Invisible Inks With Household Ingredients: Mechanisms and Properties

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Abstract

Invisible inks — colorless substances usable for writing that can be turned to color using a chemical process — have both practical value in covert communications and educational value in chemistry teaching. Publicly available invisible ink recipes are numerous and varied, but are often published without any elaboration as to their utility and usability. This paper evaluates approximately a dozen different invisible ink recipes, with focus on those that can be prepared from common household ingredients. Safety, cost, availability, shelf-life, and difficulty of use of the different invisible inks are considered. Based on this evaluation, a general recommendation is made in favor of heat-based inks for casual covert communications and chemistry education, and precipitation-based inks for more secure covert communications and chemistry education in a lab setting.

Additionally, two proposed mechanisms for action of invisible inks based on organic acids and revealed by heating are evaluated. Oxidation of ink by heat is confirmed to play a role in revealing such inks.

1 Introduction

Parents want to know about the activities of their children; generals want to know about the activities of their troops. Throughout human history, on scale from personal to international, knowledge has been a key ingredient in power.

In struggle to establish and maintain power, people often desire to communicate covertly and intercept others' covert communications. As a result, numerous technological advances have been developed primarily to deal with covert communication — both to enable it, and to intercept it. Recorded accounts of such technology go as far back as 1500 BCE[1], and touch nearly every scientific discipline, including mathematics[2], computer science[3], quantum physics[4], and chemistry[5].

In the realm of chemistry, a popular technique for covert communication — seen in science education[6], intelligence operations[5], and mass-market fiction[7] — are invisible inks.

An invisible ink is any substance that can be used for writing (typically on paper) and is not easily detected by the naked eye. The process of rendering the ink visible (ideally by the intended recipient) is known as developing the ink; the apparatus or substance used to develop the ink is the developer.

This paper reviews several substances that can be used as invisible inks, as well as their corresponding developers, with focus on those that can be manufactured from common household products and other readily available reagents.

1.1 Classification of inks by mechanism of action and development

Many ink/developer pairs share the same underlying chemical mechanism of action (on writing surface) and development. Such related pairs are often similar to each other on several of the evaluation criteria. It is, therefore, convenient to group their evaluation by mechanism.

Mechanisms present among the inks and developers evaluated in this paper include:

Sugar solutions developed by heat

Substances containing sugars (such as honey solution and sugar solution) can be developed by heating. When applied to paper and then heated, these solutions turn brown[8].

The reaction responsible for this change of color is presumably caramelization (a non-enzymic reaction that results in browning of sugars[9]).

Organic acids developed by heat

Substances containing organic acids (such as citric acid in lemon juice) can be developed by heating. When applied to paper and then heated, these inks turn brown[10].

The mechanism of action and development is unclear; two different possibilities are commonly cited — that the organic acid itself browns with heating[11,12], and that the acid reacts with the polymers of the paper, converting them into compounds that brown on exposure to heat[13,14].

Acids and bases developed by a pH indicator

pH indicators are substances whose color changes on exposure to acidic or basic solutions. Specifically, an indicator exists as two species, Ind_1 and Ind_2^-, of which one can be obtained by protonation of the other:

$$Ind_1 \rightleftharpoons Ind_2^- + \mathrm{H}^+$$

and those two species have different colors because their different bond and electronic structures result in their having different absorption spectra in visible frequencies of light.

When Ind_1 is exposed to an acidic or basic environment, the equilibrium concentrations of Ind_1 and Ind_2^- depend on the pH of the environment, and therefore so does the color of the mixture of Ind_1 and Ind_2^-.[15]

Substances containing acids or bases (such as citric acid or ammonia) can be used as invisible inks and developed by exposing them to a suitable pH indicator.

To develop a pH-based invisible ink, a pH indicator in aqueous solution is applied both to the marked regions of the writing surface and the unmarked ones. The indicator has to be chosen so that the ink produces a different indicator color than the unmarked writing surface does, which depends both on pH of the ink and the pH of the writing surface.

Inorganic salts developed by a precipitation reaction

Water-soluble salts can be developed using a precipitation reaction, if the salt solution is colorless and a colored precipitate can be produced.

The ink, containing an ion (Ion_I) in aqueous solution is applied to a writing surface and allowed to dry. To develop the ink, aqueous solution of a different ion (Ion_D) is applied to the writing surface. If the two ions combine into a salt ($Salt_P$) that has low solubility in water and forms a colored precipitate:

$$Ion_I + Ion_D \longrightarrow Salt_P\downarrow$$

then the appearance of colored precipitate of $Salt_P$ on the writing surface makes the writing visible.

2 Methods

2.1 Ink Evaluation

Inks and developers were assessed on the following criteria:

Availability

Availability of a reagent is determined to be "common" if it is readily available from common brick-and-mortar and internet stores, such as grocery stores; and "specialty" if it is only available from specialty stores, such as gardening stores.

Cost

Except where otherwise specified, cost is based on retail prices during the week of Jan 20–26 2001 at Walgreens and Stop and Shop in Malden, MA.

Preparation

Preparation is classified as "simple" if it involves nothing beyond mixing with water at room temperature, "medium" if common household processes, such as boiling water, are required, and "difficult" if specialized equipment (other than safety equipment) is required.

Shelf-life

Shelf-life was estimated based on prior experience with household products in question, assuming that the ink is not kept refrigerated.

Safety

Risks of inks and developers were determined and summarized by the following standard[16,17] risk phrases:

- R 8: Contact with combustible material may cause fire.
- R 20: Harmful by inhalation.
- R 20/22: Harmful by inhalation and if swallowed.
- R 22: Harmful if swallowed.
- R 23/25: Toxic by inhalation and if swallowed.
- R 25: Toxic if swallowed.
- R 36/37: Irritating to eyes and respiratory system.
- R 36/38: Irritating to eyes and skin.
- R 36/37/38: Irritating to eyes, respiratory system and skin.
- R 37/38: Irritating to respiratory system and skin.
- R 41: Risk of serious damage to eyes.
- R 46: May cause heritable genetic damage.
- R 62: Possible risk of impaired fertility.

Contrast

Contrast of the writing was classified as "high" if an ink yielded strokes with high contrast against the background, "low" if the strokes had low contrast against the background, and "invisible" if strokes were completely invisible.

Stroke width

Stroke width of the writing was classified as "broad" if only broad strokes (applied with a cotton swab) were discernible, and "thin" if thin strokes (applied with a nib pen) were discernible.

Sharpness

Sharpness of the writing was classified as "sharp" if strokes of ink with food dye were not visibly distorted or blurred by developing, and "blurred" if they were blurred by developing.

2.2 Choice of inks and developers

In order to be useful for development of pH-based inks, pH indicators have to be available in aqueous solution. Common aqueous laboratory indicators (such as phenolphthalein and methyl red) are deemed unsafe for consumer products in various world regions[18], and therefore are typically only available in specialized stores, such as online lab supply stores. They are toxic, often carcinogenic, and irritants, as well as being relatively expensive. Such developers were not evaluated.

A viable alternative to these is preparation of aqueous solution of flavin, an anthocyanin present in red cabbage[19]. Red cabbage is commonly and cheaply available in brick-and-mortar stores. An extract of flavin from red cabbage can be prepared with a simple stovetop process. Its shelf life is unknown, and it is not hazardous beyond risks involved with boiling water on a stove.

Numerous ionic compounds exist that participate in precipitation reactions and therefore could be used as invisible inks, but many of them are not readily available in consumer products due to their toxicity (such as copper(II) sulfate and potassium ferricyanide); they can typically only be obtained from specialty online stores. Similarly, numerous ionic compounds exist that can be used as invisible ink developers, but are also often hazardous, expensive, and difficult to obtain.

Such inks and developers (only available from laboratory supply stores) were not evaluated.

The following invisible inks were used:

- White vinegar (Stop & Shop™ Distilled White Vinegar, UPC 688267045745)
- Clear Ammonia, diluted to 5 % by H_2O (Walgreens Clear Ammonia, UPC 049022352773)
- Baking soda, 10 g dissolved in 300 ml H_2O (Guaranteed Value™ Baking Soda, UPC 688267067570)
- Starch, 10 g dissolved in 50 ml H_2O (Stop & Shop™ 100% Pure Corn Starch, UPC 688267070365)
- Sugar, 10 g dissolved in 100 ml H_2O (Domino® Premium Granulated Pure Cane Sugar, UPC 049200045701)
- Honey, diluted to 20 % by H_2O (Gunter's Pure Honey, UPC 021273100129)
- White onion water (filtrate of 50 g chopped jumbo white onion boiled in 500 mL H_2O)
- Lemon juice, diluted to 20 % by H_2O (Sicilia Lemon Juice, UPC 030849000053)
- Milk, diluted to 20 % by H_2O (Hood® Fat Free Milk, UPC 044100169250)

along with the following developers:

- pH indicator: Red cabbage water (filtrate of 170 g chopped red cabbage boiled in 500 mL H_2O; Stop & Shop® Fresh Red Cabbage, UPC 02112041383)
- Iodine: Iodine tincture diluted to 5 % by H_2O (Swan Iodine Tincture, UPC 30869385110)
- Heat: 20 min in a kitchen oven heated to 200 °C

Each ink was applied to a piece of acid-free paper of brightness 92 and weight 20 lb four times:

- Using a cotton swab dipped in ink
- Using a nib pen dipped in ink
- Using a cotton swab dipped in ink with food coloring added
- Using a nib pen dipped in ink with food coloring added

Developing a dyed ink allowed for the shape of the writing to be compared before and after development, to ascertain how well a given developer preserves strokes. Comparison of cotton swab application and nib pen application allows determination of how well different strokes are preserved.

Food coloring used was McCormick Red Food Color (UPC unknown).

2.3 Investigation of heat-based development of inks based on organic acids

To investigate two proposed mechanisms for heat-based development of inks based on organic acids, aqueous inks in a glass container were treated by heat under conditions identical to those used to develop them on paper. Because one of the proposed mechanisms requires a chemical reaction with paper, if it were the only mechanism of heat-based development of these inks, inks heated in absence of paper would not undergo the same color change.

3 Results

3.1 Mechanism of heat-based development of inks based on organic acids

Inks based on milk and lemon juice, when applied to paper and heated in an oven at 200 °C, browned in 10–20 min.

When the same inks were heated under the same conditions in a glass dish, they browned in a similar time period.

3.2 Evaluation of inks developed by pH indicator

Reagents for pH-based inks (such as vinegar and ammonia) are typically readily and cheaply available in common brick-and-mortar stores. Inks are quick and easy to prepare, and do not spoil due to their pH. Inks and reagents, by virtue of being acidic or basic, are often toxic and irritants.

See Table 1 for detailed evaluation of ph-based inks.

3.3 Evaluation of inks developed by precipitation

All precipitation-based invisible inks are difficult to obtain; none were directly evaluated.

See Table 2 for partial evaluation of precipitation-based inks available in specialty stores.

3.4 Evaluation of other inks developed by liquid developer

One other ink developed by liquid developer was evaluated; see Table 3.

3.5 Evaluation of inks developed by heat

Reagents for sugar-based inks (sugar or honey) are readily and cheaply available in common brick-and-mortar stores. Inks are quick and easy to prepare, but will spoil within 1-2 weeks, as the sugars are a growth medium for bacteria, fungi, molds, and yeast. Inks and ink reagents are safe in quantities likely to be encountered in household production of invisible ink, except for risks associated with inhalation of powdered sugar, and risks of inhalation and ingestion of spoiled ink.

Reagents for pH-based inks (such as vinegar and lemon juic) are readily and cheaply available in common brick-and-mortar stores. Inks are quick and easy to prepare, and generally keep better than sugar-based inks. Ink and reagents are often irritants.

Heat-based development of invisible inks can be performed using an incandescent or halogen bulb, an oven, or an iron. All of these can cause burns if handled improperly. All of them also run the risk of igniting the paper in the process of ink development, which is likely to cause bodily harm, as well as destroy the secret message.

Detailed evaluation of heat-developed inks is listed in Table 4.

	Reagent	**white vinegar**	**ammonia**	**baking soda**
Ink	**Active ingredient**	CH_3COOH	NH_4OH	$NaHCO_3$
	Availability	common	common	common
	Cost	0.002 USD/ml	0.001 USD/ml	0.002 USD/g
	Preparation	simple	simple	simple
	Shelf-life	indefinite	indefinite	indefinite
	Safety	R 20/22, R 36	R 36/37/38	R 36/37/38
Developer	**Reagent**	**red cabbage extract**		
	Active ingredient	flavin		
	Availability	common		
	Cost	0.004 USD/mL		
	Preparation	medium		
	Shelf-life	unknown		
	Safety	unknown		
Legibility	**Contrast**	Low	Invisible	Low
	Stroke width	Broad	—	Broad
	Sharpness	Blurred	—	Blurred

Table 1: Evaluation of inks developed by pH indicator

Ink	**Reagent**	**algicides**[a]	**copperas**[b]
	Active ingredient	$CuSO_4$	$FeSO_4$
	Availability	specialty	specialty
	Cost	0.013 USD/g	0.002 USD/g
	Shelf-life	indefinite	indefinite
	Safety	R 25, R 36/37	R 36/38, R 23/25
Developer	**Reagent**	**washing soda**[c]	
	Active ingredient	Na_2CO_3	
	Precipitate formed	$CuCO_3$	$FeCO_3$
	Availability	common	
	Cost	0.002 USD/g	
	Preparation	simple	
	Shelf-life	indefinite	
	Safety	R 20/22, R 37/38, R 41	

[a] Such as Crystal Blue Copper Sulfate Smart Crystals, UPC unknown; cost estimate based on June 24 2011 price on `amazon.com`

[b] Such as Hi Yield Copperas Iron Sulfate, UPC unknown; cost estimate based on June 24 2011 price on `marshallgrain.com`

[c] Such as Arm & Hammer® All Natural Super Washing Soda, UPC 033200030201

Table 2: Evaluation of inks developed by precipitation

Ink	**Reagent**	**starch**
	Active ingredient	starch
	Availability	common
	Cost	0.002 USD/g
	Shelf-life	indefinite
	Safety	R 36/37
Developer	**Reagent**	**iodine tincture**
	Active ingredient	I^-, I_3^-
	Availability	common
	Cost	0.13 USD/ml
	Preparation	simple
	Shelf-life	indefinite
	Safety	R 22, R 36/38, R 46, R 62
Legibility	**Contrast**	Invisible
	Stroke width	—
	Sharpness	—

Table 3: Evaluation of inks developed by other liquid developer

Ink	**Reagent**	**sugar**	**honey**	**lemon juice**	**onion juice**	**milk**
	Active ingredient	sugars	sugars	unknown	unknown	unknown
	Availability	common	common	common	common	common
	Cost	0.012 USD/g	0.012 USD/g	0.008 USD/ml	0.002 USD/ml	0.002 USD/ml
	Preparation	simple	simple	simple	medium	simple
	Shelf-life	weeks	weeks	months	months	days
	Safety	R 20	R 20	R 36/37		R 20
Developer	**Safety**	R 8	R 8	R 8	R 8	R 8
Legibility	**Contrast**	High	High	Low	Low	Low
	Stroke width	Thin	Thin	Thin	Thin	Thin
	Sharpness	Sharp	Sharp	Sharp	Sharp	Sharp

Table 4: Evaluation of inks developed by heat

4 Conclusions

4.1 Mechanism of development of inks based on organic acids

Inks based on organic acids, when treated by heat, brown in absence of paper; therefore, a possible reaction of the acids with the paper is not the only source of browning (although such a reaction may be present); inks' oxidation by heat contributes to the change of color.

4.2 Ink recommendations

Readily available inks and developers were found to be so cheap that cost is unlikely to be a concern for any except iodine.

Overall, precipitation-based invisible inks are the most difficult to obtain of those evaluated. Given that other ink/developer pairs exist that are safe, legible, and readily accessible, precipitation-based invisible inks are unlikely to hold much practical value in most applications. However, as some of these inks can only be developed by a small number of uncommon developers, they might be preferable in situations in which it is important for the covert communications to be resistant to attempts to reveal them by trying several common developers.

Another value of precipitation-based inks is in chemistry education, where they can be used to associate basic concepts of general chemistry (substitution reactions and precipitation) with a practical application (although one of limited use).

Inks developed by iodine are safe and readily available, but iodine stains skin, is toxic, and is less readily available than the inks. Overall, these inks are less convenient to use than pH-based or heat-based inks.

Educationally, iodine-developed inks can be interesting as a way of demonstrating important chemical concepts, such as starch-iodine reaction used in redox titration of iodine.

pH-based invisible inks are readily available, have a long shelf-life, and are often safe. The only readily available aqueous pH indicator (flavin) is safe and easy to prepare; its shelf-life was not evaluated. However, revealing the writing requires concentrations of the ink and the developer to be matched, so as to produce a change in indicator color. (For example, when ammonia ink and baking soda ink were developed using a particular flavin solution, only baking soda yielded visible strokes.) Furthermore, because the developer in aqueous solution has to be applied to the paper, strokes of invisible ink are blurred. As a result, only thick strokes of invisible inks were typically legible when developed by flavin.

Overall, this makes pH-based ink inconvenient to use, and unsuitable for applications that require fine strokes. They do, however, provide a practical demonstration of well-understood chemistry (acids, bases, and pH), and are therefore useful in education.

Heat-based development is readily available in many cases, and although potentially hazardous, the hazards can be mitigated by using a uniform and controlled heat source (such as a conventional oven, as opposed to a candle light or an incandescent bulb). The inks it can be used on are safe and common, but many have limited shelf-life. The development process preserves thin strokes very well. Thin strokes make detection of covert communications harder, because they distort the writing surface much less than broad strokes; therefore, heat-based inks are a good choice for covert writing, but would not be suitable where an adversary is expecting covert communications and therefore likely to try common developers such as heat.

Mechanisms involved in heat-based development of inks are either poorly understood or chemically complex, and therefore provide a simple demonstration of chemistry that cannot be explained simply. A heat-based invisible ink demonstration might be useful for getting someone interested in science, but curiosity about the details of the underlying chemistry is likely to go unsatisfied.

5 Further research

While red cabbage extract is a popular household source of flavin, there are others (such as grapes). To make an appropriate recommendation among the different sources of flavin, the extracts should be prepared and their properties evaluated.

None of the precipitation-based inks were readily available, but it is possible that some of them can be manufactured from common ingredients using other chemical processes. This was not considered for this paper, but if true would make it possible to create more secure inks from household ingredients.

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