Ozone Degradation of Ink Jet Photoquality Images

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Digital images can now be printed using a range of printer technologies. These include thermal transfer (D2T2), electrophotography, and ink jet, all of which are capable of producing photographic-like prints. There has been much interest in the environmental stability of digital images created by the different printer technologies as the overall picture quality comes closer to that of traditional silver halide photographs. The durability properties of images from a range of desktop ink jet printers have been investigated and a comparison of dye and pigment-based ink systems has also been undertaken. Some of the factors that influence the image stability of photographic-like prints produced by ink jet printers are considered. This paper reports on the influence of gas fading or ozone stability of digital images printed onto ink jet photopapers. In particular the stability of dye based inks on microporous media has been investigated. The major influences on the image properties are discussed and the importance of the ink/media interactions are considered. The environment of the colorant was found to have a significant influence on the durability of the image. Much of the research activity in ink jet has focused on attempting to solve durability issues in order to bridge the gap with silver halide photographic images.

Journal of Imaging Science and Technology 48: 153–159 (2004)

Introduction

Digital cameras are becoming increasingly popular with consumers, confirmed by the substantial sales growth seen over the last few years. They are being continually improved bringing them closer to the quality produced by the well established silver halide (AgX) technology. Traditional AgX photographs are generally of a high quality with good color reproduction, and certain photos have been projected to last up to 60 years without noticeable image degradation.[1] This is particularly so when images are protected by storing them in plastic sleeves or behind glass frames. The image permanence of ink jet photo-like images, produced using dye-based inks, is generally not as good as for images produced using AgX technology.

As new generation desktop printers are developed the printing speeds continue to increase. This represents a difficult challenge since the rate of ink absorption by the media has to be increased to keep up with the rate of ink lay-down. Currently the two main classes of ink jet recording media which can give photographic-like quality images are swellable and porous (usually termed microporous) media. These come in glossy and satin forms and typically are supported on either resin (usually polyethylene) coated substrates, well known from conventional AgX, or raw base substrates which are coated with either a layer of baryta or clay in a cross-linked gelatin binder.

The requirement for higher ink absorptivity and high quality images has led to further development of microporous pigment coatings that provide faster drying of the different aqueous ink jet ink systems. Microporous media consist mainly of inorganic pigments, which 'pack' together to form internal voids, and have an inherently 'open' structure leading to virtually instantaneous drying during printing. These media are well-suited to printers containing piezo ink jet head technology but are also suited for faster thermal printer systems. While microporous media provide instant drying they have some disadvantages associated with them, including a reduction in color gamut, a lower gloss, and a higher cost in comparison with the swellable polymer coatings. The most significant problem which has arisen for the microporous media concerns image durability, most noticeably gas fading – particularly ozone.

The photo quality media, based on swellable polymer systems, are less compatible with the current wide range of ink jet printers but are, however, generally suited for thermal ink jet printers. Swellable media are typically composed of water soluble polymer ink absorbing layer(s) and the disadvantages tend to be slow drying of the inks, tackiness of the prints, and bleed and coalescence for certain types of ink systems. Most of the problems are a consequence of the slow rate of ink absorption. Swellable polymer systems also seem to be less compatible with pigment-based ink systems in comparison to the microporous media.

The image stability for dye chromophores varies quite markedly under different environmental conditions such as light, gas, and humidity.[2] Most of the dye-based

Original manuscript received April 10, 2003

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colorants, used in ink jet inks, are water soluble and historically were derived from the textile and paper industries.[3] Some have come from the photographic industry.[4] Other dye systems have been developed specifically for ink jet.[5,6]

For dye-based inks, the image permanence tends to vary quite markedly for the different ink systems present in desktop printers, and on the different media systems available. Some magenta dye chromophores commonly used in ink jet inks have low light stability. Furthermore, these magenta dyes can also have issues with humidity and water fastness.[7-10] There are several methods for prolonging the lifetime of a digital image and these include protecting the image by lamination, and storing in a plastic sleeve or behind glass frames. However, these methods can incur extra cost and can also be inconvenient to the end-user.

Research into solving these durability issues has included the modification of the dyes and/or the recording media to make them less susceptible to fading. The most successful approach will most likely involve the development of the dyes and the media in combination, to provide the optimum performance.

Image Permanence

Some of the factors that determine the permanence of an ink jet image are listed below. This study focuses on gas fastness, which along with light and humidity fastness, are currently the most important for ink jet images.

- Gas Fastness
- Light Fastness
- Humidity
- Water Fastness
- Rubbing/Scratching
- Dark Fading

When ink jet images are exposed to atmospheric pollutants, they can degrade by an oxidizative or a reductive mechanism. The gases present in the atmosphere include nitrogen oxides, sulfur oxides and ozone. It has been determined that ozone causes the most damage and that oxides of nitrogen and sulfur have little impact.[11] Although there may be certain synergistic effects of the combination of pollutants, this paper has focused on the influence of ozone gas on print stability since this has been regarded as the most important environmental gas fading effect.[7] The open structure of the microporous photo papers allows for the rapid uptake of environmental gases, which can diffuse into the coating quite readily, where they can then degrade the colorants fixed within the coating layer. The large surface area of the ceramic inorganic oxides may also play a role providing further activation of the dyes to the fading mechanism, although this is not proven. Moisture levels may also impact the rate of fading for the dyes as they do with light fading.[12]

Initially, we compared the ozone fading of a dye-based image (HP 990cxi) on a microporous photoquality paper with that on a swellable photoquality paper along with a pigment-based ink (Epson 2000P) on microporous photoquality paper. Color blocks at 100% ink lay-down of the dyes were printed. Color changes were then measured using CIELAB colorimetry. L*a*b* values of the various color patches were measured before and after exposure to ozone. The ΔE values were then determined and plotted against time (see **Experimental Section**). Further work monitored the change not only for the primary colors, but also secondary and black colors, to give a more complete picture of ozone fading. It came to our attention that dye-dye interactions can be important in the presence of ozone and some work on this area has been reported elsewhere.[13] Catalytic fading (dye-dye interactions) has also been acknowledged with light fading.[1]

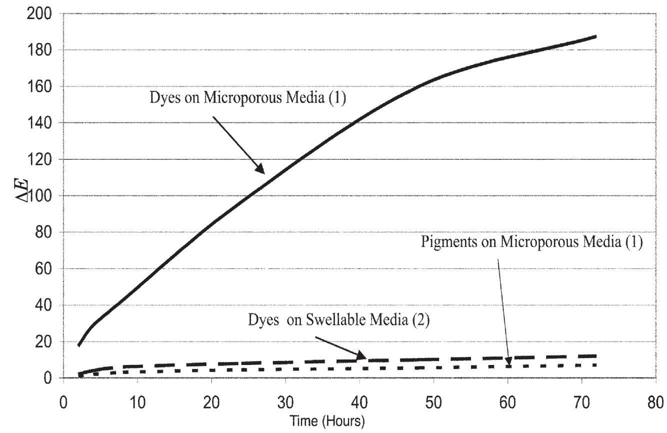

Figure 1. Comparison of Total Delta E for Color Blocks (Y,M,C,K) Printed onto Photo Quality Swellable (2) and Microporous Media (1) upon Exposure to Ozone (3.5 ppm)

TABLE I. ΔE for Dyes Printed onto Photoquality Microporous Paper (1) Upon Exposure to Ozone over Time (ppm × hours)

Ink Jet Photo Quality Printer	Ozone Exposure ppm × hours	ΔE Black	Cyan	Magenta	Yellow
HP 990cxi	84	51.2*	10.1	32.5	6.8
	168	68.4*	15.0	53.5	7.8
	252	77.4*	18.4	65.1	10.2
Epson 870	84	8.5	38.0	8.0	2.1
	168	13.5	42.7	16.0	3.5
	252	16.0	44.0	23.5	4.5
Canon S800	84	52.4	41.9	11.1	4.4
	168	61.2	44.2	12.6	6.4
	252	64.8	44.5	13.1	8.0

* 3-Color black

As can be seen from Fig. 1, the dye-based image has faded significantly on the microporous photo quality paper (**1**), whereas there is only a slight fade observed both for the dye-based image on the swellable photo quality paper (**2**) and the pigment-based image on microporous paper (**1**). Swellable photo quality media (gelatin, polyvinyl alcohol, acrylates) generally act as a physical 'barrier' layer to ozone. A thin film of the polymer probably protects dyes printed onto the swellable media and this reduces significantly the fading of these dyes in the presence of ozone.

Pigmented inks are generally resistant to ozone fading in comparison with dyes (Fig. 1). The large size of the pigment particles (typically 50-100 nm) compared to the monomolecular dyes also contributes to stability during ozone fading. However, extended ozone tests (56 days at 1 ppm) have been reported to lead to fading of certain pigmented inks.[13]

It was of interest to determine which dyes were susceptible to ozone fading on photo quality paper (**1**). From our study, the cyan dyes generally are more susceptible to ozone fading for the small format photo quality printers tested, but certain black dyes and magenta dyes are also quite susceptible to degradation depending upon

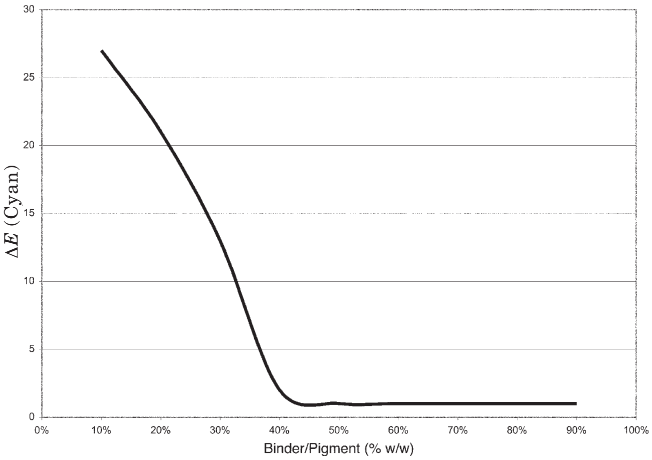

Figure 2. ΔE of Cyan Dye Printed (Canon 8200, Series 5 Inks) onto Media Comprising Different Pigment/Binder Ratio upon Exposure to Ozone (1ppm, 24h)

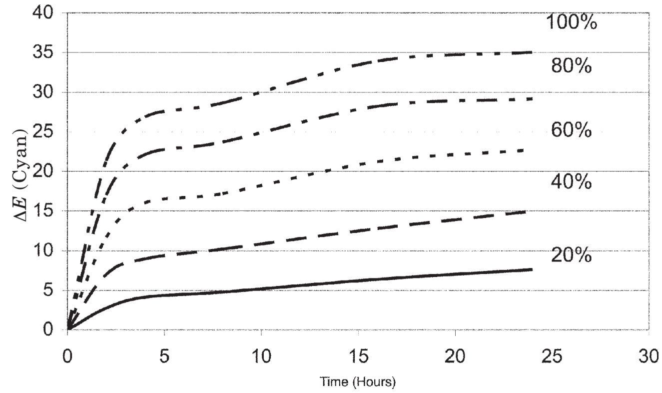

Figure 3. ΔE for Cyan Printed (Canon S800, Series 6 Inks) at Different % Ink Lay Down on Microporous Photo Quality Media (1) upon Exposure to Ozone (1ppm, 24h)

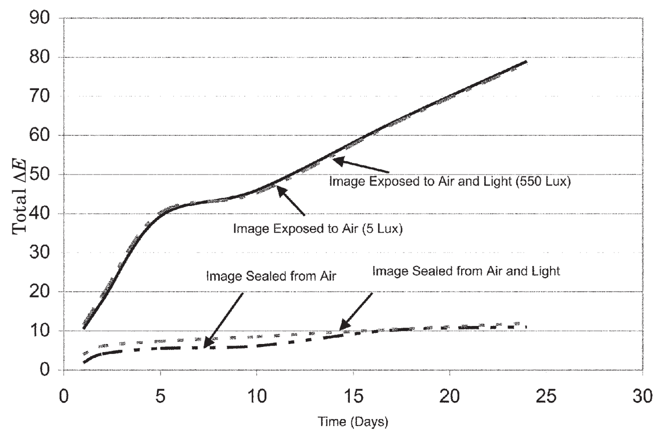

Figure 4. Total ΔE for the Fading for Color Blocks (Y,M,C,K,R,B,G) Printed (Epson 870) onto Microporous Photo Quality Media (1) Exposed to an External Environment

the conditions of exposure to ozone (Table I). In the testing carried out on this paper, the yellow dyes appear to be inherently resistant to ozone fading.

A series of experiments were run to determine when the ozone fading of a cyan dye became significant for coated media upon moving from a binder rich system ('swellable') to a pigment rich system ('microporous'). Coated media were designed with incrementally adjusted pigment/binder ratios (%w/w) of 90/10 through to 10/90 in steps of 10% (w/w). The coatings consisted of two components; polyvinyl alcohol (88% hydrolysis and 40 cps for a 4% solution at 20°C) as binder and a fumed alumina pigment (particle size range 100 to 200 nm; zeta potential of +55 mV and a surface area of 90 m^2/g). The coating was applied at 20 g/m^2 (dry) onto a modified baryta substrate.[14] The cyan (Canon 8200, series 5 inks) color block (100% ink lay-down) was printed onto the media. As can be seen from Fig. 2, the ozone fading for the cyan dyes increases dramatically at pigment (alumina) concentrations of >60%, as the coating becomes more porous. The ink dry times were reduced noticeably at this pigment concentration and higher. At pigment concentrations <60% the inks remained tacky on the surface of the media for >10 min.

It was also of interest to determine which concentration of cyan dye is the most susceptible to ozone fading. Microporous photo quality paper (**1**) was printed (Canon S800, series 6 inks) with color blocks of cyan dye at 20% (0.54), 40% (1.15), 60% (1.88), 80% (2.37) and 100% (2.45) ink lay-down. The optical density values measured for these color blocks are shown in the parenthesis. There was a greater ΔE shift seen for the 100% ink lay-down (higher optical density) compared with the 20% ink lay-down for this cyan dye (Fig. 3). Ozone fading of the cyan dye is directly related to the dye concentration (% ink lay-down). This is a different result from that observed for accelerated light fading of magenta dyes on microporous photoquality paper (**1**), where we observed that the color lay-down of 40-80% (depending on small format printer used) was most susceptible to fading.

Outdoor Fading of Images

A print (Epson 870) on microporous paper (**1**) was exposed outdoors to air only (light level at 5 Lux) and compared to the same print sealed (PVC sleeve) from air but exposed to light (light level at 550 Lux). Both samples were stored for 24 days in a 5-sided wooden box, which was shielded from rain and direct sunlight. The temperature ranged from 2 to 14°C and humidity ranged from 40% to 90%. As can be seen the photoquality paper that has been exposed to air faded significantly, whereas the print sealed from air but exposed to light showed little fade over the same time period (Fig. 4). Subsequently, a print (Epson 870) on microporous paper (**1**) was exposed outdoors to both light (light level at 550 Lux,) and gas and compared to the same print sealed from both air and light. Both samples were stored for 24 days in under identical conditions as stated above. The color print on the photoquality paper exposed to both air and light has faded whereas the print sealed from both air and light has shown little fade.

It can be seen that the fading (Total ΔE) of the colors occurs at a similar rate when exposed to both air and light in comparison to samples exposed to air in the absence of light. This suggests that after this time period, it is the atmospheric gas that contributes most to the dye fade under these test conditions. The print, sealed from the environment, does not show any significant fading. It was observed that the cyan dye faded

TABLE II. ΔE for Color Blocks (Epson 870) Printed onto Photoquality Microporous Paper (1) upon Exposure to the Environment for 24 Days

Environment	Exposure (Days)	ΔE						
		Black	Cyan	Magenta	Yellow	Blue	Green	Red
Air only	1	0.80	0.81	1.06	0.21	4.21	1.20	2.22
	2	1.36	0.72	2.39	0.54	8.48	1.40	2.81
	5	4.36	9.26	2.76	0.84	14.42	4.85	2.80
	10	6.59	12.82	1.83	1.27	14.88	7.23	1.32
	17	9.19	17.39	2.59	2.96	19.57	9.35	2.12
	24	12.10	23.10	3.10	3.50	24.50	11.50	2.16
Air and Light	1	1.29	0.53	1.28	0.20	4.36	1.01	2.88
	2	1.99	1.51	2.22	0.98	7.61	2.65	2.19
	5	4.56	9.36	2.60	1.87	13.35	6.06	2.44
	10	6.20	11.85	1.97	1.95	14.14	7.90	1.26
	17	8.59	16.46	2.55	4.02	19.30	9.81	2.03
	24	10.12	23.05	3.24	4.15	24.45	11.23	2.12

TABLE III. ΔE for Color Blocks (Canon S800, Series 6 Inks) Printed onto Microporous Photoquality Paper (1) upon Exposure to an Outdoor Air flow over 5 Days

EnvironmentOutdoor	Exposure (Days)	ΔE						
		Black	Cyan	Magenta	Yellow	Blue	Green	Red
No Air flow	5	3.4	0.3	0.6	0.7	3.2	6.2	4.3
Air -Flow	5	21.8	12.6	1.0	2.6	7.2	3.1	2.5

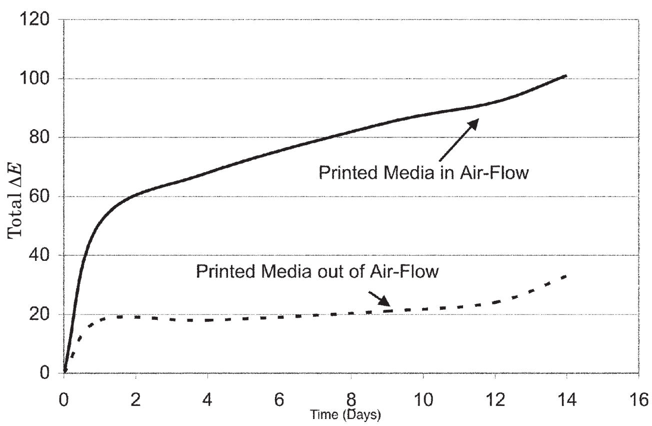

Figure 5. Total ΔE for the Fading of Color Blocks (Y,M,C,K,R,B,G) Printed (Canon S800, Series 6 Inks) on Microporous Photo Quality Media (1) Exposed to an Outdoor Environment – with and without Air-Flow

predominately in these tests, which had an impact on the ΔE for the green and blue secondary colors (Table II). The black dye also showed some fading under these conditions.

A world-wide survey to determine the outdoor ozone levels revealed concentrations from 2 ppb to 80 ppb, depending very much on the location.[16] The concentration of ozone in cities is generally lower than in the countryside and this is probably due to ozone reacting with other pollutants (NO) in the atmosphere generating NO_2, for example.[16] In rural areas away from industrial pollution this may be not so prevalent. This concentration range for ozone is relatively low and was recorded at <20 ppb at our test site. Focusing on the faded samples after 24 days and assuming an average ozone concentration of 20 ppb per day at our test site gives rise to an ozone exposure level of 11.52 ppm-hours. Repeating the test for a duplicate image placed in the ozone chamber at 3.5 ppm for 3.3 hours yielded a ΔE for the cyan dye of 8.1, magenta 4.1, yellow 2.0 and black 2.1. This amount of fading is significantly lower than the ΔE for the cyan dye of 23.1, magenta 3.1, yellow 3.5 and black 12.1 (Table II) after 24 days exposed to the environment, which may indicate that moisture, temperature, and other gases (including oxygen) may also play a role in the fade mechanism outdoors.[12]

Moreover, for the outdoor tests the air flow over the printed image seems to be significant. Two identical microporous paper (**1**) samples were printed (Canon S800, Series 6 inks) with color blocks and were exposed outdoors but kept out of light (light level at 5 Lux). One sample was shielded from the air flow while the other was exposed to natural air flow. As seen from Fig. 5 the image exposed to the air flow showed accelerated fading of the printed image. The total ΔE for the color blocks upon exposure to an outdoor air flow after just 5 days are shown in Table III. Significant fading was observed after just 5 days exposure to the air flow. The black dye has undergone the most fading (ΔE of 21.8) followed by the cyan (ΔE of 12.6). The magenta and yellow dyes appear quite stable. A similar situation was observed in an office environment (23°, 60% RH) where a printed image was exposed to an increased air flow (desktop fan) but protected from light, faded faster than a sample shielded from an air flow. The rate of fading is less than that seen outdoors but this may be due to the lower concentration of ozone indoors compared to outdoors.[12]

Investigations were carried out to determine the influence of different ozone concentrations on the fading of a printed image. Therefore, the color blocks were printed (Epson 890) onto microporous paper (**1**) and one sample was placed in the ozone chamber at 3.5 ppm for 16 hours (total exposure of 56 ppm-h) and the other placed in the ozone chamber at 1 ppm for 56 hours (total exposure of 56 ppm-h). Figure 6 illustrates that the fade rate of a printed image is faster with a higher ozone concentration of 3.5 ppm, compared to that at 1 ppm, under the

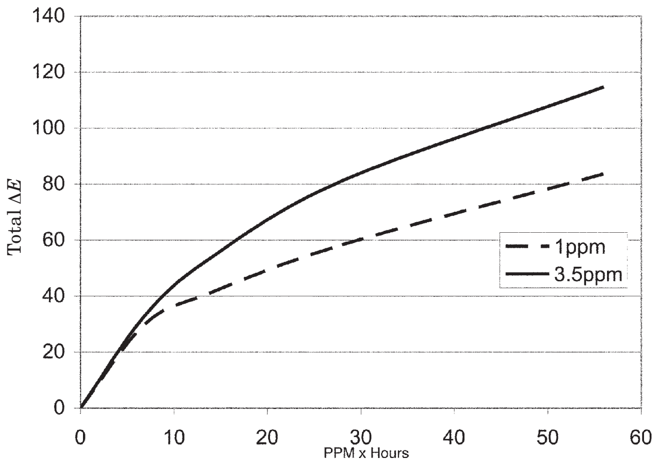

Figure 6. Comparison of the Total ΔE for the Fading of Color Blocks (Y,M,C,K,R,B,G) Printed (Epson 890) on Microporous Media (1) Exposed to 1ppm and 3.5ppm Ozone

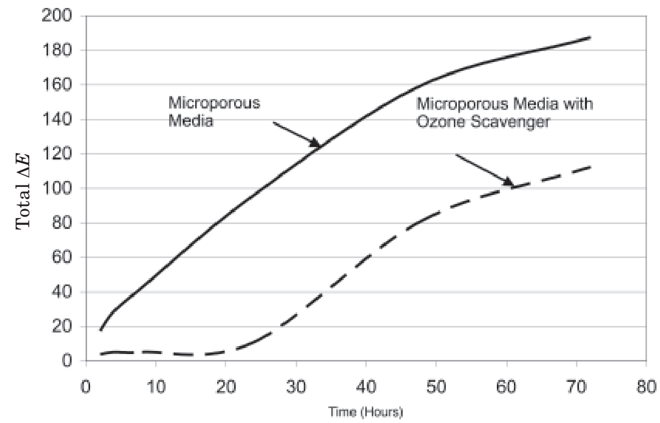

Figure 7. Total ΔE for the Ozone (3.5 ppm) Fading of Color Blocks (Y,M,C,K,R,B,G) Printed (Epson 890) onto Microporous Media (1) Containing a Reducing Additive

TABLE IV. ΔE of Cyan Dye (Epson 890) on Microporous Photoquality Media (1) upon Exposure to Ozone (3.5ppm, 24h)

Paper **1**	ΔE Cyan (Epson 890)
Uncovered Image	37.5
Image covered with aqueous polymer overcoat (0.5 μm)	0.25
Image laminated with a polyester sheet	0.25

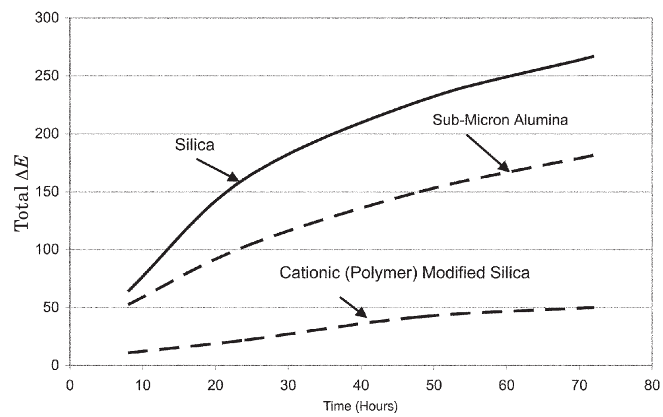

Figure 8. Total ΔE for the Ozone Fading (3.5 ppm) of Color Blocks (Y,M,C,K,R,B,G) Printed (Canon S800, Series 6 inks) onto Microporous Media Containing Silica alone, Silica 'Modified' with Cationic Polymer and Alumina

same temperature (25°C) and relative humidity (50%) conditions. This may indicate that at higher ozone concentrations other reactions occur with the dyes which do not happen at lower ozone concentrations.

Circumventing Ozone Fading of Dye-Based Images on Microporous Photoquality Paper

One method of preventing ozone to react with the dye-based image is to apply a covering layer. Thus, laminating the print with a polyester sheet or alternatively applying to the surface of the print a thin 5% polyvinyl alcohol polymer solution overcoat (0.5 μm) prevents ozone fading by acting as a physical barrier to the gas (Table IV). A further solution to the gas fading problem could be to store the image behind a glass frame. However, these approaches can be inconvenient and involve extra cost.

A second approach involves incorporating reactive antioxidant additives into the microporous coating, to assist in 'scavenging' the ozone. The ozone reacts preferably with the additive compared to the dye, thus prolonging the lifetime of the latter. Antioxidants are useful until they are consumed, after this time the fading accelerates at the expected rate (Fig. 7).

Most ink jet prints on microporous media containing inorganic pigments such as silica, alumina, calcium carbonate, clay, titanium dioxide have a problem with ozone fading. However, modification of the pigment surface can assist with this issue. As demonstrated in Fig. 8, dye-based images (Canon S800, series 6 inks) on microporous silica containing media (80% w/w silica and 20% w/w partially hydrolyzed polyvinyl alcohol binder at 25 g/m^2 (dry) on 170 g/m^2 resin coated substrate) are poor for ozone fading but for the same silica modified with a cationic polymer (<1% w/w), a significant improvement in ozone fading is observed. For example, silica modified with poly(diallyl-dimethylammonium chloride), dicyandiamide, had a zeta potential of +18 mV with a particle size distribution of between 50 and 500 nm and surface area of 200 m^2/g. The zeta potential of the 'standard' silica used was –18 mV indicating a negatively charged surface, with a similar particle size distribution. A medium containing submicron alumina (80% w/w and 20% w/w in partially hydrolyzed polyvinyl alcohol binder) also reduces the impact of ozone degradation on the dye-based image in comparison to silica. The alumina is cationic in nature; its zeta potential was +25 mV with a particle size distribution of 100-300 nm and a surface area of 90 m^2/g. Thus, there is an indication that a higher inherent cationic nature of the coated media improves the ozone fading of the dye-based images (Fig. 8).

Ozone Fading of Images on Other Media Types

Finally, a comparative study was performed of the ozone fading of an image printed onto glossy microporous photo quality paper (**1**), standard matte coated ink jet paper (**3**), and plain copier paper (**4**) with dye-based (Canon S800, Series 6 inks) and pigmented (Epson C70)

TABLE V. Ozone Fading (3.5 ppm) of Inks Printed onto Different Media Types

Media#	Printer	Ink Type	ΔE						
			Black	Cyan	Magenta	Yellow	Blue	Red	Green
1	Canon S800	Dye	37.1	34.9	9.1	4.8	40.4	4.7	14.5
3	Canon S800	Dye	4.9	15.7	3.8	2.7	14.1	1.7	1.5
4	Canon S800	Dye	0.3	10.5	1.2	0.5	5.2	0.4	1.6
1	Epson C70	Pigment	0.2	3.7	2.0	0.6	2.4	0.8	0.3
3	Epson C70	Pigment	1.0	13.5	3.8	0.8	8.6	2.4	1.2
4	Epson C70	Pigment	2.0	10.8	3.8	1.1	6.7	3.3	1.4

see Experimental Section for details

ink. The samples were placed simultaneously in the ozone chamber at 3.5 ppm for 24 h. As the results in Table V demonstrate the image printed onto the microporous photo-quality paper (**1**) showed significantly more ozone fading in comparison to the standard matte grade (**3**) and to the standard copier paper (**4**). For all media the cyan dye has faded the most and the yellow dye was the most stable. Interestingly, for paper (**1**) the black and cyan dyes have given Δ*E*'s of 37.1 and 34.9, respectively. However, with both media types (**3**) and (**4**) the cyan fading observed is much more significant than for the black dye. Moreover, with plain paper (**4**) the fading of the secondary colors is seemingly lower. The pigmented inks (Epson C70) are, as expected, much more resistant to ozone fading than the dye set. It is the cyan pigment that has faded the most noticeably with this media set but, interestingly the pigment inks have faded very little on the microporous photo-quality paper (**1**). More fade has been observed with the standard matte grade (**3**) and the standard copier paper (**4**).

The reason why the dye-based ink set fades more readily on microporous paper (**1**) in comparison with the plain copier paper (**4**) is not clear, but the large surface area of the ceramic pigments in paper (**1**) may play a role in accelerating the reaction of ozone with the dyes. It would be expected that all three media types have a very 'open' structure (as they quickly absorb the aqueous inks) and that ozone gas would readily diffuse into the media and be available to react with the dye molecules.

Why the pigmented ink set is seemingly so stable on medium (**1**) in comparison to media (**3**) and (**4**) is not clear, but is an interesting observation.

Experimental Section

Media

***Paper* (1):** Composed of >80% (w/w) alumina pigment (average particle size 80-200 nm; surface area 90-120 m^2/g; zeta-potential of +35 mV) and hydrolyzed polyvinyl alcohol binder (viscosity of 25-40 cps for 4% solution at 25°C) coated at 30 g/m^2 onto a resin coated substrate. The substrate was a double-sided resin coated paper, 150 g/m^2 raw base, with the face-side resin containing 15% TiO_2.

***Paper* (2):** Commercial HP Premium Photo Paper

***Paper* (3):** Composed of 45% (w/w) silica pigment (average particle size 5-6 μm; surface area 300-400 m^2/g) and 50% (w/w) polyvinyl alcohol binder (viscosity of 26 cps for 4% solution at 25°C) and 5% (w/w) poly(diallyldimethylammonium chloride) cationic polymer coated at 6 g/m^2 (dry) onto a 90 g/m^2 raw base.

***Paper* (4):** 80 g/m^2 office bond "plain" paper.

Methods

Photo quality ink jet media printed with small format photo printers (HP990cxi Deskjet, HP970cxi Deskjet, Epson Stylus Photo 890, Epson Stylus Photo 870 [6-color photo printers], Canon S800 Photo Printer [6-color photo printer, Series 6 inks], Epson Stylus Photo 2000P [6-color pigment ink photo printer], Epson C70 [4-color pigment ink printer]. Optical density and CIELAB L*a*b* of the color blocks (1 cm diameter) were recorded using an X-Rite Color Digital Swatchbook, model DTP22, X-Rite, Inc, Grandville, MI, USA.

All media were printed in an environment of 23°C, 50% RH and allowed to dry for 8 h under these conditions prior to any CIELAB colorimetric L*a*b* measurements. Δ*E* was determined from the difference in L*a*b* before and after fading of the primary (1°) colors cyan, yellow, magenta, and secondary (2°) colors blue, green, and red and black, and is determined by the following equation:

$$\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2}$$

Total Δ*E* was determined by summing the Δ*E* for each color block printed.

Light levels (Lux) for outdoor tests were recorded using a Photometer model SI (Inserv). Zeta potential was measured using the electro acoustic technique from a DT-1200 instrument (Quantachrome UK Ltd). External ozone levels were recorded using an EZ-1X ozone monitor (Dryden Aqua, UK).

Ozone Test

Samples were exposed in an enclosed ozone chamber (Textile Innovators Corp.) at an ozone concentration of 3.5 ppm over a specified time. Temperature was 23°C and relative humidity was at 50%. In addition further ozone testing was carried out using a 1 ppm M287 Ozone Test Chamber (SDL International Textile Testing Solutions). Temperature was 23°C and relative humidity was at 50%.

Conclusions

The development of ink jet media has advanced considerably over recent years; however, the trend towards microporous coatings for ink jet papers to provide instant drying of the ink has introduced a new problem of gas fading for the dye-based inks. In contrast to light fastness where the magenta inks tend to demonstrate the poorest stability to light, it is the cyan inks which are most susceptible to ozone fading. This appears to be a direct result of the attack by ozone on the phthalocyanine ring system destroying the chromophore. To avoid the gas fastness problem on microporous photo-like media there are several options, including modification of the dye structure, protection of the dyes using either reducing additives or certain polymer systems in order to scavenge the reactive gas, or by choice of pigment utilized in the media. These options offer an alternative to protecting the dye-based image with a barrier layer—a laminated polyester sheet, for example. Pigmented inks are much more stable to environmental fading than the dye based systems; however, the cyan pigment still shows some problems with extended ozone fading. Dye/media combinations have helped improve the light fastness of certain dyes, on microporous media, and this approach may offer the best option for circumventing the gas fade issue. Currently, swellable polymer systems provide the best environment for the protection of dyes from gas fading.

References

1. H. Wilhelm and M. McCormick-Goodhart, An overview of the permanence of inkjet prints compared with traditional color prints, *IS&T's Eleventh International Symposium on Photofinishing Technologies*, IS&T, Springfield, VA, 2000, p. 34.
2. A. J. Lavery, J. Provost, A. Sherwin, and J. Watkinson, The influence of media on the light fastness of ink jet prints, *Proc. IS&T's NIP14*, IS&T, Springfield, VA, 1998, p. 123.
3. P. Gregory and P. Gordon. *Organic Chemistry in Colour*, Springer, Berlin, 1983.
4. A. J. Lavery and J. Provost, Colour-media interactions in ink jet printing. *Proc. IS&T's NIP13*, IS&T, Springfield, VA, 1997, p. 437.
5. P. Gregory, Ed., *The Chemistry and Technology of Printing and Imaging Systems*, Blackie, London, 1996.
6. M. Fryberg, R. Hofmann and P.-A. Brugger, Permanence of ink jet prints: a multi-aspect affair. in *Recent Progress in Ink Jet Technologies*, Vol. II, IS&T, Springfield, VA, 1999, p. 419.
7. P. Wight, Issues in ink jet stability. *Proc. IS&T's NIP16*, IS&T, Springfield, VA, 2000, p. 95.
8. S. Schüttel and R. Hofmann, The influence of diluted inks and drying on the lightfastness of dye-based ink jet prints. *Proc. IS&T's NIP15*, IS&T, Springfield, VA, 1999, p. 120.
9. M. Fryberg and R. Hofmann, Influence of dye structure on permanence. *Proc. IS&T's NIP16*, IS&T, Springfield, VA, 2000, p. 95.
10. A. J. Lavery, Photomedia for ink jet printing. *Proc. IS&T's NIP16*, IS&T, Springfield, VA, 2000, p. 216.
11. H. Onishi, M. Hanmura, H. Kanada, and T. Kaieda, Image permanence of ink jet photographic prints. *Proc. IS&T's NIP17*, IS&T, Springfield, VA, 2001, p. 192.
12. B. Vogt, *Stability Issues and Test Methods for Ink Jet Materials*, Thesis, Department of Image Engineering, University of Applied Science, Cologne, Germany, 2001.
13. D. E. Bugner and P. Artz, A comparison of the image stability of digital photographic prints produced by various desktop output technologies, *IS&T's NIP18 Conference on Digital Technologies,* IS&T, Springfield, VA, 2002, pp. 306–309.
14. R. A. Barcock, A. Dodds, K. Werner, D. Becker, Inkjet recording material comprising pigment layers , US Patent 6,502,935 (2003).
15. http://www.thesalmons.org/ozone/ozonemap.html