Forensic Science International 278 (2017) 269–279

Contents lists available at ScienceDirect

Forensic Science International

journal homepage: www.elsevier.com/locate/forsciint

On the behavior of certain ink aging curves

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ARTICLE INFO

Article history:
Received 16 March 2017
Received in revised form 8 June 2017
Accepted 11 July 2017
Available online 19 July 2017

Keywords:
Inks
Dating
Aging

ABSTRACT

This work treats writing inks, particularly ballpoint pen inks. It reviews those ink aging methods that are based on the analysis (measurement) of ink solvents (e.g., 2-phenoxyethanol, which is the most common among ballpoint pen inks). Each method involves measurements that are components of an ink aging parameter associated with the method. Only mass independent parameters are considered. An ink solvent from an ink that is on an air-exposed substrate will evaporate at a decreasing rate and is never constant as the ink ages. An ink aging parameter should reflect this behavior. That is, the graph of a parameter's experimentally-determined values plotted against ink age (which yields the ink aging curve) should show this behavior. However, some experimentally-determined aging curves contain outlying points that are below or above where they should be or points corresponding to different ages that have the same ordinate (parameter value). Such curves, unfortunately, are useless since such curves show that an ink can appear older or younger than what it should be in one or more of its points or have the same age in two or more of its points. This work explains that one cause of this unexpected behavior is that the parameter values were improperly determined such as when a measurement is made of an ink solvent that is not completely extracted (removed) from an ink sample with a chosen extractor such as dry heat or a solvent.

1. Introduction

Besides the colorants (dyes or pigments), all inks contain at least one solvent, which is volatile and thus capable of volatilizing (evaporating) over time. Consequently, all inks that lay on a (porous or non-porous) substrate and are exposed to the air are capable of losing their solvents over time through evaporation; they leave behind their non-volatile components (their residue), which includes their colorants and resins. The amount of each ink solvent always decreases with time and never remains constant until no more evaporates (i.e., some remains, but it evaporates at a very small rate). Inks inside a container like an ink cartridge evaporate very slowly since the amount of air-exposed ink is extremely low — it appears only on the tip and on the top opening of the cartridge. It can be said that an ink inside a cartridge is in a closed system while one that is exposed to the air is in an open system. Any change over time of an ink in a closed system is minimal compared to the change over time of an ink in an open system. Thus one can say that the length of time since an ink was placed on a substrate (like a document) is the age of the ink entry. It should be noted that any change in an ink over time (which is a cause for ink aging) is the result of a change over time in at least one of its components (a solvent, a colorant, a thicken agent, etc.). In this work only changes in an ink solvent are considered. Several researchers have treated the various methods for dating writing. The two general approaches are referred to as the static approach (which relies on the existence a reference collection of ink formulas whose date of first production are known) and the dynamic approach (which relies on following changes in an inks properties as it ages) [1–4]. Most of these researchers agree that for the dynamic approach, following the changes in the inks solvents shows the most promise.

There is one class of inks (commonly known as the conventional ballpoint pen inks) that, besides the ink solvents and the colorants, contains resins to help increase their viscosity. For such conventional ballpoint pen inks, the evaporation process causes the ink to become thicker (more viscous) as it ages and, consequently, the evaporation process is not linear (i.e., the rate at which an ink solvent evaporates is not constant as the ink ages). The amount of a solvent in an exposed ink plotted against time produces a graph (curve) that decreases in a curvilinear way as the ink ages, levels off asymptotically to a value close to zero, and is never constant.[1] It thus decreases in an exponential-like manner.

[1] An ink is said to be "aged out" with respect to the solvent being measured when no more of this solvent can be detected by the analytical method used to detect it. However, the solvent continues to evaporate albeit at a very slow rate; so slow that it makes it seem to remain constant.

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http://dx.doi.org/10.1016/j.forsciint.2017.07.011

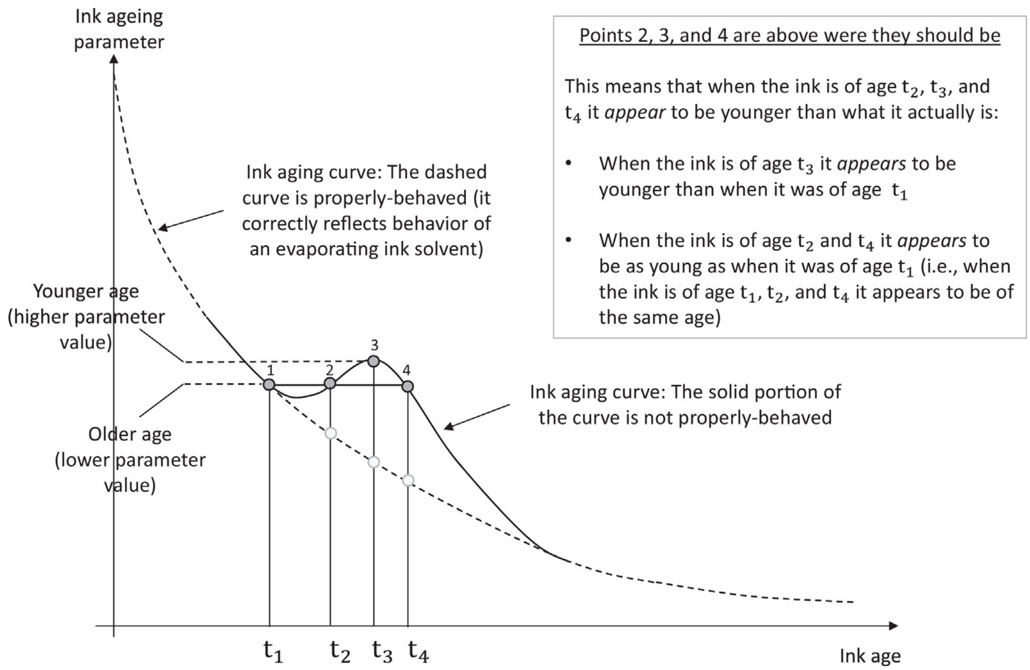

Fig. 1. Example of an improperly-behaved ink aging curve.

The term "strictly decreases" is sometimes used to emphasize that whatever is decreasing is never constant. The above is also true for inks that have little or no resin since, as the ink solvents evaporate, these inks also have to become thicker due to the presence of their non-volatile colorants; however, they evaporate much more quickly than those containing a greater content of non-volatile components (e.g., resins).

An ink aging parameter consists of experimentally-determined measurements associated with an ink property that changes with time. Such a property is the level of an ink solvent of an exposed ink. This will be the only property considered in this work. There are several ink aging parameters that involve the level of an ink solvent with ink age. This work considers only those parameters defined in such a way that they decrease as the ink ages and do not depend on the amount of ink examined (i.e., they are mass independent/invariant). Furthermore, all ink samples of different age considered here are taken to be from the same source (e.g., the same pen), placed on the same substrate (e.g., the same paper), made with the same pen pressure, and exposed to the same storage condition. The experimentally-determined values of an ink aging parameter, when plotted against ink age, should generate an ink aging graph (curve) that reflects the aging behavior of an ink solvent. However, there are ink aging curves associated with these parameters that do not reflect this behavior; they, for example, may have points that are below or above where they should be or points that remain constant as the ink ages. One of the causes of such outlying points is that, at these points, there was incomplete extraction[2] of the analyte; this is the topic of this work. Obviously such behavior is unacceptable as it can lead to errors in determining the age of an ink, see Fig. 1. An ink aging curve that correctly reflects the aging behavior of an ink solvent could be called a *properly-behaved ink aging curve*. Such curves are not only decreasing curves without ever being constant (i.e., they are strictly decreasing curves), but every point corresponds to the correct ink age.

As an illustration of how these ink aging parameters are used, suppose one wants to know when ink entry was placed on a document. Furthermore, suppose there is another ink entry on the same document that meets the following three conditions: (a) this ink entry is known to have been made with the same ink (e.g., with the same pen or ink formula), (b) the date when this ink entry was placed on the document is known, and (c) this ink entry and the questioned ink were kept under the same storage conditions. If such a second ink is found,[3] then the two inks can be compared to determine their relative age. This is done as follows: each of the two inks is examined by taking the necessary measurements needed in the ink aging parameter selected; when the resulting parameter values are compared, the ink with the higher value is the younger of the two. If this happens not to be the case, then it could be that the measurements used to determine the parameter were not properly made such as when some of the extractions of the analyte were incomplete (this idea of improperly-determined measurements is further developed in this work since it is its focus). There could be other reasons that can cause this unexpected behavior. This is for inks of different age that are of the same formula (e.g., those from the same pen) and on the same paper. Such reason include (1) the possibility that not all the inks that were placed on paper were made with the same pen pressure (causing differences in the amount

[2] In this work, complete extraction of an analyte (e.g., an ink solvent) by a given extractor (e.g., heat or a solvent) shall mean that all that can be extracted by that extractor is what gets extracted. A weak extractor does not remove all the analyte present in a sample, as some may remain; if it is used in a closed vessel, a state of equilibrium will eventually be reached where any analyte molecule that gets extracted is replaced by one already extracted (thus, extraction of more analyte molecules ceases when equilibrium is reached). A strong extractor will eventually remove all the analyte present unless saturation occurs.

[3] If the document does not have another ink for comparison, one can just keep the ink for several weeks and examine it every week (using an ink aging parameter) to see how it decreases. A steep decrease indicates the ink is relatively fresh otherwise it may not be fresh (but naturally, accidentally, or artificially aged). One can also estimate the age of the questioned ink by inducing aging on a removed part of the ink sampled and comparing the values of the ink aging parameter used. A large difference indicates the ink is relatively fresh. If one has a pen containing the same ink as that in question, then a sample of its ink is planted on the document and after about 24 h a portion of it is removed and heated. The resulting three inks can be compared to estimate the freshness of the questioned ink.