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DOCUMENT FORGERY DETERMINATION METHOD: INK AGING

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ABSTRACT

Document forgery is one of the most common crime types. The Forensic Judicial System needs the knowledge and experience of experts working in the field of judicial document review for the detection and elucidation of this crime. Determination of the text and/or numbers added to the document afterwards or the date of the issuance of the document can only be realized through determining the structure and date of the ink forming the suspicious texts.

To determine the age of ink, changes in the structure of the ink in the document are determined and interpreted analytically. While there are many laboratories and experts in this field abroad, the work in this field in our country has just begun to spread.

In this study, we will explain how date of the ink is determined and discuss the studies in this field along with their advantages and disadvantages.

Introduction

Since age determination dates the ink in the document, it is one of the important and controversial fields in the field of forensic science. The reasons for being one of the controversial areas include the fact that there are too many ink producers in the market and each of these producers uses various substances in producing ink. However, the aging process begins as soon as the ink is on the paper. This process is also affected by environmental factors (light, temperature, humidity).

Even the examination of one of the changes (evaporation of solvents, hardening of resins and dyestuff) in ink structure on paper provides information about when the document was created.

Document review specialists pay attention to 3 main factors. These are paper, writing instruments and ink. Writing instruments can be divided into 2 main groups. These are ballpoint pens and pens other than ballpoint pens.

Table 1 shows the chronological order of writing instruments according to their release dates on the market.

Table 1: Release dates of writing instruments on the market

2-Ink Structure

The ink structure consists of a colorant (one or more), a solvent (one or more), a resin (one or more), and additives.

Dyestuff forms 50% of the structure of the ballpoint pen ink. Dyestuffs are used to give color to the ink. Triaryl methane dyes are preferred as dyestuff. Due to their vivid colors and cheap costs, the most commonly used dyestuffs are crystal violet, methyl violet and Victorian blue.

Solvents are used to dilute dyestuff and facilitate their application to paper. They constitute 25% of the ink. When the solvent is selected, solvents with high-boiling point which do not evaporate quickly and cause ink to dry are selected [2]. Commonly glycol based solvents are used. The most commonly used solvents are phenoxyethanol, phenoxyethoxyethanol, dipropylene glycol, phthalic anhydride, oleic acid, benzyl alcohol, 2-prolidone, butylene glycol, etc. [4].

Resins are polymers with high molecular weight. Increasing the ink lubrication quality and film durability and the adjustment of the viscosity is necessary to establish a bond between the ink and the paper. Most commonly used resins are insoluble in water but soluble in organic solvents present in the ink formulation. The most commonly used resins are alkyd resin, polyester resin, colophon resin, phenolic recycle, chlorine and polyvinyl acetate, oleylamine, ethoxylate, phthalic acid ester, hydrogenated acetophenone and condensed formaldehyde [2,4,6].

3-Age Determination

Determining and interpreting the changes occurring in the structure of the ink as soon as it is transferred to the paper with analytical techniques is called age determination of ink. These changes are demethylation (degradation) of the dyestuff, evaporation of the solvents and hardening of the resins [1].

Degradation Of Dyes:

As soon as the ink is transferred to the paper, it starts aging due to light and O_2. Crystal violet loses the methyl group in its structure and transforms into methyl violet and methyl violet also transforms into a tetramethyl pararosanile by losing a methyl group. [2,3].

Evaporation of solvents:

Evaporation times of the solvents in the ink applied to paper are different from each other. Studies have shown that the solvent that takes the longest time to evaporate is phenoxyethanol and that it takes 2 years for phenoxyethanol to be completely removed from the paper [1].

The evaporation of phenoxyethanol from paper takes place in two phases, fast and slow evaporation. In the fast drying phase, as the amount of phenoxyethanol present on the paper surface is much, evaporation is faster. However, as time progresses, the rate of evaporation slows down as phenoxyethanol is trapped on the paper surface. The evaporation equation of phenoxyethanol from paper (Figure 1) is as follows. In this equation, (Y) is the amount of decreasing solvent with time (aging), (M_0) is a constant, (M_n) is the mass of the fast evaporating part, (My) is the mass of the slowly evaporating part and (t) is the corresponding time. [5].

Figure 1: Equation of evaporation of phenoxyethanol from paper

Polymerization and Hardening of Resins:

The hardening of the resins in the ink begins immediately after the application of the ink to the paper. The resins harden and trap solvents and dyes between the cross links. Thus, an inverse proportion occurs between the aging of the ink and ink extractability. Through the method of determination of polymerizations of resins, documents between 8 months and 2 years can be dated [2].

4-Methods Used in Age Determination:

Three different approaches are used to interpret the analysis of chemical changes in ink structure, namely static, dynamic and relative dynamic approach [1].

The static approach is based on the analysis of time-invariant

components (rare earth elements, etc.) in the ink. The forensic lab has a database which it updates every year by taking the production prescriptions from manufacturers. Thanks to this database, the ink composition that makes the suspicious writing allows the determination of the possible dates of production; thus a clear idea of whether or not ink exists in the market in the alleged date is created [7].

The biggest disadvantage of determining the age of the ink with static approach is that the databank cannot be updated continuously and cannot cover all types of ink [1-2]. Because of these disadvantages, dynamic approach is preferred more.

The absolute dynamic approach is based on the detection of chemical changes that occur in the ink structure due to the influence of environmental factors after it is transferred to the paper. There are many factors such as paper properties, storage conditions, etc. that affect age determination of ink. In order to minimize the error margin resulting from these factors, time interval is preferred instead of direct time [2].

Relative dynamic approach is based on the comparison of the ages of the ink in the same document. In this way the ages of the writings in a document can be ordered chronologically. The relative age determination comparison is possible only for inks that have the same formula and are applied on the same paper and for documents kept under the same storage conditions. The best example of these documents is diaries. In other words, relative age determination can only be applied when the only difference between writings in documents is the time when they are written [2].

5- Age of Ink Analysis

The first of the age determination work was done by Mitchell with a ball-point pen ink and this work was published in 1904 in the book "Ink and Their Composition and Manufacture" and in 1920 in the journal The Analyst with the name "Examination of the Age of Ink in Writing".

With the widespread use of ballpoint pens in the 1950s, studies on determination of the age of ball-point pen ink gained speed. In 1959, Kikuchi measured the period of dissolution and dispersion of the ink on paper. He found that the new inks dispersed faster than the old ones. This study laid the foundations for the solvent extraction technique used today [8]. In the early 1960s, Werner Hoffman identified the date of production of ball-point pen ink, which he collected from the market, in his work he conducted at the Zurich Cantonal Police Laboratory. He compared the components of the ball-point pens he collected with the standard reference ink collection in the lab, setting the dates for their release to the market. He used paper chromatography, thin layer chromatography (TLC), Spectrophotometry, and optical methods that did not damage the document. The success of this work led to the work of Brunelle in the United States in the Alcohol, Tobacco and Firearms Bureau in 1968. In 1975, Brunelle and Cantu developed the ink labeling program in this office. The program aimed to determine the production year and to be able to form an opinion about the date of suspicious writings. These studies laid the foundation of the static approach [6]. In 1963, Witte developed direct sampling techniques for ink analysis on paper. Brunelle developed a similar sampling technique in 1968. These studies were important because they did not cause any significant damage to the document.

In 1982, Stewart's work identified the components in the structure of the ink with TLC and compared it with the library results. With Gas Chromatography-Flame Ionization Detector (GC-FID), he found that the organic solvents decreased over time after the ink is transferred to the paper [6].

In 1985, he found a relationship between the reduction in the ratio of ink solvents to 3100/3500 cm $^{-1}$ (OH / CO) and age with Humecki Fourier Transform Infrared Spectroscopy (FTIR). He worked on documents aged between 0 and 22 years. It was observed that there was a decline in the ration for 30 years, but rapid decline was determined in the first 10 years [7].

In 1987, Cantu and Prough developed the Solvent Extraction Technique to measure the relative age of the ink. Before developing the method, they defined conditions such as ink being in the same formula, being on the same paper or having waited in the same storage area, taking samples from different pieces of paper at the same quality. Thus, since extraction of the ink that has remained on the paper for a longer time is difficult, the extraction efficiency will be lower. They proved the hypotheses that the less the ink waits on the paper surface, the more the extraction efficiency will increase. Thus, the extraction rate was calculated using the "efficiency" of the extraction and its dependency on time was revealed [8-9]. In 1987 Brunelle et al. used single solvent extraction technique in relative age studies. They used weak solvents on the ink stain and extracted the sample and looked at the amount of ink extracted by thin layer chromatography. Unlike Cantu, Brunelle et al. did not use the extraction ratio in their methods. In this study, the age of the unknown ink has been compared with the ages of the known inks. Therefore, the disadvantage of the method is that it is dependent on the mass. To eliminate this disadvantage, in 1989, Brunelle and Lee developed a method using a mass-independent and dye-ratio technique, and proposed two views. According to the first of these, as the ink ages, it is less soluble in organic solvents. According to the other, the degradation of dyes and the fading of their colors depend on their aging [10-11].]

In 1990, Isaacs and Clayton extracted the samples they drew with the same pen in different months with polar solvents analyzed with the diode array UV / visible spectrophotometer and formed extraction curves. They found that fresh ink samples were extracted completely. However, they did not find satisfactory results regarding aging. The most important reason for this is the degradation in the dyestuff takes place for years [12].

In 2001, Andrasko et al. developed a method that allows the HPLC analysis of dyestuff. In their study they stored and analyzed the samples from different brand blue ballpoint pens under different light conditions. He stated that in all the pens he examined, there is CV, MV. He stated that while there was no change in the samples kept in the dark for 3 weeks, there were changes in the ink compositions that were kept in the daylight during various hours. He observed that while there was a decrease in the amount of CV and MV, there was an increase in the amount of TPR [13].

In 2007, Weyermann et al revealed the relationship between time and evaporation of phenoxyethanol from the paper surface after the ink is applied to the paper. For this, they analyzed phenoxyethanol, ethoxyethanol, dipropylene glycol, and phenoxyethanol in 1.5-year-old documents on GC-MS. They found that other small quantities of solvents outside the base solvent quickly evaporated after ink has penetrated into the paper, the reduction in the amount of ethoxyethanol stopped within 10 days, there was a rapid decline in 2 weeks in the amounts of dipropylene glycol, phenoxyethanol and phenoxyethoxyethanol and phenoxyethanol, ethoxyethanol and dipropylene glycol in the papers stored in contact diffused to the paper on or under the paper with the ink. They also stated that when relative peak area (RPA) -Time curve is used, they could detect phenoxyethanol in the documents as old as 562 days and that phenoxyethanol was found in more than 90% of the samples they examined. In addition they determined that the age of ink in the document depends on the type of paper, the type of ink, and the storage conditions of the paper. They reported that when they evaluated the results they achieved, precise dating is not possible but age ranges can be specified and the ink in fresh, old or older documents can be compared. In their subsequent (ENFSI-EDEWG) reports following these studies, they stated that this comparisons can be made and interpreted in the first 3 months, 3-6 months, 6-9 months, 9-15 months and more than 15 months after the writing [14].

In 2007, Samandiou et al. verified their methods in their paper by analyzing ballpoint pen ink by reverse phase HPLC method. In their method, they extracted the samples cut from the paper with

acetonitrile, used ammonium acetate (0.05M), acetonitrile and methanol as the mobile phase and used interstil 5m (250x4mm) as the column. The retention time for CV is 17.83 min, and the retention time for victoria blue is 20.39 min. LOD and LOQ values of CV were 0.07 ng and 0.2 ng, and LOD and LOQ values of VB were 0.3 ng and 1 ng [15].

In 2008, Bugler et al. took 0.5 cm square sections from 85 different ink samples ranging from 1 week-old to 1.5-year-old documents and gave to TD-GC/MSe. They subjected the samples to two different thermal discharges, first at 70°C and then at 200°C. They collected the substance at -100 C in trap. They used 5-MS column in GC. They drew the time curve against % V. They obtained a curve that declined by up to 15 months and then the declines almost stopped [16].

In 2015, San Roman et al analyzed ink solvents by MHS-SPME-GC-MS. In this study, Hexyleneglycol, phenoxyethanol, Diethyleneglycol, ethyleneglycol and propylene glycol were analyzed as solvents. They drew the age curve between 0 and 5 years. [37].

Table 2 shows the chronological ordering of studies on ink age determination.

Table 2: Chronological ordering of age determination studies

CONCLUSION

In the US and Europe, many laboratories carry out routine analyzes of ink age. These laboratories use phenoxyethanol analysis especially in determining the age of documents aged between 0 and 24 months. In recent years, the age of the ink has been reported on a curve by looking at the amount of phenoxyethanol in the artificially aged state and non-aged state of the ink sample. Thus, the error margin is minimized. At the same time, in phenoxyethanol analyzes, the sample taken from the ink-free area should also be analyzed. This is because solvents are diffused horizontally and vertically from the paper. Thus, detection of phenoxyethanol in the blank sample evidence that the document has been contaminated.

In documents older than 24 months, the method of detection of dyestuff is used. The demethylation reaction used in the determination of age can be easily determined by chromatographic and spectroscopic methods. Between two suspicious ink samples to compare, the number of studies conducted with methods that do not harm the document in recent years has increased steadily.

Table 1: Release dates of writing instruments on the markt

YEAR	PRODUCT
1945	Ball-point pen
1950	Use of glycol-based solvents in ink
1955	Use of copper phthalocyanine
1963	Felt Tip Pens
1967	Roller Pens
1984	Gel Pens

Table 2: Chronological ordering of age determination studies

Year	Author	Method of determining the age of ink	Reference
1984	McNeil	Scanning microscopy for ink age determination on manuscripts	17
1985	Humecki	Determination of age of ink on the document using FTIR	18
1985	Stewart	Ink age determination through the determination and comparison of the volatile components in the structure of ball-point-pen ink with GC-FIG (flame ionization detector)	6
1988	Cantu	On relative aging of the ink - Use of Solvent extraction technique	8
1994	Aginsky	Use of thin layer chromatography to determine the age of ballpoint pen ink	19
1995	Aginsky	Determination of ink age using microspectrophotometric method	20
1996	Aginsky	Determination of ink age by GC-MS method in artificially aged documents	21
1998	Aginsky	Why is it more accurate to measure ink extractability as an age function and to measure ink volatile components more than dyes?	22
2000	Gaudreau and Brazeau	The use of solid phase microextraction SPME-GC-MS in developing a method to determine the aging properties of ink	23
2001	Lyter and McKeawn	Secondary ion mass spectrometry based on volatility Ink age determination study using (TOF-SIMS)	24
2002	Gaudreau and Brazeau	Ink age determination through determining the solvent loss ratio in the structure of the ballpoint pen ink using GC-MS	25
2002	Lafontaineue and Brazeau	Examination of ballpoint pen ink using GC-ESI-MS (ion electrospray ionization mass spectrometry)	26
2004	Hofer	Determination of age of ballpoint pen ink	27
2004	Laporte and his friends	Identification of 2-phenoxyethanol in ballpoint pen ink through GC-MS (gas chromatography / mass spectrometry)	28
2004	Lociciro and friends	Dynamics of the aging of ballpoint pen ink: Determination of phenoxyethanol with GC-MS	29
2005	Siegel et al.	Analysis of ink on documents using laser desorption / ionization mass spectrometry	30
2006	Andrasko	Examination of ballpoint pen ink through Microthermal Desorption GC-MS	31
2006	Kirsch	Determination of resins and aging products in ballpoint pens with GC-MS	32
2006	Xu et al.	Examination of black ballpoint pen and gel pencil ink with gas chromatography and UV-vis spectrophotometer	33
2007	Gaudreau and Brazeau	Quantitative analysis of solubilizers of ballpoint pen ink by solid phase microextraction	34
2007	Weyermann et al.	A GC-MS study on the drying out of ballpoint pen ink on paper	14

2008	Jürgen, Bügler,, Buchner and Dallmayer	Thermal Desorption and Gas Chromatography - Aging Findings of Pen-ink Using Mass Spectrometry	16
2008	Wang et al.	Identification and dating ball-point pen inks on documents with ion coupling high performance liquid chromatography	35
2015	San Roman et al.	Methodology for the date of ballpoint pen examined by MHS-SPME-GC-MS methods	36
2017	Diaz Santana et al.	Study on the use of gas chromatograph-mass spectrometry and high-performance liquid chromatography for the dating of ink on the document	37

Figure 1: Equation of evaporation of phenoxyethanol from paper

$$y(t) = m_o + m_f e^{-(t/t_f)^{1/2}} + m_s e^{-(t/t_s)^{1/2}}$$

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