Effect of Ozone Exposure on Inkjet Prints

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Abstract

With the penetration of inkjet printers into the professional photographic market, image permanence of the prints produced on an inkjet printer has become a much-debated issue. One of the factors affecting the image permanence is the effect of ozone. Certain organic dyes present in the inkjet inks have been found to be vulnerable to degradation by atmospheric ozone, a strong oxidizing agent.

In order to understand and observe the effect of simulated ozone exposure on prints made on an inkjet printer, tests were performed under controlled conditions. We believe this to be the first such test performed on inkjet prints by an unbiased third party. The results did provide indication that the degradation of the prints had some dependency on the substrate. The results showed that for one particular dye colorant set the fading of Cyan colorant caused objectionable color differences. Compared to dye based colorant, pigment colorant set proved to be very stable. Two different substrates on a pigment based inkjet printer and four different substrates on a dye based inkjet printer were tested.

Introduction

Professional photographers are increasingly adapting the digital platform for their complete imaging chain. The use of inkjet printers for color photographic reproduction has increased tremendously over the past couple of years. With better image quality, faster prints as compared to traditional process, and lower cost of the printers; the use of a higher end desktop inkjet printer has found acceptance in the professional photographic community. The longevity of the photographic prints on inkjet media has become a much-debated issue. Some of the durability issues are lightfastnness, water fastness, gas fastness etc. This study investigated the effect of atmospheric ozone of prints made with inkjet printers on different substrates using dye colorants and pigment colorant. The effect of ozone is quantified in terms of their color change.

Background

Atmospheric Ozone and Other Pollutant Vapors

In recent years, many studies on the effect of pollutant vapors on printed images and books have been undertaken. Ozone, sulfur dioxide and nitrogen oxides have received attention in view of permanence of printed material.[1] Ozone, which is a strong oxidizing agent, reacts with the double bonds of organic dyes and changes the structure of the delicate complex structural arrangement within the dye molecule. Studies have been conducted previously on, the effect of ozone on the colorant solutions without the influence of an inkjet receptive layer[2] and on the effect of ozone on one type of inkjet media using different dye based colorant sets.[3] In this study the combined effect of colorants and inkjet media was evaluated.

Inkjet Media

Inkjet media is either the simple sized paper or those formulated by coating an ink receiving layer onto a substrate either paper, film or resin-coated paper. The coating layer is a complex mixture of binders, pigments, fixing agents, optical brighteners etc. In media with porous structures, like simple sized papers, primarily the capillary movement of the ink droplets from the media surface absorbs the ink. In most coated inkjet media, the ink is absorbed by molecular diffusion of the ink droplets into the media through ink medium interaction.

Inkjet Inks – Dyes and Pigment Based Colorants

There are two different types of colorants used in inkjet printers today. One type is the soluble organic colorants which are the ‘dyes’ and the other being insoluble inorganic colorants which are the ‘pigments’. Dye colorants have low molecular weight and are relatively small in size. Pigments are insoluble colorants, which are applied as fine particles to the media.

The chemical nature of the colorant largely determines the extent of interaction with media. Upon printing, dye based inks will diffuse into the substrate with the solvents. Whereas the pigment particles essentially remain at the surface of the ink jet layer while the solvent diffuses into the substrate.

Experimental

In order to test the effect of ozone on inkjet prints, two different kinds of substrates – paper glossy media, and resin coated media were selected. Two different colorant sets – dye based and pigment based colorant sets were chosen to test the effect of ozone on these different colorant sets.

The test samples upon being printed by the two different inkjet printers were sealed in a light blocking box and were transferred to the ozone chamber at the Image Permanence Institute (IPI) at Rochester Institute of Technology. The ozone chamber which has been described in previous studies,[1] was used for testing the samples at 1ppm of ozone gases at 25°C, 50% RH. The control prints were also stored at these relative humidity levels without any ozone gases, in order to make a true comparative analysis. Table 1 below lists the ozone levels as recommended by EPA and the test conditions. The prints were left in the ozone chamber and one set was retrieved after every 24 hours for five consecutive days.

Table 1. Ozone levels and the tested rate

Upper limit ozone levels as per EPA	0.2ppm/8hr day
Ozone level tested in this study	1ppm
24 hrs exposure in ozone chamber ~	40 days exposure
48 hrs exposure in ozone chamber ~	80 days exposure

Methodology

The test target consisting of 288 color patches evenly sampled in the CIELAB color space, was printed on all the different substrates on two different printers. One inkjet printer using dye based inkjet colorants and another large format inkjet printer using pigment based colorants, were used to reproduce the test target. With the large format inkjet printer two different substrates – paper glossy substrate and resin coated substrate; were used to produce the samples. On the desktop inkjet printer, four different substrates – two paper glossy substrate, two resin coated substrates; were tested. Of the two resin coated substrates tested on the desktop inkjet printer, one was known to have a microporus coating.

For each substrate tested, a total of six prints were made. One set of prints from each substrate was retained as control print and saved in a light tight box. The other five prints on each substrate were then placed in the ozone chamber for accelerated ozone fading. Prints were retrieved every day for five consecutive days.

For monitoring color changes caused by ozone exposure the patches on the test page were measured with a GretagMacBeth SpectroLino spectrophotometer. The CIELAB color coordinates under D50, 1931 2° observer were obtained for the prints removed from the ozone chamber and for the control prints. The color difference expressed as ΔE^*_{ab} was quantified for each print between the control print and the print which had been subjected to accelerated ozone exposure.

Results and Discussions

Overall Color Changes

The results seemed to suggest that the color changes were dependent on the colorant. The prints made with pigment inks did not show any significant color change whereas the prints made with dye inks showed tremendous color change. This has already been reiterated by previous studies.[4,5,6] The color changes were noticeable for all but three substrates even with a simulated 40 days ozone exposure. Calculating the ΔE^*_{ab} from the measured data, showed that the substrate by itself did not display a fade. The average ΔE^*_{ab} for the substrate are as shown below, in Fig. 1. From the graph it can be observed that for three of the six different samples, the average ΔE^*_{ab} was greater than 3. For four out of the six samples, ozone exposure of 12 months would produce a very huge color difference as shown in Fig. 1. Table 2 below lists the minimum, maximum and average ΔE^*_{ab} for all the samples.

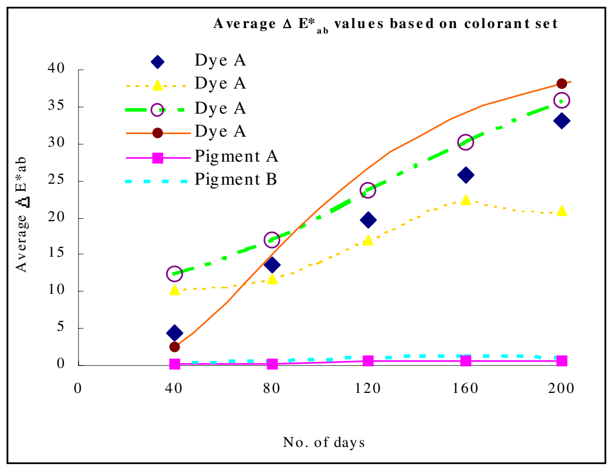

*Figure 1. The average ΔE*ab for all the printed samples.*

Table 2 . The minimum, maximum and average ΔE*ab for all the substrates.

Substrate	Minimum ΔE^*_{ab}	Maximum ΔE^*_{ab}	Average ΔE^*_{ab}
Resin coated	0.592	60.891	19.326
Clay coated	0.262	37.041	16.475
Microporus	0.032	66.313	31.306
Paper glossy A	0.073	2.013	0.450
Paper glossy B	0.051	4.437	0.956
Paper glossy C	0.066	66.109	23.852

The hue differences between the control and the prints taken from the ozone chamber were also calculated for all the patches. From the analysis the following observations were made.

(i) All the patches, which primarily were composed of Cyan colorant, showed that the colorants were fading. The measurement data supported this with the lightness component of ΔE^*_{ab} having the largest difference.

(ii) Those patches, which were composed of Cyan and Yellow, appeared to have faded too due to the fading of the Cyan colorant. Hence some of the green patches turned yellow.
(iii) The patches that were a combination of Cyan and Magenta turned orange from violet on those patches, which had higher dot area coverage of Cyan.
(iv) The significant hue shift that was noticed was in those patches that were a combination of all the three primary colors – Cyan, Magenta, and Yellow. Due to the fading of the Cyan colorant, most of these patches turned orange.
(v) On those patches, that were composed of all the four primary colors – Cyan, Magenta, Yellow and Black, the patches turned brown. These patches, which were black on the control print, showed a huge color difference because the Cyan colorant was faded and the combination of Magenta, Yellow, and Black produced a brown, which reduced the D_{max} of the print.

Figure 2 below demonstrates the individual colorant fade rates. The figure above denotes the average trend found in most of the samples that showed a tendency to fade. From Fig. 2 above it can be noted that the patches with Cyan and Magenta colorant have had the huge color difference and the patches with all the four colorants also have very large color differences.

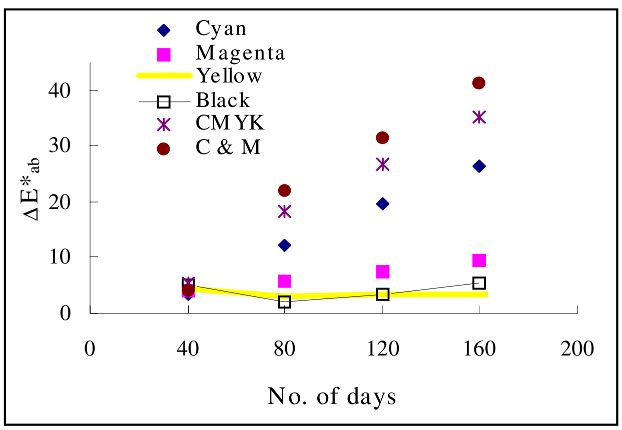

Figure 2. The trend of individual colorant fading based on the Resin coated sample. Average ΔE^*_{ab} are shown

Different Behaviors of Dye and Pigment Colorants

From the experimental data, we can see that print samples made with pigment colorants did not fade in the ozone chamber. The print samples made with dye colorants demonstrated significant color shifts and fading.

Previous studies have described this phenomenon. This study quantitatively demonstrates the difference in the behavior of the dye and pigment colorants in terms of ΔE^*_{ab}. Fig. 3 below shows that for the two samples produced with pigment colorants, the color shift is negligible as compared to huge objectionable color shifts for prints produced with dye colorants.

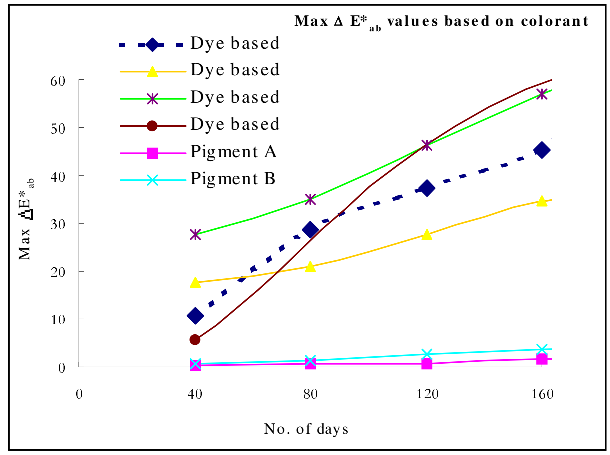

Figure 3. The maximum ΔE^*_{ab} for all the printed samples based on the colorant.

Table 3 . The minimum, maximum and average ΔE^*_{ab} for all the substrates.

Substrate	Colorant	Printet
Resin coated	Dye based colorant	Desktop inkjet printer
Clay coated	Dye based colorant	Desktop inkjet printer
Microporus	Dye based colorant	Desktop inkjet printer
Paper glossy A	Pigment based colorant	Large format inkjet printer
Paper glossy B	Dye based colorant	Desktop inkjet printer
Paper glossy C	Pigment based colorant	Large format inkjet printer

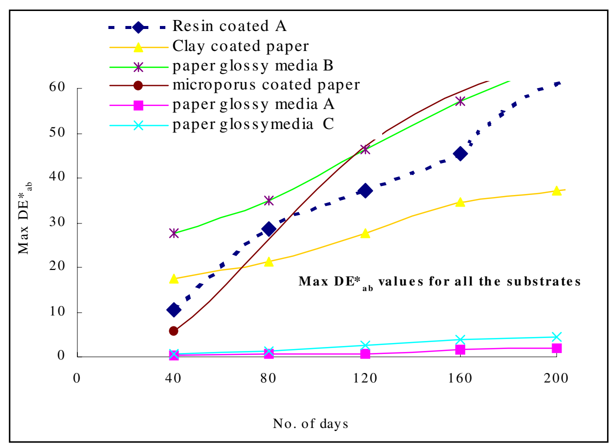

Figure 4. The maximum ΔE^*_{ab} for all the printed samples based on the substrate.

Role of Substrate in Ozone Fading

It was noticed that different substrates behaved differently in the accelerated ozone exposure tests. Fig. 4 below shows that there is a difference in the fading rate for different kinds of substrates. In this study the samples printed with pigment colorants showed only negligible color differences. On further inspection of all the substrates used in conjunction with the dye colorant some dependencies on the substrate were noticed. Table 3 above matches the substrate with the colorant and printer.

Different kinds of coatings that are applied to the base media that is used in inkjet applications. Some of them are non-porous coatings on resin-coated paper, non-porous coatings on white PET film, porous coatings on resin coated paper, porous coatings on white PET film and porous coatings on plain paper. In this study, it was found that despite the fact the same dye colorant was used to print on different substrates, the rate of fading was dependent on the substrate. For instance, the clay coated paper, which is a polymer swellable media, did not fade at the same rate as others. In comparison the 'Paper glossy media B' showed larger color differences and the fade rate was faster. Since the actual substrate composition was not known for this substrate, it is assumed that this substrate had a non-porous coating on resin coated paper.

With the demand for better substrate to be used in inkjet printers, microporus substrates are being developed. Microporus coatings have resulted in substrates which have fast drying capability. The ink is absorbed into the micro pores and the colorants are fixed in the top coat or upper receiving layers. But this leads to the issue of being vulnerable to oxidation. The O_3 free ion now has a pore to enter the coating layer and oxidize the anionic dyes.

As has been observed that the lightfastness of ink jet prints have some dependency on the media[7], the ozone fading of inkjet prints seems to show similar dependency.

Conclusion

This study has quantified the effect of accelerated ozone exposure on inkjet prints. The simulated ozone exposure was so undertaken that other factors like humidity, light exposure were not affecting the samples. To test the effect of ozone exposure on different colorants, both dye based colorant and pigment based colorant sets were used. A number of different substrates were also tested.

From the results it appears that the substrate has an influence on the ozone fading too. This study reiterated the fact that dye based colorants are not resistant to fading due to ozone exposure.

The results of this study have shown that for this particular dye colorant set, the fading of the Cyan dye has caused significant color shifts. The color shifts were noticed even at a short duration of simulated 40 days. This suggests that this particular dye set is not very stable. A further study to quantify the effects of ozone exposure on different dye colorant sets, on the same substrate and different substrates on the same dye colorant sets will provide more answers to help in the formulation of better matched media and colorant sets.

References

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Biography

Deepthi has an MS in Graphic Arts System and an MS in Color Science from RIT. She is the Associate Imaging Scientist at RIT Research Corporation, NY. Her work is primarily focused on image quality evaluation. She is a member of IS&T and ISCC.