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Technical Report With Case Studies on the Accelerated Aging of Ball-point Inks

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ABSTRACT

This paper presents the results of several actual case examinations in which accelerated aging was used to estimate the age of ball-point inks on questioned documents, All of the results described in this paper were admitted as evidence in court. The results obtained using accelerated aging were verified either by the examination of known dated writings, examination by another examiner, or by the identification of dating tags in the inks. While the data presented does not satisfy the requirements for this to be a research paper, (actual cases rarely provide adequate known dated writings) the data shows that accelerated aging is an effective and reliable way to estimate the age of inks when known dated writings are not available for comparison with questioned inks. The authors have collectively testified approximately 50 times over the last 10 years using accelerated aging to date inks. Other private examiners have also testified to the results of accelerated aging. The case results described in this paper are just a sampling of the results that were accepted as evidence. Also presented in this paper is a demonstration of the reverse extraction phenomenon which is the fact that some inks extract faster or more completely as the ink ages.

Introduction

The concept of accelerated (artificial aging) as away of estimating the age of paper, as measured by the folding endurance test, is well established and documented (1-5). Cantu established an equivalence between natural and induced aging of a Fisher black ball-point ink written on Nashua photocopy paper (6). The aging parameter used was the extent of extraction into a weak solvent (water:methanol =3:1) of a fluorescent Rhodamine-type dye found in this ink. Fluorescent measurements were done on solutions (10). For this ink, paper and aging parameter, 4 minutes of induced (accelerated) aging at 100 degrees C is equivalent to 72 days of natural ink aging at 22 degrees C. Brunelle (7,8) and Aginaky (9) have since responded on the use of accelerated aging of ink to estimate the age of inks on questioned documents and both have used their technique on actual cases. Both used different approaches. Brunelle measures the extraction of ink dye components into solvents. For all the inks

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tested to date, these measurements detect changes in ink up to approximately 6 years. Aginsky measures the extraction of ink solvent (vehicle) components into solvents. For all the inks tested to date, these measurements detect changes in ink up to 6 - 12 months. Canto reported an excellent summary and discussion of all techniques reported to date on the aging of ink (11).

Although the use of accelerated aging to estimate the age of inks has been widely reported, only a limited amount of actual experimental data has been published. This paper presents data obtained from the use of accelerated aging on actual cases, since 1988. while the data is only a sampling from the hundreds of cases examined by this technique, the data demonstrates the reliability of accelerated aging to estimate the age of ball-point inks on questioned documents. Case 10 establishes that accelerated aging can also be applied to non-ball-point inks. The data presented was verified by comparing the results obtained by accelerated aging with the results obtained from known dated writings, by the identification of dating tags in the inks, and/or by verification by a second examiner.

Experimental

Equipment

Shimadzu Model 930 TLC Recording Scanning Densitometer (All inks and dyes were scanned at 535mm in the Reflectance Linear Mode.) Standard Glass TLC Developing Chamber to accommodate 8" X 8" plates Temperature controlled oven with +/- accuracy of 0.5 degrees C Supplies

Merck Pre-coated high performance Silica Gel TLC plates Analtech Pre-calibrated Micro-pipette (lOuL and 20uL. sizes) Analtech pre-calibrated disposable pipettes (4uL) Hand made syringe and needle plunger (20 gauge) for removal of ink samples VMR Scientific 1 dram glass vials with screw caps

Chemicals

Reagent grade 1 -butanol, pyridine, ethyl acetate, ethanol and benzyl alcohol Solvent Systems

I (ethyl acetate, ethanol and water) 70:35:30 II(l-butanot ethanol and water) 50:10:15

Procedures (Ball-point Inks)

Ten to twenty micro-plugs of ink and paper were removed from the documents using the syringe and needle plunger described above and then placed into the glass vials. Weak solvent extractions were performed using I-butanol (I0 uL for 10 plugs or less and 2OuL for over 10 plugs). Strong solvent extractions were performed with either pyridine or benzyl alcohol. Samples taken for accelerated aging were heated in a temperature controlled oven for 30 minutes at 100 degrees C. Then, these samples were allowed to equilibrate at room temperature for 30 minutes before performing the solvent extractions.

For R-Ratio and Percent Extraction measurements, the weak solvent was added to the ink samples with the micropipet and stirred immediately by rotating the vials 5 times, making sure the ink plugs were completely covered with the extracting solvent. Four micro-liter aliquots were removed at various time intervals up to 10 minutes, stirring before removal of each aliquot. Each aliquot was spotted on a Merck HPTLC plate approximately 3/16" apart and about 5/8" up from one end of the plate. After removal of the last weak solvent aliquot, the remaining weak solvent extract was evaporated in an oven at 80 degrees C. After the vial reached room temperature, the strong solvent was added and allowed to extract 5 minutes, after stirring as above. Then, after complete stirring, 4uL of the strong solvent extract was spotted adjacent to the weak solvent spots on the TLC plate. (The spotting was done with just one continuous application of the pipet to the TLC plate until all solvent was gone from the pipette, except when pyridine was used as the strong solvent. To keep the ink spot small, pyridine extracts had to be spotted intermittently).

The ink spots on the plate were completely dried by placing the plate in a temperature controlled oven at 8O degrees C for at least 10 minutes. When benzyl alcohol was used as the strong solvent, the plate was heated until the white ring around the spot completely disappeared. After the plate cooled to room temperature, the TLC plate containing the ink spots was scanned in the scanning TLC densitometer, which recorded the relative concentrations of each spot on the plate in relative percentages. The percent extractions in the weak solvent at each time interval were compared (heated vs. unheated samples) R-Ratios were calculated by dividing the concentration of each spot by the concentration reading for the longest extraction time of 10 minutes. Both the R-Ratio results and the Percent Extraction results are independent of the amount of ink taken for analysis. The R-Ratios were plotted R-ratio vs. time of extraction to produce R-Ratio Curves.

After readings were completed for the R-Ratios and Percent

Extractions, the spots on the plate were developed in the TLC Developing Chamber using solvent systems I or II. After the plate was completely dry, the plate was again scanned in the densitometer; however this time the plate was scanned along the direction of the separated dyes. This scan determined the relative percentages of each dye present in the ink. Dye-Ratios were calculated by dividing the dye with the highest percent concentration by each of the other dye concentrations. The various dye-ratios of the heated vs, unheated samples were compared. Bar Graphs were prepared from the data obtained to show the results of the percent extraction and dye ratio tests. Line graphs were prepared to show the R-ratio curves.

Procedure For Non-ball-point Inks

The procedure for the non-ball-point ink described in Case 10 is the same as for ball-point inks, except for the choice of weak and strong solvents. Ethanol was used as the weak solvent and ethanol:water (1:1) was used as the strong solvent. The addition of water to ethanol increases the polarity of the solvent which in turn increases its extraction power.

The Issue of Replicate Testing

Replicate testing (testing each sample in duplicate or triplicate) can be performed in 2 ways. One way is to test each sample 2 or 3 times to determine the range of variation in the test procedure used and the examiners ability to reproduce results. Normally the mean is calculated and this value is used for comparison with the mean value of other samples compared.

A second approach that satisfies replicate testing is testing different samples of the same formula ink that is known to have been written at the same time, For example, this is the approach that was used for Cases 1, 3, and 4. This approach is equivalent to multiple testing of the same sample of ink.

After examiners have performed. these tests several hundred times and know their ability to reproduce results, then multiple testing is not essential. This approach should not be used until the examiner has become proficient in all aspects of the testing procedure. It takes a lot of experience to perfect the spotting of ink samples on TLC plates in a precise and uniform manner and to obtain reproducible solvent extraction results.

The Effect of Paper on Test Results

The cases described in this paper all involved tests that were performed on the same paper or the same papers within a file with the same storage conditions. It has been established that tests performed on different paper may produce different results. Therefore, comparison of ink on different paper should not be performed, unless it can be determined with the actual documents received for examination that the different papers had no effect on the test results. For example, if the same ink of the same page appears on two different papers and the results are the Same, then it can be concluded that paper had no effect on the results.

Results and Discussion

Scientific Premise

All tests performed were based on the scientifically proven and published premise that as inks age on paper, the ink undergoes changes that effect the ink's ability to dissolve or extract into various Organic solvents. Generally, as ink ages, it extracts more slowly. and less completely than newer inks. Therefore, by comparing these extractability properties of inks of the same formula on the same type paper using either or all of the extraction techniques (R-Ratio, Dye-Ratio and Percent Extraction), one can sort and order those inks that are still aging (drying) according to the date they were written. To do this requires knowing whether the ink extracts slower and less completely with age or vice versa. When these inks include known dated inks, more precise dating is possible. To know if an ink is still aging, a difference should exist when the ink is tested at a later time or after it has been artificially aged. This also determines the direction of the aging parameter. If an ink is found to be totally aged out (dry) using these techniques, then all one can conclude is that the ink is over a certain number of years old. The actual age depends on how long it takes that particular ink to completely dry on the particular paper involved and how it has been stored. Fresh inks exposed to strong age-inducing conditions may appear older than If stored under "normal" conditions and older inks (but not dry) stored under very age preserving conditions may appear fresher than if stored under "normal" conditions. Normal storage conditions are considered to be documents stored at room temperature in a file or drawer with minimum exposure to light.

R-Ratios (which measure rates of extraction) and extent of extractions are monotonic (increase or decrease with age). They usually decrease with age, but increases have been observed. However the direction of dye ratios with age is not predictable. The reason for this is yet is to be determined. Dye ratios also have the potential of reversing themselves with age (11), although this has never been observed with inks tested to date.

The scientific premise of accelerated aging is that heat can be used to mimic natural aging as measured by the same aging parameter For example, heating an ink sample for 30 minutes at 1OO degrees C may make a fresh ink have the extraction characteristics of an ink generally no older than 6 years (the ink has dried or aged out as measured by these techniques). We have found with all ball-point inks tested using the techniques described in this paper, that ball-point inks completely dry within approximately 6 years. Of course, some inks become completely dry in less than 6 years. Therefore, accelerated aging has limited effectiveness for estimating the actual time a writing was made. It is more effective to determine whether two or more inks were written at the same time, as long as the inks being compared are still drying. Or, if one ink is found to be dry (no change caused by heat) and the other still drying (significant change caused by heat) using accelerated aging, one can conclude the two inks were written at different times. How different in time depends on the magnitude of change caused by heat and knowledge of how long it takes that particular ink to totally dry. (See 2(A) and 2(B) is also possible to determine which ink is newer, depending on which ink's extraction properties change the most with heat. Again the direction (increase or decrease with age) indicates if the ink in question extracts faster or slower as it ages on paper, respectively.

While newer inks usually extract faster and more completely than older inks into organic solvents, this is not always the case. (11). For example, Bic blackball-point ink is frequently, but not always, found to extract older inks faster and more completely than newer inks. (See figures 1 and 2) The reason for this unexpected phenomenon is not fully understood, but it may be due to the fact that the vehicle in Bic black ball-point ink is benzyl alcohol as opposed to the variety of glycol solvents and resins other companies use. Another possible explanation is that the Bic black ball-point ink composition is less susceptible to polymerization and oxidation and the binding properties of fresh ink break down with age, allowing the ink to extract more easily with age. Whatever the reason for the reverse extraction phenomenon, conclusions can be reached as long as the ink is heated first, to determine if it extracts faster and to a greater extent or slower and to a less extent with age.

Cases 1-13 demonstrate the effectiveness of accelerated aging in a number of different circumstances, Figure 1 and 2 and Cases 1 4, 9, 10B, and 12 demonstrates the reverse extraction phenomenon in the rates and extents of extractions, as well as in dye ratios. Note that in Case 10, the percent extraction (Case 10A) decreases with age (heat), while the dye ratio (Case 10B) increases with age (heat). Dye ratios that increase with age can be inverted to reflect decrease with age. Since the various figures are self-explanatory. no further explanation is required here, except to say that in all cases presented, accelerated aging helped to render reliable conclusions which were helpful to the judge or jury in reaching their verdicts. Readers should also be aware that 1) known dated writings in these cases were limited to those that were available on the documents received for examination and 2) all ink comparisons were performed on either the same piece of paper or the same type of paper submitted with the case. These papers were known to be stored under the same conditions.

Conclusion

Accelerated aging was determined to be an effective method for estimating the age of ink within the limitations described in this paper. Using known dated writings is always the preferred way of estimating the age of inks on questioned documents; however when these are not available in the case at hand, accelerated aging has proven to be a useful and reliable tool. The technique has been routinely accepted in court throughout the United States, as well as in Israel, and Australia.

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