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REVIEW ARTICLE

Effect of Thermochromic Ink on Different Types of Papers

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ABSTRACT

Frixion Roller Thermochromic ink pens are incorporated with an erasure in each pen, which can be used to generate heat through friction which, in turn, decolourize the writings. Application of heat by other sources also have a similar effect. Thermal ink has a unique characteristic which makes it disappear, when heat is applied at a specific temperature. Due to this significant property of thermal ink, it is widely used for frauds. Easy availability and the unique characteristic of thermal inks attracts criminal minds and therefore increases criminal activities. The main purpose of this research paper is to describe different properties of thermal ink along with the derivation of an easy, inexpensive and non-destructive process to restore disappeared writings. Reaction of thermochromic ink with different varieties of papers has also been examined in this paper.

INTRODUCTION

KEYWORDS | erasable ink, thermal ink, ink analysis, forensic science

Invisible ink is prepared by special chemical process specifically for some industrial purposes. Invisible ink pen looks just like any other pens available in the market but the ink is made of different chemical composition. It is commonly known as magic pen. Auto-vanishing fluid inks are easily available in the market which raise great deal of concern.[4,14,15] Two kinds of invisible inks are: disappearing ink and thermal ink. Disappearing ink is a mixture of different chemicals which causes the ink to become visible for a very short time duration after which it disappears.[17-18] It works on the principle of acid/base chemistry and is an irreversible reaction. This research paper is focussed on thermal ink only.

Thermal ink is a type of erasable ink which is removed easily by the friction produced by rubbers incorporated in each pen.[9-13] It has different colours like red, blue, green and black. Such inks can be removed from the paper surface mechanically through erasure or by exposure to 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. For the ink to disappear or fade the ink requires an external heat such as friction through eraser or through direct exposure to temperature.[4,5]

These inks are used for committing various crimes. Criminals use thermal ink pen to erase the original writing and then rewrite with the intent to defraud. Such obliterations are not visible to the naked eyes and are difficult to detect.[19,21,28] Forensic document examiners are very much familiar with these type of thermal ink ball-pen manufactured by Paper Mate, they are sold in UK under the name "Replay". "Eraser Max" is a new brand

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name for Replay erasable pens in the UK. A latest collection of erasable pens are manufactured by Pilot under the name "Frixion" erasable roller ball pen.[3,6]

A small eraser is fitted at the tip or end of the erasable pen which helps remove the writing. While removing with rubber eraser small traces of writing remained visible to the eyes. Rubbing the rubber eraser on the paper generates heat by the action of friction and decolourize the writings but does not abrade it.[3,6]

Pigment-forming microcapsules are made up of mainly three substances: first, leuco dye which can switch between colored 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 the color but it can produce color only when it is chemically bonded with the color developer. The bonding of leuco dye

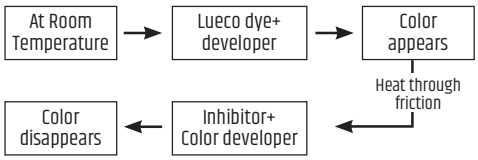

Figure 1: Reaction of Thermal Ink

and color developer is prevented by an inhibitor [color change temperature regulator] that inhibits bonding of the two above a particular temperature and makes the color disappear. There are several temperature regulators available that regulate colour change at different temperature.[7,22]

The solvent system used in thermal inks are leuco dye developer system. In the presence of a solvent an interaction between a colour former [leuco dye] and the developer results in the formation of the three components due to which colour change takes place.[20] Spirolactone molecule is commonly used as a colour former. One such possibility is CVL (CcrystalVvioletLlactone), which is colourless in grounded form. Opening of lactone ring gives colour to CVL, which results in increased conjugation due to the increased polarity or hydrogen bonding nature of 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 acid-base sensitivity. It can be studied by adding 3M HCL or 3M H2SO4 to dry erasable ink at low temperature. This results in spreading of the colored form on the paper that helps to partially keep their colour at high temperatures. When acid is added to same dry ink after conversion at high temperature, it reverts back to coloured form.[1] However, addition of 3M NaOH or 3M NaCl showed negligible or little effect on the behavior of ink at high and low temperature.[8]

Examination through optical microscopy reveal the granular structure of ink which may be the result of micro-encapsulation of ink. Most of the granules are in the range of 1-2μm in size and some are upto 8μm 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 favoured colored form at low temperature and colorless at high temperature. Differential Scanning Calorimetry (DSC), when heated on a sample of black Frixion ink showed that the dominant endothermic transition takes place between 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 dry ink, wet ink and aqueous solution inks like NH3, HClor NaOH added.[8]

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 coexist 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.[8] It was found that α-anthracene terminated methoxy polyethylene glycol (An-PEG) aqueous solution can be used as a new type of ink to be written on conventional paper.[16,27]

METHOD & MATERIALS

Samples are made using Pilot Frixion Clicker Roller Pen (Blue) on three different types of papers. The papers used to prepare samples are White Copier paper (70gsm), Bond paper (90gsm) and Glossy paper (180gsm). There are total 90 samples recorded, 30 samples for each type of paper. In this process three ink removing methods are used i.e. erasure incorporated at the backside of each pen, hair dryer and domestic iron. A total of 10 samples with each method is prepared. Domestic freezer is used to restore all the writings. Observations were made by using a hand magnifying glass and unaided eye.

Observations

Frixion Roller pens are incorporated with an erasure at the tip of each pen which can be used

Figure 1: Pilot Frixion Clicker

to generate heat through friction which, in turn, decolourize the ink lines. This erasure can affect the physical properties of the paper depending upon the quality and type of the paper used.

We also used a domestic hair dryer to remove the writings made by thermal ink pen. It takes only 1 or 2 minutes to remove the writings from the paper. It was observed that the ink reappears in specific region of page with the movement of air stream.[6]

Domestic iron at a moderately hot, "two dot" setting was also used to remove the thermal ink writings. To protect the study paper, another sheet of paper is placed above the study paper before using the iron. The same effect was achieved when "one dot" setting of the iron was used to apply heat.[6]

All the samples with decolourized writings were placed in a domestic refrigerator (low temperature) to restore the writings. The following results were observed:

Sl.No.	Type of Paper	Method of Removal	Time taken to remove ink-lines	Reappearing Time at Low Temerature
1.	Copier Paper	Pen Erasure	1min.	45min
		Hair Dryer	1-2 min.	20min
		Domestic Iron	Few seconds	20min
2.	Bond Paper	Pen Erasure	1min.	1hour
		Hair Dryer	1-2 min.	20min
		Domestic Iron	Few seconds	20min
3	Glossy Paper	Pen Erasure	1min.	Doesn't reappear*
		Hair Dryer	1-2 min.	30min
		Domestic Iron	Few seconds	30min

Table 1: Pilot Frixion Clicker Roller [Blue]

It was observed that writings on the copier paper reappeared when removed with all the three methods i.e., by using erasure, hair dryer and domestic iron after putting it under the domestic refrigerator. Writings on the bond paper also shows similar results as shown by the copier paper.

Glossy paper reacts differently as compared to copier paper and bond paper. Glossy paper has a very smooth surface. When friction erasing

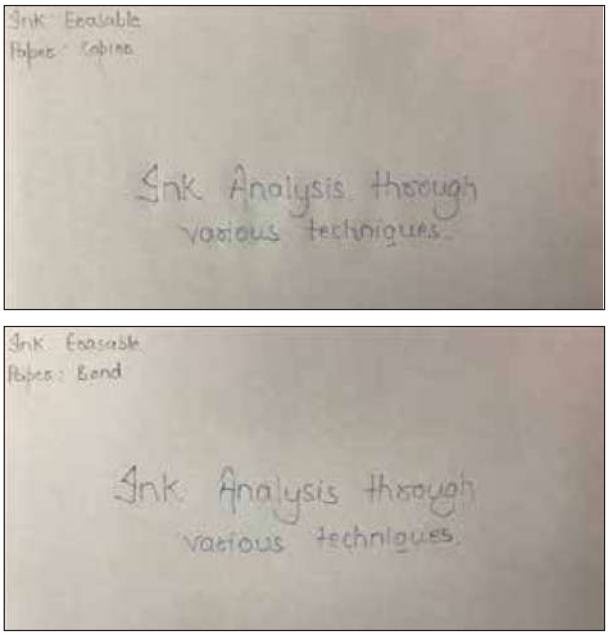

Figure 2 & 3: Reappeared writing on Copier, Bond papers respectively, by using domestic refrigerator (Blue)

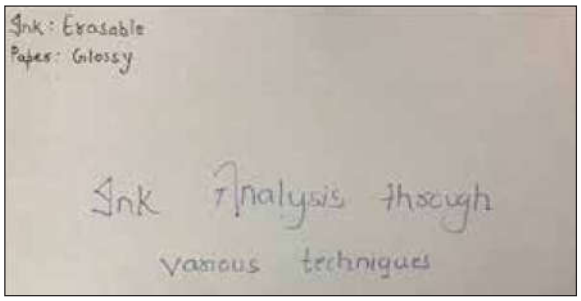

Figure 4: Reappeared writing on glossy paper using domestic refrigerator

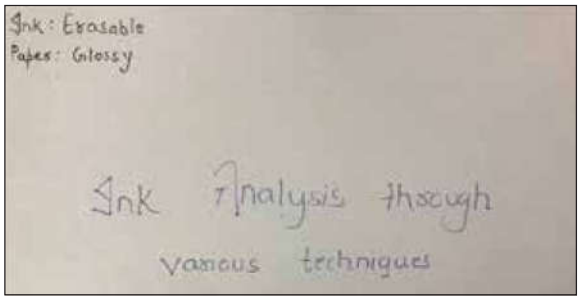

Figure 6: Reappeared writing on glossy paper using domestic refrigerator

method was used to remove ink lines from the glossy paper, it was observed that even after keeping it in a domestic refrigerator for sufficient time, the writings doesn't reappear. Only traces at the end of strokes reappeared. It was also observed that when ink lines were removed by using a hair dryer and a domestic iron then it reappears within 30 minutes when kept under the refrigerator.

CONCLUSION

It is difficult to detect disappeared thermal ink writings with naked eyes. Easy availability and unique quality of thermal inks attract criminal minds to indulge in increasing frauds. It was observed that applying heat by iron is the fastest method to remove thermal ink writings. This research paper provides information and alerts the forensic science community about the existence of thermal erasable roller ball-point pen and also describe an inexpensive, easy and non-destructive

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Figure 5: Few traces at the end of strokes reappeared when writings on the glossy paper is removed by using friction (rubber erasure)

method to decipher such writings. Some of the important features and properties of erasable ink are also elaborated in this paper. Restoration of disappeared writing by using an easily available domestic refrigerator provides a new avenue to detect these temperature dependent ink writings. Refrigeration method doesn't work on glossy paper when ink-lines are removed by pen erasure. In all other cases restoration by putting the samples in a refrigerator is possible. IJFMP

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