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The pH Pen—A Means of Comparing Paper Products

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ABSTRACT: Printers may use a pH pen to test the alkaline/acid content of paper stock to determine if it will be compatible with a given formulation of printing ink. Questioned-document examiners may find the pH pen useful as an additional discriminator when attempting to determine if two paper products (known and questioned) could have originated from a common source. A total of 68 different fine white paper products were compared. From a total of 2278 possible pairs (questioned and known), all but six pairs were discriminated by a combination of physical characteristics, fluorescence under UV light, and the pH pen.

KEYWORDS: forensic science, questioned documents, pH pen, paper comparisons, printing, counterfeiting

A kidnap ransom note and envelope, and paper and envelopes found at the lodgings of the suspects; a note a bank robber gave to a teller, and paper found in the suspect's vehicle; a threatening or sexually harassing note, and paper found in the suspect's home; the possibility of page substitutions within legal or travel documents: these are all examples of cases in which questioned document examiners may be asked to examine paper products (known and questioned) to determine if they may have originated from a common source.

Depending on the chemical processes used [*1*], paper may be commercially produced leaving a finished product with a residual relative acidity ranging anywhere from acid, to neutral, to alkaline. Until recently, most fine white commercial papers were made by using titanium dioxide as a filler and coating pigment to add brightness and opacity. That process left the paper acid, but today many paper companies have switched or are in the process of switching to a calcium carbonate (chalk) production process, which produces a paper that is relatively alkaline.

A company publication[2] lists five primary reasons for the "decision to convert to alkaline production:

1. Economics: It is less costly to produce an alkaline sheet than an acidic sheet. Calcium carbonate is less expensive than titanium dioxide. Hence, to remain competitive, it will be necessary for all fine white paper mills to produce alkaline paper.

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[2]Printers Research Pacific, Inc., personal communication, 1992.

2. Environment: The paper companies share our concerns for the environment and are responding to the need to clean up the pollution that is created by metallic papers.
3. Availability: Calcium carbonate is more readily available than titanium dioxide.
4. Longevity: Acidic papers yellow with age, that is, the Library of Congress Archives are discoloring. Calcium carbonate has shown to resist discoloration.
5. Color: The mills are able to produce a 'whiter white,' using calcium carbonate."

The National Information Standards Organization (NISO) has established a standard for permanent paper. For a $10 purchase price, a copy of this standard may be obtained from Transaction Publishers, Dept. NISO Standards, Rutgers University, New Brunswick, NJ 08903 (202/932-2280). Paper conforming to this standard may be identified by the infinity sign in a circle: ♾, which is a registered trademark of NISO. Permanent paper is "not only alkaline, but buffered, free of groundwood, and able to meet fairly modest strength requirements for tear and fold" [2].

By February 1991, mills in several states had converted to the alkaline process [3] (Table 1).

100% Alkaline Companies [4]

As of January 1991 all of the fine paper made by several companies is neutral or alkaline (Table 2).

TABLE 1—*Mills that had converted to the alkaline process as of February 1991* [3].

Alabama
Jackson—Boise Cascade
Mobile—International Paper
Selma—Hammermill
Kentucky
Hawesville—Willamette
Wickliffe—Westvaco
Maine
Brewer—Eastern
Hinkley/Skowhagen—Warren
Massachusetts
Dalton—Crane, Byron Waston
Holyoke—(NVF)
Millers Falls—Strathmore
Turners Falls—Esleeck
Michigan
Alpena—Fletcher
Muskegon—Warren
Plainwell—Simpson Plainwell
Minnesota
Brainerd—Potlatch
Cloquet—Potlatch
International Falls—Boise Cascade
North Carolina
Pisgah Forest—Glatfelter
Plymouth—Weyerhaeuser
New Hampshire
Groveton—James River
New York
Cohoas—Mohawk
Glens Falls—Finch Pruyn
Lyons Falls—Lyons Falls
Newton Falls—Papyrus Newton Falls
Potsdam—Potsdam
Ticonderoga—International Paper
Ohio
Chillicothe—Mead
West Carrollton—Cross Pointe
Oregon
St. Helens—Boise Cascade
West Linn—Simpson
Pennsylvania
Erie—Hammermill
Johnsonburg—Penntech (Willamette)
Spring Grove—Glatfelter
Tyrone—Westvaco
South Carolina
Bennettsville—Willamette
Texas
Pasadena—Simpson Pasadena
Washington
Hoquiam—Grays Harbor (Hammermill)
Longview—Weyerhaeuser
Wallula—Boise Cascade
Wisconsin
Kimberly—Midtec
Menasha—Whiting
Merrill—Ward
Neenah—Glatfelter
Nekoosa—Georgia Pacific
Park Falls—Cross Pointe
Rothschild—Weyerhaeuser
Stevens Point—Consolidated

TABLE 2—*Companies whose fine paper is neutral or alkaline, as of January 1991.*

Company	Number of Mills Making Fine Paper	Capacity (tons per day)
Boise Cascade	5	3270
Crane	3	120
Cross Pointe	2	675
Eastern	1	180
Finch Pruyn	1	575
Fletcher	1	85
Glatfelter (incl. Ecusta)	3	1680
Hammermill	3	1800
Lyons Falls	1	220
Mohawk	2	230
Papyrus Newton Falls	1	400
Potlatch/Northwest	2	595
Potsdam	1	?
Simpson Pasadena	1	750
Simpson Plainwell	1	260
Weston	1	70
Weyerhaeuser (U.S. only)	3	1610
Whiting	1	25
Willamette (incl. Penntech)	3	1700

Due to the costs involved in replacing existing equipment, not all mills will switch over to the alkaline process right away. The larger corporations are switching over mill by mill in the next two years. It is unknown if all mills will switch over, and it is likely that acidic papers will exist for some time due to specialty mills and products.

The amount of calcium carbonate in the finished product will vary from mill to mill, and therefore so will the relative acidity/alkalinity, or pH. This may present a problem to printers using colored ink with the offset printing process. Initially the colors produced will be true, but after several runs, the relative alkalinity of the paper may produce a change in the pH of printer's fountain solutions, and toning may occur.

If printers are aware beforehand that a pH imbalance between their paper stock and their fountain solution may produce toning problems, they may be averted by the addition of the proper buffers. The pH pen (Fig. 1) can quickly and easily tell them whether the paper falls in the acid, neutral, or alkaline range. Resembling a felt tip marker in both appearance and use, the tip of the pH pen marks the surface of the paper, leaving a small colored area. The brand shown in Fig. 1 (Printer's Research Pacific, Inc., Sutter Creek, CA) produces a color spectrum range between yellow, green, or blue, depending on whether the paper falls in the acid, neutral, or alkaline range, respectively.

Paper finish, dimensions, weight, color, watermarks, and fluorescence under ultraviolet light (UV) [5], are some of the many tests that document examiners may use in trying to determine if known and questioned paper materials could have originated from a common source. The pH pen can provide a quick additional test by determining the pH level of the paper.

We purchased our first pH pen at a large paper products store in San Diego, Kirk Paper & Graphics. This store also had available a sheet that listed the alkaline/acid content of printing papers they had in stock in May 1991.[3] From a total of 101 products, 48 were listed as acid, 39 alkaline, and 14 neutral.

Also, a total of 18 were additionally marked with an asterisk, indicating that their pH might vary from lot to lot and therefore printers should use a pH pen to validate the pH

[3]Kirk Paper & Graphics, San Diego, CA, personal communication, 1992.

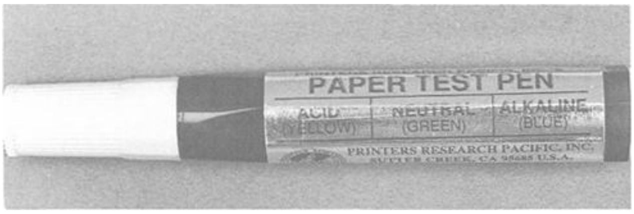

FIG. 1—*pH pen (pen #1), Printer's Research Pacific, Inc., Sutter Creek, California.*

level. This suggested to us that at this time there might be sufficient variation in the alkaline/acid content of commercial paper products to warrant the use of the pH pen by document examiners as a quick and easy test whose results might serve to either eliminate a questioned paper as having a common source with a known, or add support to the possibility of commonality of origin.

We also wondered if extremes in relative paper acidity could result in a chemical reaction with entries from pens having water soluble inks. If such a reaction were to occur it might alter the color of the entry. If the relative paper acidity could in some cases affect the visual appearance of an inked entry, this could present a problem to document examiners. An example would be if the question is "Could the same pen (which is not available) have been used to make entries on two or more different documents?," but the acidities of the documents differ.

Materials and Methods

Materials

A total of 68 fine white paper products from 12 different mills were examined. These were obtained from two large paper products companies in San Diego, either Kelly Paper, or Kirk Paper & Graphics.

Three different types of pH pens were tested initially. First, the three-color pen shown in Fig. 1 (and designated pen #1), and then two additional types which were provided by Donald R. Trammell, Vice President, Operations, Printers Research Pacific, Inc., Sutter Creek, California.

All three types are similar in appearance and in use, and all three have the corresponding color shades for the various pH's shown on the side of the pen. All three are manufactured in Japan and bear the logo "Astro." Pen #1 covered the full pH range but just had three colors, depending on whether the paper was relatively acid (yellow), neutral (green), or alkaline (blue). Pen #2 covered the pH range from 5.2 to 8.2 in eleven increments of different shades yellow to green. Pen #3 covered the full range of pH from 1.0 to 12.0 in 12 whole-number pH increments whose colors ranged from mauve through various red and orange shades to an eventual dark green. (A pH of 7 is neutral, below 7 is in the acid range, and above 7 is alkaline.)

Paper Testing

Similar size marks in the form of streaks were made on all 68 paper samples using all three pens. The tip of each type of pen has an initial color, but as test streaks are made, the color shift on the paper is instantaneous. However, the authors would recommend that at least 10 min be allowed for ink drying time, for thorough chemical reaction, and for paper fiber saturation of the ink when comparing known and questioned samples.

Initially we were concerned that carryover on the pen tip from one paper sample to the next might influence the resulting final color. To prevent this, the pen tips were streaked on a clean glass plate between paper samples, but this precaution proved to be unnecessary.

Physical Characteristics

No special equipment or conditions were used for examining the physical characteristics of the 68 white paper samples. Samples were merely examined side-by-side visually, examined for differences in paper weight, texture, and whiteness, and compared for opacity using fluorescent room lights.

Video Spectral Comparator

All 68 samples were each examined and compared for visible fluorescence under UV light excitation using a Foster & Freeman Video Spectral Comparator (VSC-1). Examinations were conducted by comparing the appearance on the monitor of two samples side-by-side, using the longwave UV light source with the FS1 Filter Slide at the LP1 filter position.

Possible Color Changes in Ink Entries

Test marks from over twenty different makes/models of roller ball and felt-tip pens were placed on two sheets of paper that tests with the pH pen had shown to be at the extremes of acidity and alkalinity of the 68 samples. No visual differences in ink color were noted when the same pen was used to mark the two sheets.

Results and Discussion

Based upon the information when the 68 fine white paper samples were collected, they were all from different mills or were different products from the same mills. We placed identifying marks on each sample so that they could be traced back to their original source. In comparing the 68 samples, we used the rationale that one would logically proceed first with those tests that were easy to perform, highly discriminating, and made no alterations to the sample. Therefore, the samples were first segregated into groups according to physical characteristics. Next, all samples were grouped according to their fluorescence under the VSC-I, and lastly they were all grouped according to their color reaction produced with pH pen #1. Although more powerful semidestructive discriminating tests based on fiber analysis, trace metal content, and chemical analysis of paper additives and coatings are available for paper comparisons [5,6], these were not considered in this study.

Physical Characteristics

Although watermarks were present on many samples, these were ignored because one might not always have a full sheet to compare and the watermark might be absent. The 68 samples could be grouped and are illustrated in Table 3.

For 68 samples there are a total of 2278 pairs (questioned and known), so if all but 55 pairs were discriminated the discrimination index (D.I.) [7] based on discrimination by physical characteristics alone is:

$$\text{D.I. for physical characteristics} = 2278 - 55/2278 = 0.976$$

TABLE 3—*The 68 samples as grouped.*

Sheets (samples)/Group	Number of Groups	Number of Sheets	Indistinguishable Pairs
1	29	29	...
2	5	10	5
3	3	9	9
4	1	4	6
5	2	10	20
6	1	6	15
		68	55

TABLE 4—*Samples grouped by category.*

Category	Sheets/Category	Indistinguishable Pairs
0	9	36
I	1	...
II	1	...
III	11	55
IV	6	15
V	25	300
VI	1	...
VII	6	15
VIII	4	6
IX	1	...
X	3	3
	68	430

VSC-I

The 68 samples were grouped into categories from least fluorescent (0) to most fluorescent (X). Samples could be distinguished by fluorescence between categories, but not within (Table 4).

$$\text{D.I. for VSC-I} = 2278 - 430/2278 = 0.811$$

pH Pen

Of the three pH pens tested, the color differences were most apparent and most easily interpolated in the three-color pen, or pen #1. Although in pens #2 and #3 there are supposed to be up to 12 different shades of color depending upon the pH, in practice, slight color shifts were very hard to differentiate. Therefore, discrimination tests on the 68 samples were based on the results with pen #1 alone. Pen #1 leaves a yellow mark if the paper is acid and a blue mark if it is alkaline, but around the neutral range (pH = 7) it was possible to distinguish three shades of green, that is, light green, green, and dark green. Therefore, the 68 samples could be grouped into five categories (Table 5).

$$\text{D.I. for pH pen} = 2278 - 598/2278 = 0.738$$

When using the pH pen, just a small test area on the paper will yield satisfactory results. In fact, even edges of the paper may be used. When dealing with a coated paper surface as found on slick, glossy, magazine paper coated with latex, only the surface of

TABLE 5—*Samples grouped into five color categories.*

Color Category	Sheets/Category	Indistinguishable Pairs
Yellow	5	10
Light green	14	91
Green	29	406
Dark green	11	55
Blue	9	36
	68	598

D.I. for pH pen = 2278-598/2278 = 0.738

the paper is tested, and the true pH of the paper can be determined by testing the edge or tearing the paper against the grain to reveal paper fibers under the latex coating, The pH level and test results may be apparently different between coating and actual fiber. When carbonless paper was tested different results were obtained, depending upon which side of the paper was tested, the coated front or the coated back.

False Readings

Just as fluorescence level readings may be rendered invalid due to prior treatment of the paper [*8*], the pH pen will not function properly or may give false results if the paper has been previously treated with ninhydin, DFO, or soaked in water. These may change paper pH levels and give false readings. Small chemical changes (due in part to solvent evaporation) that could produce slight variations in tone could occur as a pH pen is used over time, or there might be variations between different sample lots of pens. Therefore, questioned and known paper samples should be tested at the same time using the same pH pen.

Counterfeiters in the Far East use the pH pen to test paper before counterfeiting currency and travel documents to establish a similar pH level. A small color dot is placed on the counterfeit paper to establish pH. If need be, the pH level of the counterfeit paper can be altered to the desired pH level by chemical treatment before printing.[4]

Case Example

The potential of the pH pen for detecting counterfeit currency was demonstrated by a recent evidence submission from a special agent of the Naval Investigative Service. Figure 2 shows the questioned United States twenty dollar bill on the right and a genuine bill on the left. Although physical characteristics readily showed the bill to be counterfeit, this was quickly substantiated with pen #1. Intelligence has not as yet identified the source of the counterfeit bill.

Discrimination of Combined Methods

When discrimination based on physical characteristics was combined with discrimination based on fluorescence under the VSC-I, nine groups were left undiscriminated, consisting of one group of four sheets, three groups of three sheets, and five groups of pairs. This is a total of 20 possible indistinguishable pairs left out of the initial 2278, and the D.I. for the two methods combined is:

D.I. (physical char. and VSC-I) = 2278 − 20/2278 = 0.991

[4]James River Paper Co., Cypress, CA, personal communication, 1992.

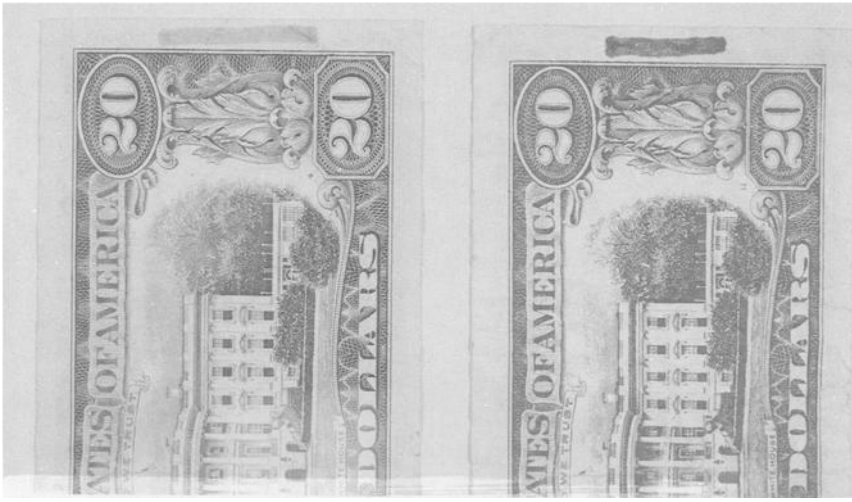

FIG. 2—*A blue streak made by the pH pen (pen #1) on a counterfeit United States twenty dollar bill (top, right), and a yellow streak made with the same pen on a genuine bill show the papers to be alkaline and acid, respectively.*

When discrimination based on the pH pen is added to the above combined discrimination, six groups of indistinguishable pairs remain.

$$\text{D.I. (all three methods)} = 2278 - 6/2278 = 0.997$$

Summary

Based on visual tests run on a limited number of inks, there were no indications that the pH of the paper could produce a change in the visible appearance of the inks.

Out of 68 fine white paper samples, which would make a total of 2278 pairs (questioned and known) for possible discrimination, all but six pairs were discriminated by the three combined methods of physical characteristics, fluorescence under the VSC-I, and pH level as indicated by the pH pen. This was an improvement from 55 indistinguishable pairs left if physical characteristics alone were used, or 20 indistinguishable pairs for combined physical characteristics and fluorescence. Although the addition of microscopic and chemical semidestructive techniques would doubtless give improved discrimination, the discrimination index (0.997) for the three combined methods is already very close to one. Of course, these statistics are only valid for these 68 samples. The average quality of the papers sampled was probably higher than what is most commonly encountered by document examiners.

As more and more mills change over to alkaline paper production, the ability of the pH pen to discriminate between different samples may decrease. However, it will take time to exhaust the stock of acid paper on the market, and even when almost all mills are producing only alkaline paper the pH in the neutral to alkaline range may vary. Also, most large paper companies in the United States are recording changeover dates for the switch from acid to alkaline mill by mill, and this could become advantageous when attempting to establish the date of a document aside from known dating procedures.

Although the pH pen was the least discriminating of the three methods, its use is worth considering since it does improve the overall discrimination, the pen is inexpensive, and the test is quick and easy.

Acknowledgment

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