

## A BRIEF REVIEW ON INVISIBLE INK: IT'S VARIOUS TYPES AND EXAMINATION METHODS

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### ABSTRACT:

The analysis of ink in forensic examination has come up as a great challenge. There are a number of techniques and processes available for ink forgeries. Some of them are tricky but routinely practiced to commit crimes related to deeds, bills, cheques, will, contracts and certain other financial documents. Invisible ink or magic ink is one of the modern technology widely used for committing financial forgeries. It is of two types, erasable ink and disappearing ink. Disappearing ink fades away without leaving any trace after few hours upon exposure to CO<sub>2</sub> (any other acid) in the air. Another type of ink is erasable ink which can be easily removed by certain rubbers incorporated in each pen. The present review represents the type, nature and different properties of invisible ink. Different techniques used to decipher these invisible inks are mentioned.

**Keywords:** Invisible ink, erasable ink, disappearing ink, magic ink, forensic science, ink analysis

### INTRODUCTION:

With the increase in literacy, shrinking job opportunities, globalization of the economy and access to superior technology, white collar crimes have increased dramatically. Increasing Research and Development in various fields of science has led to a increase in more advanced technology which results in both positive as well as negative applications(1). Banks are one of the most common and easy target for a forger where the entire banking system is based on physical documents. Criminals cheat banks with false identification, bank instruments, fabricated or altered cheques and stolen financial information. It is observed that most of the bank frauds cost millions of rupees and losses are mounting day by day(2). Other financial related crimes like those related to deeds, will, contracts, bills, and various other documents are also increasing.

It has been observed that criminals are continuously using and developing new *modus operandi* using new advanced technology to cheat different organization and individual victims(1). Erasable and disappearing ink, a.k.a. magic inks are among the latest techniques used by criminals in committing different forgeries. Development and advancement of new research and technology has enhanced the availability of different types of pen with magic ink which are being used by criminals for forgery. Vanishing ink/invisible ink are the type of

ink which are prepared by special chemical reactions. Invisible ink pens, commonly called as magic pens looks like other normal ink pen, but there ink composition differs from other pens. They enter the country through illegal means and are available at very cheap price which attracts the common people. Auto-vanishing fluid inks are available in the local market which makes them accessible to local people and raises a great deal of concern.

It has been revealed in literature review that there are mainly two types of ink that are used to prepare invisible ink pens - (i) Thymolphthalein based (disappearing ink), (ii) Thermochromic based ink (thermal erasable ink) (2). Recent years have witnessed that these inks are being used in legal documents which results in heavy loss to the third party because these inks leave no sign of chemical or physical alteration or deletion on the document. For example, suppose a promissory note signed by a normal regular ink but the details like amount are filled by a disappearing ink. After the disappearance of vanishing ink, a different regular ink pen can be used to fill a different amount, causing a fraud(12).

Ink in general is a composition of pigments or dyes along with additives to bring about desired physical properties. Today, a variety of ink composition is available consisting of different combination of organic, inorganic and synthetic material with different characteristics and properties.(14)

### DISAPPEARING INK:

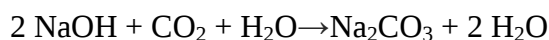
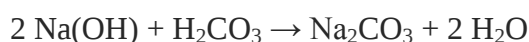
Disappearing ink is a substance consists of a mixture of chemicals which makes the ink visible to the eye for a short duration of time. It is an irreversible reaction based on the principle of acid/base chemistry[3].

Disappearing ink is a water soluble pH (acid-base) indicator that when exposed to air changes from a colored to a colorless substance. The chemistry behind this reaction is the water present in the ink reacts with CO<sub>2</sub> present in the air to form carbonic acid. The carbonic acid formed reacts with sodium hydroxide to form sodium carbonate. Due to this reaction neutralization of the base, pH changes and makes indicator colorless, hence ink disappears [3,11,12,13,14]:

Carbon dioxide(CO<sub>2</sub>) in the air reacts with water(H<sub>2</sub>O) to form carbonic acid(H<sub>2</sub>CO<sub>3</sub>):



The neutralization reaction :- sodium hydroxide + carbonic acid -> sodium carbonate + water:

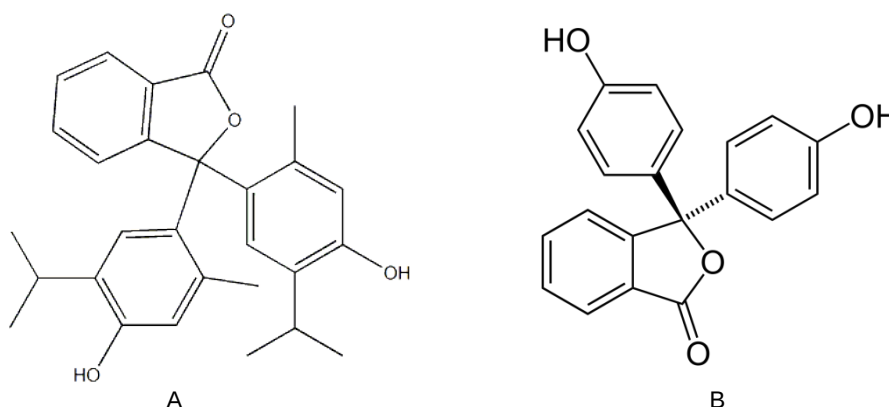


- Sodium hydroxide and CO<sub>2</sub> reacts with each other in the presence of air to form sodium carbonate. Sodium carbonate is less basic as compared to sodium hydroxide.

- Sodium carbonate changed the colour of the indicator from blue to colourless. The transition range of thymolphthalein is pH 9.3-10.5, above this pH range it is blue and below this range it is colourless.
- Only colourless residues are left behind and alcohol gets evaporated(4).

Disappearing ink is a mixture of acid-base pH indicator like thymolphthalein, ethyl alcohol, base like sodium hydroxide solution, and water at pH 11. The most common pH indicators used in the preparation of disappearing inks are thymolphthalein ( $C_{28}H_{30}O_4$ ) and phenolphthalein ( $C_{20}H_{14}O_4$ ).

In solid form they both are found as white powders. Thymolphthalein gives blue color so it is used to prepare blue ink and phenolphthalein gives pink color so it is used to prepare red ink. Mixture of thymolphthalein and phenolphthalein is used to generate a purple solution according to their pH values(3). Amount of sodium hydroxide and thymolphthalein/phenolphthalein in a solution decides the fading period a disappearing ink, it range from a few hours to few days. These vanishing ink on paper may not be detected even under high-resolution magnifier, IR light and UV light(3,12).



**Figure 1:** A- Thymolphthalein, B- Phenolphthalein(13)

Sodium hydroxide with thymolphthalein gives blue color ink, with phenolphthalein gives pink color and the mixture of all three gives purple color. As the concentration of sodium hydroxide in a solution increases the stability of ink also increases, low or decreased concentration of sodium hydroxide produces colourless writing. Increasing concentration of phenolphthalein and thymolphthalein also increases the stability of writing(4).

Disappearing ink are used for a variety of purposes, For example, it is used as a marking tool by the painters. in sports, dance classes, textile industry, fashion industry and many other different activities which require a marking system(3,4,14). It is also used as a tool in education system by the teachers while preparing papers, only questions are visible and the answers became visible by using a colouring assistant(3,4,14).

## **OTHER TYPES OF INVISIBLE INK:**

### **IR-active invisible ink**

Infrared- active invisible ink shows high absorption in IR spectral region, but it is transparent in the visible region of the spectrum. There are two types of IR-active ink, IR absorbing ink and IR penetrating ink. Silicon (IV) 2,3 naphthalocyaninebis (trihexyl-silyloxy) (SiNc) based Infrared-active invisible ink shows strong absorbance at 790nm and highly transmitting characteristics in the visible spectrum. Colorants which are chemically and physically compatible with the ink base are used in the preparation of IR invisible ink. Infrared inks that satisfy these requirements are further mixed with suitable binders and pigments. Examples of pigments which are used mostly are BASF Lumogen IR 765, 729nm SiNc and Lumogen IR 788 and binder such as polyethylene terephthalate resin (PET) are used(15).

### **UV-active invisible ink**

Ultra Violet - active invisible ink fluoresce due to the presence of dyes upon exposure to UV light source. When excited by UV light, a portion of energy is absorbed by the material and fluorescence is emitted in the visible range. Some invisible inks which are commercially available glow brightly in a variety of colors when exposed to UV light. Tonic water, optical brighteners containing laundry detergents, body fluids and soap are some of the examples of UV-active ink materials(15).

## **ERASABLE INK:**

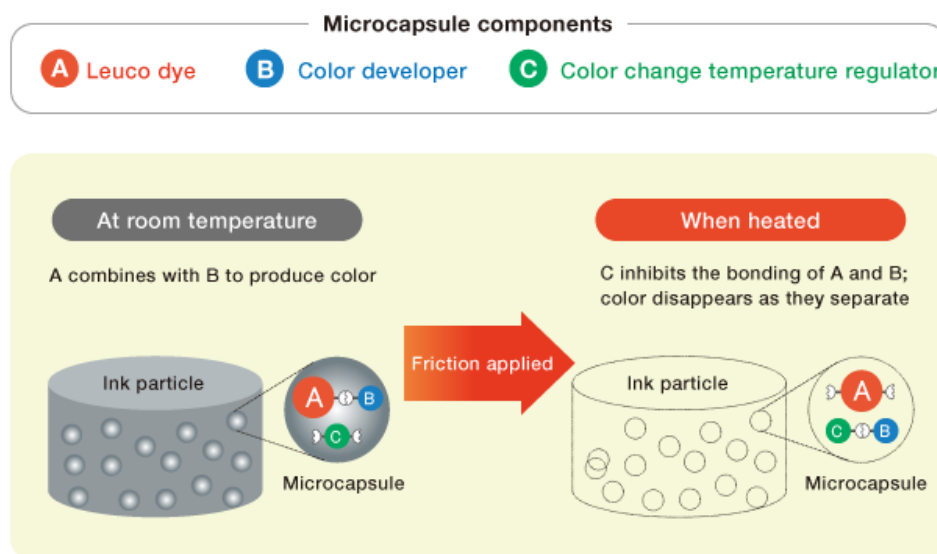
Thermal or thermochromic ink is a type of erasable ink which is removed easily by the friction produced by rubbers incorporated in each pen. It has different colors like red, blue, green and black. Such inks can be removed from the paper surface mechanically through erasure or by the exposure effect of heat and cooling simultaneously. It is a type of viscous ink that depends largely on the heat generated during erasure which affects the solvent of ink. The fading of this type of ink requires an external heat factor such as friction due to eraser or by direct exposure of temperature(6).

These inks are used for committing various crimes. Forensic document examiners are very much familiar with these type of erasable ink ball-pen manufactured by Paper Mate, they are sold in UK under the name "Replay". "Eraser Max" is a new brand name for Replay erasable pen in UK.. A latest collection of erasable pens are manufactured by Pilot under the name "Frixon" erasable roller ball pen(3,9).

A small eraser is fitted at the tip or end of the erasable pen which helps to remove the writing. While removing with a rubber eraser a pale trace of writing remains visible to the unaided eyes. Rubbing the rubber eraser on the paper generates heat by the action of friction and decolorize the ink line but does not abrade it(3,9).

Pigment forming microcapsules are made up of mainly three substances: first, leuco dye which can switch between coloured and colourless forms, second, a color developer which chemically bonds with the leuco dye to produce color and third is a temperature regulator which changes color according to temperature. The leuco dye is the one which actually determines colour but it can produce colour only when it is chemically bonded with the colour developer. The bonding of leuco dye and colour developer is prevented by an

inhibitor(colour change temperature regulator) that inhibits bonding of the two above a particular temperature and makes the colour disappear. There are several temperature regulators available that regulate colour change at different temperature(16).



**Figure 2:** Frixion erasable ink(16)

Leuco dye developer solvent system is used in thermochromic/thermal erasable inks. The leuco dye-developer-solvent system is a thermochromic pigment present in a polymer shield. Color change takes place due to the formulation of three components based on the interaction of a color former (leuco dye) with the developer in the presence of a solvent. Colour former may be a spiro lactone molecule. Such one possibility is the CVL (CcrystalVvioletLlactone), which is colorless when in grounded lactone form. CVL attains colour when lactone ring opens. This is result of increase in the polarity or hydrogen bonding ability of the environment (developer) increasing the conjugation. Generally, phenols are used as developers. Solvents used in these inks are amides, esters, alcohols or acids having long chain aliphatic character(2).

The solvent system used in thermal inks are leuco dye developer system. In the presence of a solvent an interaction between a color former (leuco dye) and the developer results in the formation of the three components due to which color change takes place. Spiro lactone molecule is commonly used as a color former. Such one possibility is the CVL (CcrystalVvioletLlactone), which is colorless when in grounded lactone form. Opening of lactone ring gives color to CVL, which results in increased conjugation due to the increased polarity or hydrogen bonding ability of the developer. Phenols are generally used as developers. Some of the solvents which are commonly used in these inks are esters, acids having long chain aliphatic character, amides or alcohols(2).

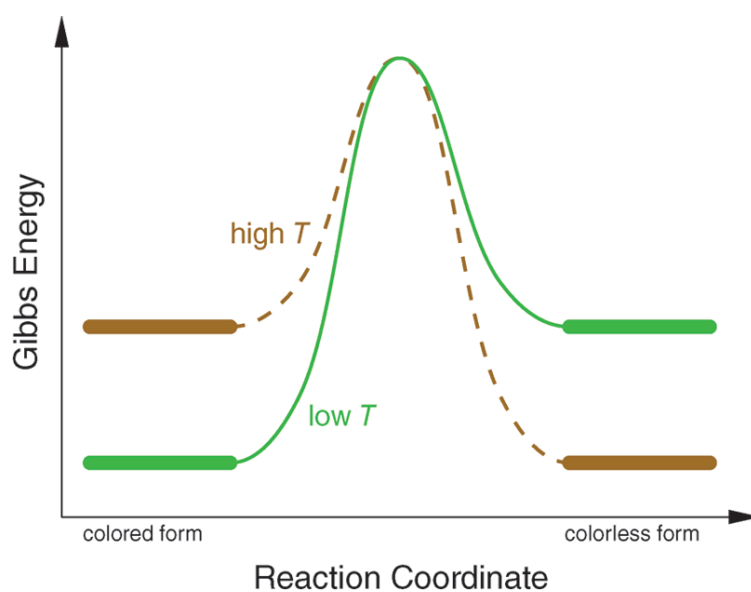
### Properties of thermal ink:

Erasable ink has acide-base sensitivity that can be studied by adding 3M HCL or 3M H<sub>2</sub>SO<sub>4</sub> to dry erasable ink at low temperature which results in spreading of the coloured form on the paper that help to partially keep their colour at high temperatures. Addition of these acids to these same dry ink colors after conversion to the high-temperature, colorless form caused

them to revert to their coloured form. However, adding of 3M NaOH or 3M NaCl had negligible or very little effect on the behaviour of ink at high and low temperature(17).

Examination through optical microscopy reveal the granular structure of the inks which may be the result of micro-encapsulation of ink. Most of the granules are in the range of 1-2  $\mu\text{m}$  in size and some are upto 8  $\mu\text{m}$  in size. Most of the aqueous solutions does not affect the physical structure of ink granules, but some of the acids and bases can affect the granular structure by penetrating the granules and thus affects ink ability to change color.

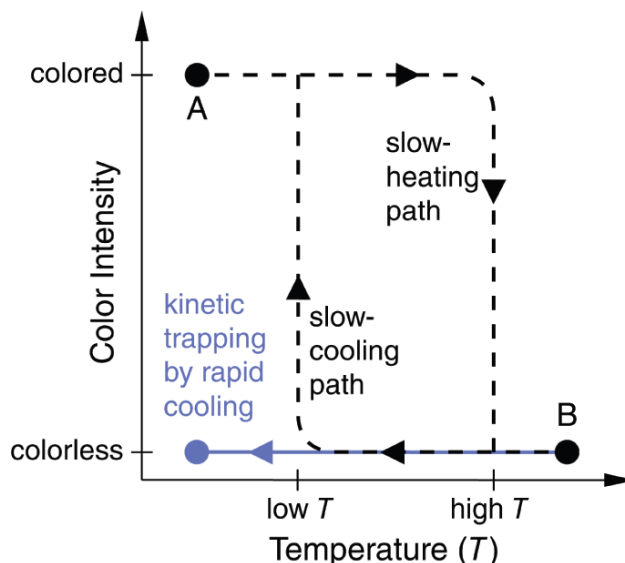
Given enough time, the components of the ink reach their thermodynamically favored colored form at low temperature and colorless forms at high temperatures. Differential Scanning Calorimetry (DSC), when heated on a sample of black FriXion ink revealed that the dominant endothermic transition takes place at about 57°C to 60 °C (without any exothermic transition in given range). When the ink was cooled, its dominant exothermic transition takes place at about -3°C to 0 °C (without any endothermic transition in the given range). As observed it was found that these temperature ranges were consistent for wet ink, dry ink, and aqueous solution inks like HCl, NH<sub>3</sub>, or NaOH added(17).



**Figure 3:** Activation barriers between the coloured and colourless forms at different temperatures.

The activation barrier that is responsible for the inter-conversion of different forms of ink components is high enough that at room temperature both the forms can exist for a longer period of time. This is called as colour hysteresis which can be explained as the ink form at room temperature that depends on the way from which that room temperature is reached or achieved. To begin with coloured ink below the color transition range at point A, the ink traverse through the upper pathway as it is heated by the action of rubbing and attains a high temperature ( $\sim 60^\circ\text{C}$ ) before changing the color and then ends up at point B. At point B when the ink gets cooled slowly, it traverse through the lower pathway and attains low temperature ( $\sim 0^\circ\text{C}$ ) before changing of the color and then ends up at point A. The cooling pathway of the

ink gets changed when the high temperature or colourless form of the ink gets rapidly cooled to low temperature with liquid N<sub>2</sub>, this kinetically traps the ink in colourless state. When this ink is warmed up back from these low temperature, it gets converted from colourless to coloured form(17).



**Figure 4:** Schematic colour hysteresis curve for the thermochromic ink, including the kinetic trapping of the colourless form of the ink(17).

## DIFFERENT EXAMINATION TECHNIQUES:

### 1. Color measurements

Color measurements are very useful evidence and can be examined by changing of inks color. The color strength (K/S) for erasable and disappearing ink can be determined on paper sheet samples by calculating the value of K/S from the Kubelka- Munk equation.

$$K/S = (1-R)^2 / 2R$$

Where,

R= average observed reflectance

K= absorption coefficient

S= scattering coefficient

K/S= corresponding strength of colour

The corresponding K/S value can be calculated for each ink sample using Data Color SF 600+ Relative color(6).

### 2. Colour strength measurements

**Fading time** :Fading time of writing is defined as the time from writing to its colour disappearance (complete fading).

Different brands of disappearing ink were spread on the surface of paper samples and allow drying at room temperature then measuring the reflectance from two hours up to three days and calculating the changes in value of the color strengths (K/S) using the Kubelka-Munk equation. The change in color strength values (K/S) give an indication on fading of inks,

Where each color is measured at 254nm. It was found that Phenolphthalein loses its color faster than Thymolphthalein.

Similarly, different brands of blue erasable ink are disseminated on surface of one type of paper sheet samples and allow them to dry at room temperature. Then, the fading of ink color is determined for each sample by measuring the reflectance of ink (R) at different time intervals, ranging from two hours to three days, either at room temperature between 20-25°C or by exposing to ultra violet light at 254 nm(6).

### **3. Microscopic examination**

The optical examination of documents was carried out by hand magnifiers and stereo microscope (magnification 20X-60X) with direct light and oblique light(6,12). The whole document is examined carefully with the help of different tools to find out minute differences like lingering effects, use of erasures or traces of erasures, different strokes of ink lines etc. Different types of tools like hand magnifiers, binocular and illuminated magnifiers are available which can be used for microscopic examination of documents. Strokes of invisible ink contain minute streaks and striations which can be used to individualize the writing(7).

### **4.Examination with VSC**

Video Spectral Comparator 6000 (VSC6000) or other different versions of VSC are used for the optical examination of documents. VSC is one of the most versatile instrument which can be used for non-destructive examination of different documents by using different instrumental parameters. It is very easy to use and gives instant results. VSC consists of an imaging device which helps the examiner to analyze different inks, examine alterations, and study hidden security features. VSC allows the forensic examiner to identify forgery in questioned documents by using a special inbuilt feature of spot illumination of infra-red, visible or UV portions of the spectrum which makes the hidden strokes glow and disappeared ink fluoresces under the influence of ultra-violet light(6,7,12,14).

### **5.Examination with Projectina Docucenter4500**

Projectina Docucenter is an instrument used for the examination of photo-copied and scanned documents. Projectina is especially designed to examine documents by the method of superimposition and side by side comparison. It is also called as a micro-projector. The main feature of this instrument is that it examines and compares objects which appear to be identical. It proves that two objects that first appear to be identical have in fact many minute differences(7).

### **6.Electrostatic detection apparatus (ESDA)**

In late 1970's Foster and Freeman commercially produced Electrostatic Detection Apparatus (ESDA). It is a non-destructive method to examine indentations in a suspected document. It is a very easy to use technique, it helps to produce life-size transparencies of indented writing without causing any damage to the original document. It does not interfere with other forensic tests and the same document can be processed number of times without any loss of sensitivity. This technique can be used to individualize the writer and can also be used to reveal invisible writing.

### **7.Chemical Method**

Ammonium  $\text{NH}_3$  vapour was used to decipher the disappearing ink. When the disappearing ink comes in contact with  $\text{NH}_3$  vapour, invisible entries turned blue successfully without harming the paper/substrate. Similar results are observed by using iodine fuming and dilute

sodium hydroxide(NaOH). Reappeared writings were photographed using digital camera as the writing will remain visible only for few seconds and then again becomes invisible (3,7,12,14). It was found that NaOH solutions when sprayed on paper may harm the paper/substrate.

### 8.Heat effect

Heat can be used to disappear erasable ink writing. This can be studied by using oven, electric iron and hair dryer(7). Disappearing ink doesn't have any effect of heat.

### 9.Examination under refrigerator (at low temperature)

Invisible writings can be revealed by putting the samples in the freezer of any household refrigerator. At such low temperature of the refrigerator the thermal ink become coloured and visible. It is a very simple, easy to use, sensitive, fast, cost-effective and non destructive technique to examine and detect alterations and manipulations on a suspected document(2).

### 10.Examination of physical properties of paper

When erasures are used on a paper, some of the surface layer is removed by the erasing process which also affects the thickness and other physical properties of the paper. Thickness of the paper should be measured from different positions of the document. Roughness and texture of the document are also measured by using microscope. The thickness of the paper will decrease at positions where erasures are used due to the removal of the coating layer. As thickness decreases, roughness increases due to the removal of the coating layer from the surface of the paper(7). Different mechanical properties of the paper are also studied by different test like tearing resistance test, strength test, elongation test and bursting test.

### 11.Examination of chemical composition the Ink

Erasable ink consists of different components like elastomeric polymer, volatile solvent, non-volatile solvent, pigments, dyes, and lubricants(7). Disappearing ink are mostly made by using thymolphthalein, water, sodium hydroxide and ethyl alcohol(3,12). Examination of composition of the inks are very important.

**Difference between erasable and disappearing inks on paper using Scanning Electron Microscopy (SEM) :** Erasable ink remain on the surface and are not absorbed by the paper as it belongs to the viscous ink family. On the other hand disappearing inks are absorbed by the paper as it belongs to the liquid inks family(6,7).

**Table 1:** Difference between disappearing ink and erasable ink(6)

| S.No. | CATEGORY              | ERASABLE INK<br>(THERMAL INK) | DISAPPEARING<br>INK      |
|-------|-----------------------|-------------------------------|--------------------------|
| 1.    | COLOR                 | All Color                     | Pink(red) & blue         |
| 2.    | Shape of Strokes      | Ink on the surface of paper   | Ink penetrates the paper |
| 3.    | Erasing method        | By erasure or heat            | A spontaneous erasure    |
| 4.    | Type                  | Viscous writing material(dry) | Liquid writing material  |
| 5.    | Colorant material     | Pigments & dyes               | Indicators               |
| 6.    | Effect of alkali sol. | No effect                     | Reappearing of ink       |
| 7.    | Pressure of writing   | Smooth                        | Rough                    |

|    |                           |                         |           |
|----|---------------------------|-------------------------|-----------|
| 8. | State of ink on the paper | On the surface of paper | penetrate |
|----|---------------------------|-------------------------|-----------|

## CONCLUSION:

Invisible ink pen are easily available in the market and can be used by the forger for committing forgeries. Once the ink becomes invisible, it becomes difficult to detect it by naked eyes. So, it becomes very important to develop a practical and non- destructive method to decipher these inks easily. Invisible inks are becoming one of the latest techniques used in committing forgeries in writing various bank cheques, withdrawal forms, wills, deeds and other important documents. Many different varieties of these pens are easily available locally, this makes easy for the criminals to use them and commit forgeries. Various examination methods are available to decipher such vanishing inks like VSC, ESDA, Projectina docucenter 4500, chemical methods etc. Invisible inks are abused by the criminals because of its easy availability and unique quality, therefore it becomes our duty to create awareness about this issue among different investigating agencies and laboratories to ensure that it is being used judicially. It will be of great advantage to the society as well as law and enforcement agencies.

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