Stain Resistance as Part of Image Permanence for Consumer Digital Inkjet and Thermal Imaging Systems

Kristine B. Lawrence, Deborah L. Cigna, Wendell J. Brattlie, David Erdtmann, and Joseph E. LaBarca, Eastman Kodak Company, Rochester, NY, 14650-2116, USA

Abstract

Methods for determining overall print permanence or image stability for digital inkjet and thermal photographic prints have been well defined and are used to represent typical "long-term, home storage conditions" for consumer prints. What these methods do not take into consideration are instances where a consumer might accidentally spill substances onto unprotected prints resulting in unwanted staining. Typical substances can range from high staining materials such as coffee to lower staining materials such as milk. In these instances, stain resistance could certainly impact the long-term preservation of consumer prints. To date, the only existing international standards for this type of image degradation include an ASTM procedure for stain resistance and an ISO procedure for water resistance. This paper will discuss the importance of considering stain resistance as part of long-term image permanence criteria for digital consumer color prints and shortcomings associated with the current international standards. In addition, supporting data from several digital inkjet and thermal imaging systems using a variety of staining substances will be discussed.

Introduction

In today's society, many consumers are "going digital" whereby their "precious moments" are captured using digital cameras and prints are made with either home inkjet or thermal printers. With this shift from conventional silver halide capture/professional imaging to digital capture/home printing by consumers, it was necessary to develop procedures that would predict how long digital prints imaged at home by consumers might last. This can also be referred to as overall print permanence or image stability. For the scope of this paper, overall print or image permanence can be defined as all methods necessary to predict how long a consumer print might last once printed. The factors typically used to determine this have included: light (office or daylight illumination), environmental gas (ozone stability), moisture (exposure to high humidity), and heat (album or dark storage at elevated temperatures). These methods have been well documented by several individuals as well as companies for home inkjet and thermal printer systems [1,2].

What has not been well documented in the literature relates to the category of "print or image durability." Print durability can be defined as damage that affects the physical integrity of the print and/or degradation of the image on the print. Factors that can contribute to this type of damage include: excessive moisture causing the print to curl or cockle; image degradation such as smudging, fingerprinting or colorant bleed; and staining of prints caused by accidental spills of common household beverages such as coffee or smearing with foods like peanut butter. With the shift to consumer home printing, there is an increasing likelihood that the overall print quality or image durability could be impacted by one or more of the above factors. If a consumer does not take extra precautions to protect their prints from this type of degradation, the outcome could be that the print is rendered "unacceptable."

Another consideration deals with the limited number of procedures available that can quantify this type of print or image degradation. In fact, there are only two international standards for this type of image degradation in the literature (an ASTM procedure for stain resistance [3] and an ISO procedure for water resistance [4]. As a result, many companies rely on very qualitative metrics to rate image durability and do not always include this metric as part of the overall image permanence ratings.

The remaining portion of this paper will focus on only one aspect of image durability: stain resistance. The first section will present an overview of what methods are currently being used to describe stain resistance and will briefly describe advantages and disadvantages for each. The next section will propose a new test procedure for staining of printed images taking into consideration the positive attributes from current methods in conjunction with the development of a more quantitative method of analysis. The third section will briefly outline what the common household beverages currently are, leveraging data from an international marketing study [5]. From this marketing study, the top 8 beverage categories were selected and 2–4 brands from each category were used in the preliminary evaluation using a relevant inkjet printing system (a system in this context refers to making prints using the default driver settings for the particular ink-media combination recommended for that printer). These results will be summarized and a smaller subset of beverages will be used to evaluate stain resistance across several inkjet and thermal home printer systems, and results from this study will be tabulated. The last section will capture conclusions from these studies along with a proposal of future work needed to move towards development of an international ISO standard for stain resistance.

Literature/Historical Background

As mentioned earlier, there are only two international standards currently in the literature that are used to describe image permanence as a function of image durability (one for stain [3] and the other for water [4] resistance). In addition, Wilhelm briefly describes two additional tests for water resistance (water drip and a water drip with gentle wiping) as part of his procedure for determining water resistance [6]. At first glance, one might think that water and stain resistance are "one and the same" in that most common household beverages that could stain a print are also water based. Although this may be true in some cases, there are other instances where prints having "good water resistance" may still be vulnerable to staining when exposed to the range of substances consumers typically have in their home environments. In a paper published by Sony [7], the author describes use of coffee as part of their method for assessing water resistance. The test involves soaking half of a printed image in coffee and when removed, illustrates how the treated side of the image becomes "stained". This raises the question of whether the prints are truly water resistant or are just more prone to staining with liquids that are highly colored.

In a technical brief published on Epson's website for DURABrite Ultra inks [8], there is a very general description of a procedure for water-resistance and illustrates damage to text of varying colors caused by an excess of moisture or accidental spills. This method is limited to only describing water resistance.

Although the ISO procedure for water resistance [4] takes into consideration several types of damage related to durability, it does not include any metric for capturing unwanted staining of prints that could occur when using water-based solutions that are highly colored such as coffee or fruit punch. In addition, it lacks a quantitative method for analysis causing any results to be very subjective.

For these reasons, it became evident that an evaluation method was needed to differentiate water resistance from stain resistance. The ASTM procedure for stain resistance [3] mentioned earlier is currently the only published international standard for this type of image degradation. In addition, the only other literature references found for stain resistance were within two US patents [9] and the test procedures described in both were very similar to the ASTM methodology.

A brief description of the ASTM procedure for stain resistance is as follows. The test target is composed of blocks of colorant containing color patches at four density fill levels (see Figure 1 below). A measured amount of a staining agent (beverage or food) is placed at the center of each block of colorant so that it wets all density patches within that block of color.

Figure 1: *Example of Block of Colorant from ASTM Test Target*

The staining agents were allowed to stand at room temperature for approximately 15 min, and then blotted off using a paper towel followed by gently wiping with a moistened paper towel. The analysis involved a visual ranking process whereby the treated target was compared to an untreated target and assigned a score ranging from a 1 (no change) to a 4 or 5 (significant stain and/or removal of colorant).

In attempts to follow this procedure several issues became apparent. First of all, the treatment time was too long and would not necessarily reflect what would happen if a consumer spilled something on their print. Secondly, the color patches were too close together, resulting in uneven wetting of each color patch and cross-contamination attributed to colorant bleed. Another concern was the use of a moist paper towel to remove the excess staining agent. This could confound the results because of the introduction of water into the test procedure. Lastly, the method of analysis was very subjective and as stated earlier may vary between different individuals performing the test.

New Procedure Development

This section will describe steps taken to develop a more robust procedure for stain resistance that would combine the positive attributes from existing procedures with necessary modifications. In addition, incorporation of a more quantitative method of analysis will be proposed. The ultimate goal would be to develop an international standard for describing stain resistance that differentiates from water resistance and more closely simulates how a consumer's print might be impacted by accidental spills of common household beverages. For the scope of this paper, the test development will focus on the use of only liquids and beverages as staining agents. Any modifications to this procedure that would broaden the test development to include typical household foods such as mustard or peanut butter will be the topic of another paper.

In efforts to determine the validity of the proposed test methodology, staining agents were evaluated using prints made from a variety of home inkjet printer systems. Printer systems were selected from what is currently in the marketplace and spanned the range of ink (dye or pigment based) and media (porous or swellable) technologies. One thermal and one silver halide system were included in the final phase of evaluation. Because the focus of this paper is test development and not OEM benchmarking, the printer manufacturers will not be disclosed with any results but will only be generically referred to (see Table 1 below).

Table 1: Printer Systems Used for Stain Resistance Test Development

System ID	Ink (Dye or Pigment)	Media (Porous or Swellable)
A	Pigment	Porous
B	Pigment	Porous
C	Dye	Swellable
D	Dye	Porous
E	Dye	Porous
F	Dye	Porous
G	Pigment	Porous
H	Thermal	Thermal
J	AgX	AgX

Currently, Eastman Kodak Company has several test procedures that evaluate ink-media performance as a function of print durability, one of which includes stain resistance of inkjet and thermal consumer prints. This procedure differs from the ASTM procedure as follows: shorter treatment times (30 s in place of 15 min), dry-dabbing excess staining agent (in place of a wet wipe) and utilization of Delta E2000 [10] calculations to quantify the amount of stain present (in place of a visual rank). The test target was quite different from the ASTM method in that it contained patches of red, green, blue, and D-min at only one fill level (70%). This target was quite limiting in that the highest level of staining tended to occur in the lower density regions of a print. Because of this, a new test target was designed to incorporate the positive attributes of the ASTM target (multiple colors at different fill levels) but differed in that all density patches were separated from one another to minimize uneven wetting and cross-contamination of colorant (see Figure 2 below). In addition, three patches containing no colorant (D-min) were added to the target to simulate regions of prints that have little to no colorant present such as a white wedding dress or white bath towel.

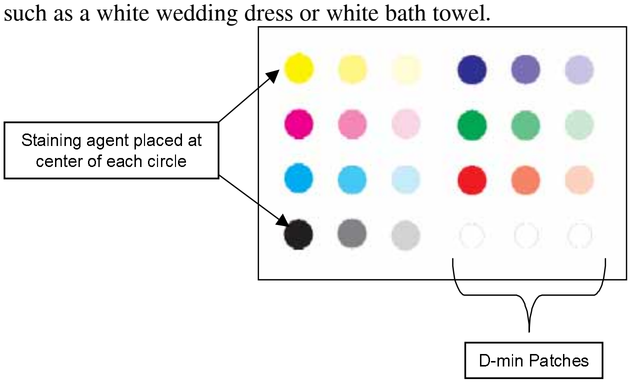

Figure 2: *Proposed Stain Target*

To illustrate these differences, a 2 × 2 experiment was designed using fruit punch as the staining agent with prints made using "Printer System A" (from Table 1 above). The two variables investigated were treatment time (15 min-ASTM vs. 30 s-Kodak) and removal methods (wet wipe-ASTM vs. dry dab-Kodak). Analysis involved collecting density and CIELAB values for all patches before and after staining using a Spectrolino SpectroScan [11]. A Delta E2000 was calculated based on the CIELAB differences before and after staining. The results from this experiment are illustrated in Figure 3 (see Appendix).

From these results, several conclusions were drawn. The level of staining increases when the color density fill level decreases. This was true for all color records and in most cases, the D-min patches where no colorant was present tended to show the largest amount of stain. For both removal methods, the longer treatment times (15 min) yielded significantly higher levels of staining across all color records and fill levels relative to the shorter treatment time (30 s).

When comparing removal methods, differences were only seen at the 15 min treatment time where the "wet wipe" tended to show slightly lower levels of staining than the "dry dab" method. One potential cause for this difference was that "wet wiping" of the stained target introduced water into the test method and removed more of the staining agent than when performing the "dry dabbing" technique. Interestingly, at the 30 s treatment time, the removal method (wet wipe vs. dry dab) had no impact on the amount of staining. For these reasons, it was decided to set the treatment time at 30 s and to use the dry dab method for the removal of excess stain agents from the surface of the prints.

Beverage Selection as Staining Agents

The next portion of the test development was to expand the staining agents to cover typical beverages that might be found in a consumer's household. The ASTM procedure does specify use of coffee and cola in addition to fruit punch as part of its procedure. Two questions to consider at this point were: do these three beverages adequately represent what consumers might accidentally spill on their prints, and secondly, do these liquids span the range of stain severity (low staining to high staining)?

In order to address the first question, data was collected from an international marketing study by Beverage Marketing Corporation to determine what the top beverage categories were worldwide [5]. The projections presented in this paper were determined by Beverage Marketing Corporation and based on data collected from industry executives, trade and research organizations from over 200 countries. A comparison was made between actual volumes from 2005 with projections out to 2010 and the results were quite similar. Because of this, only the projections for 2010 were used to determine what the top beverage categories are worldwide and the results are found in Table 2 below [12].

Table 2: Top Beverage Categories Worldwide

PROJECTED GLOBAL BEVERAGE MARKET
Categories Ranked by Size of Consumption Volume

Category	2010(P) Rank	Thousands of Hectoliters	Thousands of Gallons	Share of Volume
Milk	1	2,785,000.00	73,524,000.00	5.60%
Tea	2	2,565,500.00	67,729,200.00	5.20%
Bottled Water	3	2,050,000.00	54,120,000.00	4.10%
CSDs[1]	4	1,907,000.00	50,344,800.00	3.80%
Beer	5	1,715,490.00	45,288,936.00	3.40%
Coffee	6	1,408,687.00	37,189,336.20	2.80%
Fruit Beverages	7	554,800.00	14,646,720.00	1.10%
Wine	8	263,000.00	6,943,200.00	0.50%
Distilled Spirits	9	180,100.00	4,754,640.00	0.40%
Subtotal		**13,429,577.00**	**354,540,832.20**	**27.00%**
Others**		36,297,944.50	958,265,733.80	73.00%
TOTAL		**49,727,521.40**	**1,312,806,566.00**	**100.00%**

(P) Projected
[1]CSDs refers to Carbonated Soft Drinks
* Includes all beverages, commercial and noncommercial, like tap water
Source: Beverage Marketing Corporation

In a press release dated March 7, 2007; Beverage Marketing Corporation described what the future beverages in the US would be and included carbonated soft drinks (CSDs), sports beverages, bottled water, ready-to-drink (RTD) tea and coffee, fruit beverages, and energy drinks [13].

Keeping the above statistics in mind, two to four brands of beverages were selected from the top seven categories and used as potential staining agents (see Table 3 below). An additional category was added to cover the energy and sports drink arena. Whenever possible, brands that were classified as being "top sellers" for their category were used [13].

Because many of the beverages had different consistencies and wetting properties and varied in acidity (pH range 2.2–7.1), it was of interest to evaluate each one on a variety of unprinted inkjet papers. This was done as a quick screen to determine how robust the application of, time duration, and removal method for each staining agent would be, given the wide range of physical properties for the beverages selected. One drop (0.05 mL) of each beverage was placed on each of the unprinted inkjet papers that were selected, allowed to sit for 30 s, and then dabbed off with a dry paper towel. A visual ranking process (stain severity) was used to quickly assess the level of stain present for each beverage-media combination where 0 = no stain; 1 = light amount of stain; 2 = moderate staining; 3 = high level of staining. The results from this preliminary screening process are summarized in Table 3 below.

With the exception of chocolate milk, yogurt smoothie, and V8 juice (see Table 3), the proposed methods for application and removal of all other beverages worked well. In theses cases, the beverages were problematic in that they were difficult to remove with a dry paper towel and tended to leave either a hazy film and/or solid residue on the media surface. As previously demonstrated, when the time duration for staining was shorter (30 s), the removal method did not impact the final Delta E result (see Figure 3 in the Appendix). Another observation was Media C tended to become tacky when wet, causing the paper towel to physically stick to the media surface during the removal process. When encountering issues such as the ones just described, the wet wipe method of removal is preferred, with the assumption that the result would be the same as dry dabbing.

Bottled water and beer categories showed very little to no staining across all of the media variations evaluated. Because of this, these categories were dropped as potential staining agents.

Hot beverages such as tea or coffee and highly colored fruit drinks such as red fruit punch tended to show the highest levels of stain relative to other beverages. With the exception of Media B, coffee in any form showed significantly higher levels of staining on all media variations.

Table 3: Stain Severity on Unprinted Media

			Stain Severity on Un-Printed InkJet Media[1]						
Category-Ranking	**Proposed Staining Agents (by Brand)**	**Staining Agent Temp**	**Media A**	**Media B**	**Media C**	**Media D**	**Media E**	**Media F**	**Media G**
Milk (cat #1)	Chocolate Milk	11C	2	1	3	1	3	2	3
	Yogurt Smoothie	12C	1	1	2	1	1	1	1
Tea (cat #2)	Lipton Green Tea	23C	0	0	2	0	0	1	1
	Nestea Iced Tea	23C	0	0	2	1	1	1	1
	Red Rose Tea	23C	2	0	3	3	3	2	3
	Red Rose Tea	**60C**	3	0	3	3	3	2	3
Bottled Water (cat #3)	Aquafina Raspberry	23C	0	0	2	0	0	0	0
	Vitamin Water, Balance	23C	0	0	2	0	0	0	0
Carbonated Soft Drinks-CSD's (cat #4)	Coca-Cola	23C	1	0	2	1	1	2	1
	Pepsi	23C	1	0	2	2	1	3	1
	Pepsi One	23C	1	0	2	3	2	3	2
	Mountain Dew-regular	23C	1	0	2	0	0	0	0
	Mountain Dew-Code Red	23C	3	0	2	3	3	3	3
	Mountain Dew-Live Wire	23C	3	0	2	2	3	3	2
Beer (cat #5)	Labatt Blue	23C	0	0	2	0	0	0	0
	Michelob Ultra Light	23C	0	0	2	0	0	0	0
Coffee (cat #6)	Black Coffee	23C	3	1	3	3	3	3	3
	Black Coffee, hot	**63C**	3	1	3	3	3	3	3
	Expresso, Black	**51C**	3	2	3	3	3	3	3
	Starbucks Expresso Double Shot w/Cream	14C	2	1	3	3	3	3	3
Fruit & Vegetable Juices (cat #7)	Fruit Punch	23C	3	1	3	3	3	3	3
	Welch's grape juice	23C	3	1	3	3	3	3	3
	V8 Juice	23C	3	2	3	3	3	3	3
Sports/Energy Drinks (New Age)	Gatorade Frost	23C	1	0	2	1	1	1	1
	Gatorade Cool Blue	23C	2	0	2	2	2	2	1
	Gatorade Fruit Punch	23C	3	1	3	3	3	3	3
	MVP Green Apple	23C	1	0	2	1	1	1	1
	Red Bull Energy Drink	12C	0	0	1	0	0	0	0

[1]Visual ranking for the level of stain present on unprinted media where:

0=no stain ; 1=light stain ; 2=moderate staining; 3=high level of staining; nd=not done

Quantification of Stain Severity

The next step taken as part of the test development process was to determine whether the Delta E2000 metric would be suitable for quantifying stain severity. Prints were made from the new test target (see Figure 2 above) using "Printer System A" and the default driver settings for that printer-media combination. All prints were allowed to dry at room temperature overnight. Each target was then read before staining using the Spectrolino SpectroScan, then two drops (0.10 mL) of each beverage (or staining agent) were placed on each color patch, allowed to stand for 30 s, and any excess liquid was then blotted off using a dry paper towel. The targets were then allowed to dry at room temperature before rereading and a Delta E2000 was calculated for each color patch and recorded. The maximum Delta E across all color patches was determined for each beverage and the results plotted (see Figure 4 in the Appendix). The results from this study both confirmed observations made during the preliminary screen using the unprinted media as well as validated the use of Delta E2000 as a metric for quantifying stain severity.

Results using New Test Method

The last segment needed to complete the test development for stain resistance was to select beverages that spanned the range of stain severity from the study done with "Printer System A" (see Table 3 above) and evaluate them across additional inkjet, thermal, and silver halide printer systems. Beverages selected for this portion of the test development included: chocolate milk, ready-to-drink (RTD) green tea, Red Rose™ tea (brewed), Coca-Cola®, Mountain Dew LiveWire, black coffee (brewed), fruit punch (Red), and Gatorade® Cool Blue™ sports drink. All beverages were allowed to equilibrate to room temperature (23 ºC) before beginning the experiment. The maximum Delta E2000 was calculated for each beverage-printer system combination and the results are summarized in Figure 5 (see Appendix).

From these results, one can see that a wide range of stain severity was achieved across all printer system-beverage combinations. Printer System C exhibited the highest level of stain independent of beverage type, whereas Print Systems B and H showed the lowest levels of stain. Generally speaking, highly colored beverages such as coffee, fruit punch or highly colored CSDs showed more staining than the RTD green tea (very little color). Interestingly, although the Gatorade Cool Blue beverage is not highly colored, several systems showed fairly high Delta E2000 values caused by color changes that occurred with some of the color records when treated. The beverages that span the range of severity as well as represent those most commonly found in consumer's homes were: coffee, fruit punch, Gatorade Cool Blue, and. Mountain Dew Live Wire.

Conclusions and Future Work

With the shift to printing digitally captured photographs in consumer's households, determination of print durability as part of overall print permanence has become extremely important. Several factors that contribute to print quality or image durability were discussed. In addition, literature searches uncovered very few internationally accepted methods of analysis that could quantify the numerous factors that contribute to print or image degradation.

This paper discussed preliminary steps taken towards developing a more robust procedure for stain resistance caused by accidental spills of common household beverages. Marketing studies identified top beverage categories currently consumed worldwide. Method selection was based on the ability to differentiate between unwanted staining of images from water damage. The preferred method to date involves printing a target containing color patches at three density fill levels, placing two drops (0.10 mL) of a staining agent at the center of each patch for 30 s, then blotted off using a dry paper towel. The level of staining present was determined by calculation of the maximum Delta E2000 from CIELAB reads before and after staining across all color patches. Additional work is planned to implement a VOC study that will aid in determining what Delta E2000 values represent acceptable vs. unacceptable levels of print staining to consumers. Additional work is planned to demonstrate any correlation of stain severity with physical properties of the beverages like pH and/or wet properties of the media.

The preferred beverages of choice that spanned the range of stain severity and covered beverages most commonly found in consumer's homes were: coffee, fruit punch, Gatorade Cool Blue, and Mountain Dew LiveWire. Given the fact that an international standard would not allow for the use of actual brand names in a procedure, the recommended beverage categories for a standard would be: coffee, fruit punch and carbonated soft drinks (CSDs). Future work is needed to determine what components in CSDs cause more staining. Once this is determined, a recommendation would be made to better describe the CSD category for use in an international standard.

When dealing with beverages such as milk or juice with pulp, the blotting method was adjusted from "dry dabbing" to a "wet wipe". Additional work is needed to confirm that this method of removal does not confound the final results caused by the introduction of water.

As previously mentioned, this procedure was limited to only beverages. Future work is planned that will describe method development for use of staining substances such as peanut butter or mustard.

Appendix

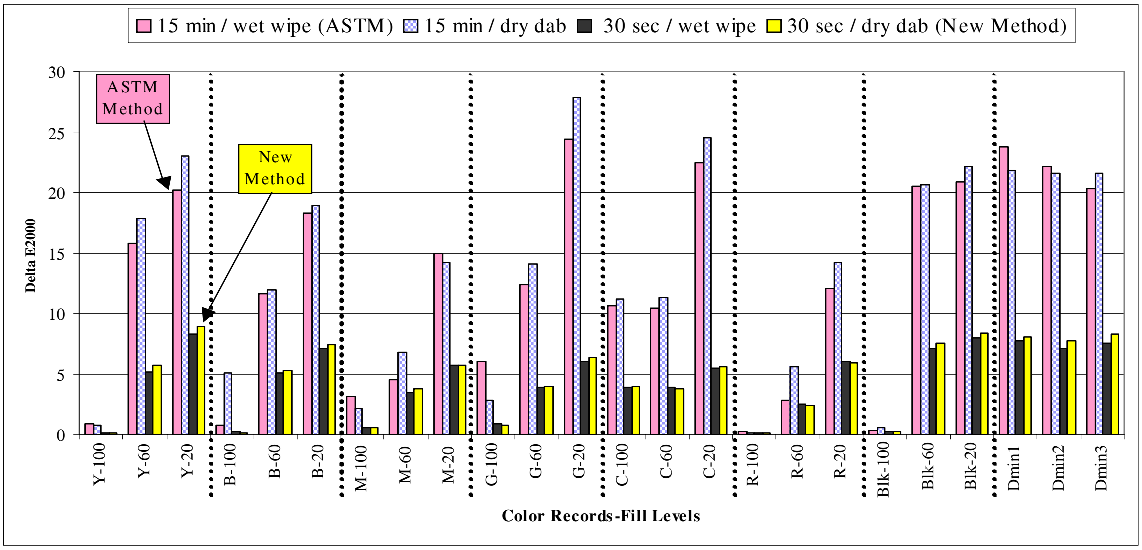

Figure 3: *Stain Severity as a Function of Treatment Time and Removal Methods*

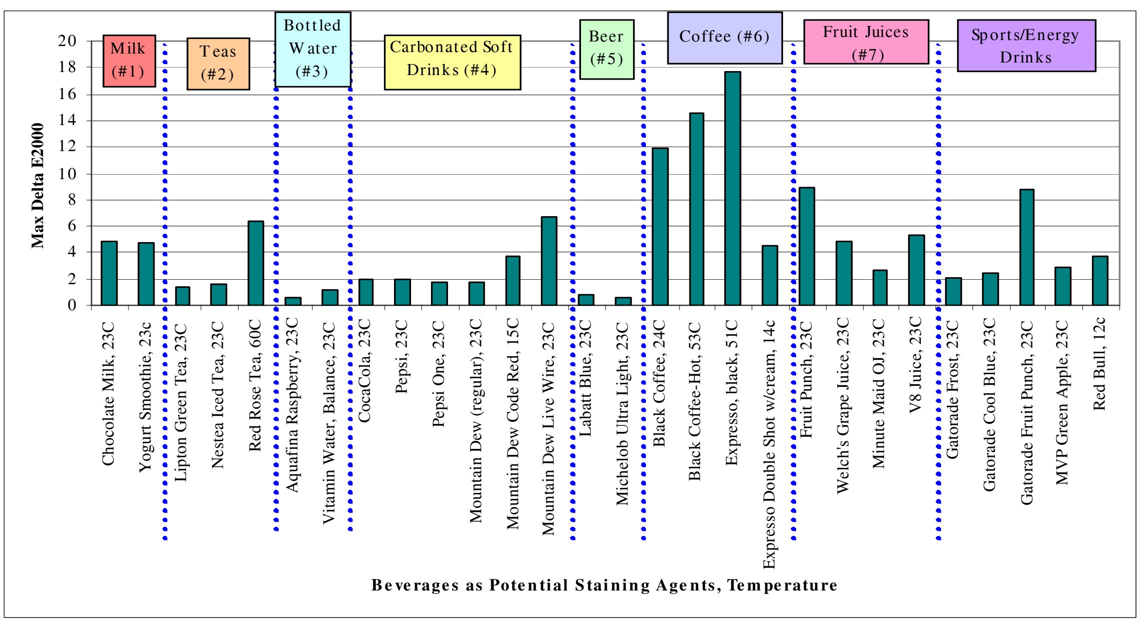

Figure 4: *Maximum Delta E2000 as a Function of Beverage Using Printer System*

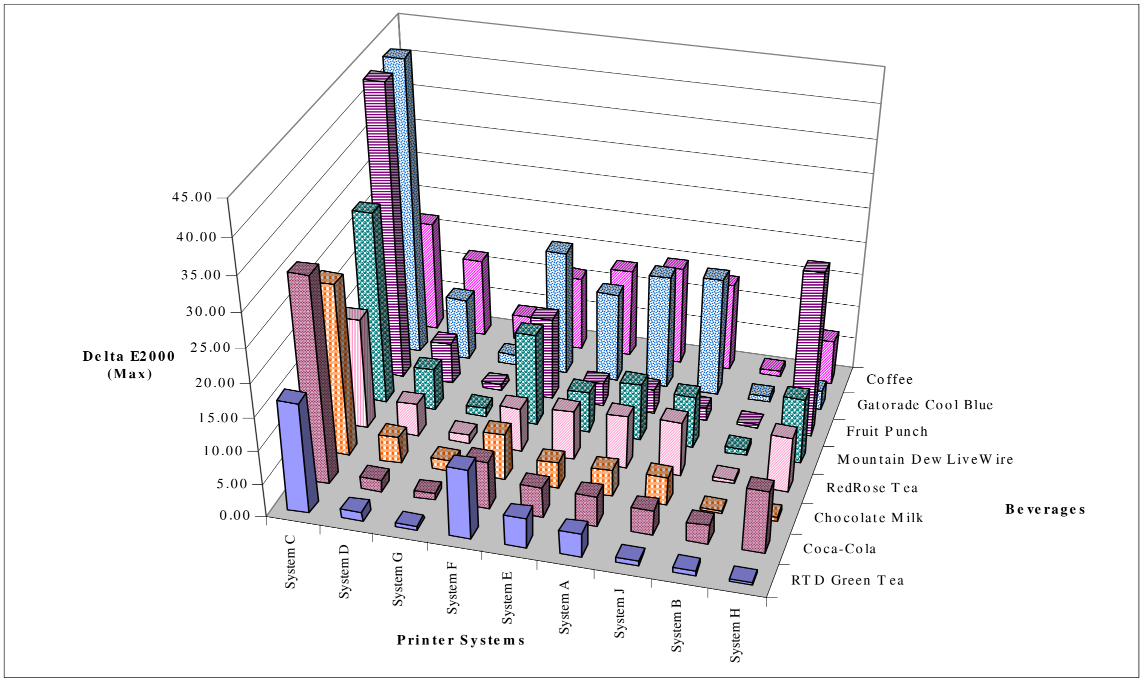

Figure 5: *Stain Severity (Maximum Delta E2000) as a Function of Beverage-Printer System Combination*

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[11] Manufactured by GreyTag Macbeth. Settings include: D50 illuminant, 2deg observer angle, ANSI A density standard, white base=Abs, no filter.

[12] Same as [5], table taken from page 345.

[13] Obtained on internet from Press release dated March 7, 2007 regarding an article published by Beverage Marketing Corporation entitled: "The Future of Liquid Refreshment Beverages in the U.S."

Author Biography

Kristine Lawrence received an Associates degree in Chemical Engineering Technology from Broome Community College in 1982 and a Bachelor's degree in Chemistry from Rochester Institute of Technology in 1989. She has been employed at Eastman Kodak Company in Rochester, New York for 25 years and has worked as a materials scientist/systems evaluator on a variety of digital imaging programs including inkjet, thermal dye transfer, and microencapsulation. She has co-authored 49 issued patents, received a Team Achievement Award in 1990, and was inducted into Kodak's Distinguished Inventor's Gallery in 1999. She has co-authored outside publications in NIP12 and the Journal of Medicinal Chemistry. Kristine is currently working in the Inkjet Photo Materials Lab at the Kodak Research Laboratories in areas of image permanence and durability, and was a key contributor to the recent launch of Kodak's new inkjet system.