed with 10 cm^3 of water is sufficient.

The discussion can be approached using the Special Operatives Executive (SOE) properties for 'ideal' invisible ink as the evaluation criteria.

The invisible ink could be dried with a hairdryer or on a warm radiator initially.

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The hotplate can be used on a low heat without the white tile, but it will have to be supervised as the paper could burn. It is safer to use a white tile on the hotplate to place the paper onto. It takes about 20–30 seconds on average on a low to medium heat setting for the message to appear. This means that a class practical could be carried out using a hotplate without congestion.

The oven method takes longer and there is less control over when to discontinue heating.

There is more control over the chemicals if paintbrushes, etc. are used instead of spray bottles.

Results:

After writing, the message should not be visible either by inclining the paper and using oblique incident light or seeing any residue on the surface of the paper.

When developed the message should be visible and readable so students should be able to inform others of the message. The message is given to another group who develops the message and reports to the group on what the message said.

Good results can be obtained from the heat method on milk, sodium hydrogen carbonate solution, vinegar (ethanoic acid), sugar solution and soapy water (sodium carbonate solution).

The following work well from the chemical reaction method, copper sulphate and ammonium hydroxide, copper sulphate and sodium carbonate, phenolphthalein and sodium carbonate.

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