

Image Permanence of Ink Jet Photographic Prints

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Abstract

Color ink jet printers have become extremely popular in homes and corporate offices thanks to technological improvements that deliver better image quality at higher speeds. With these improvements, ink jet printer users, including novices and experienced amateurs, are able to print with ease photographic quality images that are comparable to traditional silver halide photographs. Taking advantage of digital printing, the digital photographic market is expected to expand rapidly in the very near future. With this background, image permanence on ink jet recording prints is strongly desired, and this leads to the improvement of dye inks and media matching for ink as well as the development of new media that are optimized for pigment inks. The general approach that is taken for dye inks is to match the recording ink and the recording media in order to improve image permanence, employing photographic quality attained through the use of photo-output quality media. In the case of pigment inks, a variety of approaches are being studied, such as applying gloss and the pigment's own metamerism to attain photographic quality, employing the fastness of the pigments themselves.

This paper reports on storage performance with respect to the effects of water, thermal, humidity, plasticizers, light and gases, for ink-jet recorded images which use dye inks and photo-quality recording media, and which have a level of image-quality equivalent to silver-halide photographs.

Introduction

It has been five years since the advent of a six - color Epson Stylus Photo Printer that used color ink jet recording technology to produce photographic quality images. Strides made in ink jet recording technologies such as advanced micro dot (higher resolution), advanced multiple-sized dot, and higher speed technologies in the ensuing years led to faster printing and better photographic quality. With these advances, Seiko Epson Corporation has been trying to produce ink jet digital photo prints that produced permanent images equal to or better than that of traditional silver halide photographs. The first step was to improve the lightfastness of magenta, which had long been a problem with conventional water-soluble dye inks. The next step was to

develop special papers optimized for photo output as well as a water-soluble ink set that resolved the problem of relatively rapid loss of color balance due to light degradation. The last step was to match recording inks with recording media to improve lightfastness, which was another long-standing problem with conventional dye inks.

Ink jet recording media for photo output are classified as either the swellable type made up mainly of gelatin, polyvinyl alcohol and other water-soluble polymer ink absorbing layers, or the porous type with ink absorbing layers made up mainly of inorganic pigments that form gaps which can rapidly absorb ink. The porous - type is far superior when it comes to photographic quality and high-speed printing.

This report describes dye ink permanence performance on porous-type photographic recording media based on the results of image stability evaluations with respect to factors like water, thermal, humidity, light, plasticizers and gases that most markedly affect the permanence of images on ink jet recording material.

Experimental

The critical factors that determine the permanence of ink jet recorded images are listed below.

- 1) Water
- 2) Humidity
- 3) Thermal
- 4) Plasticizer
- 5) Light
- 6) Atmospheric gases

The permanence of images recorded using the following ink jet printer, recording ink and recording media were tested and surveyed as described below based on the preceding factors.

Table 1. Test Conditions

Ink jet printer	Epson Stylus Photo 870
Recording ink	Genuine inks (six colors)
Recording media	Premium Glossy Photo Paper (porous ratio of Approx. 70%)

1) Waterfastness: Waterfastness was tested by printing 5 cm x 5 cm patches of yellow, magenta, cyan and black at an initial density of 1.0, and then allowing the patches to dry for 24 hours. Each patch was moistened with 2 ml of water, covered after 1 minute with cotton wiper, BEMCOT M-1 (Asahi Kasei Corp.), placed under a 100 g weight and slide horizontally under the weight. This same test was conducted for comparison on other glossy papers available from other brands.

2) Humidityfastness: Humidityfastness was tested by printing patches of yellow, magenta, cyan and black at an initial density of 1.0, and then allowing the patches to dry for 24 hours. The patches were left uncovered for seven days in a constant temperature-constant humidity chamber at 40°C \pm 2°C and 85% \pm 2% humidity. Each patch was subsequently evaluated by measuring the change in color (delta E) using CIELAB colorimetry.

3) Thermal degradation (Dark stability): Accelerated tests were run to evaluate image permanence in dark places like albums where the image will presumably be stored. The forced thermal degradation tests run in several temperature ranges at a constant humidity confirmed that the logarithm of discoloration and fade reaction time was linearly related to the inverse of the reaction temperature (absolute temperature), and image permanence at room temperature had to be inferred from that.

The yellow, magenta, cyan and black patches were left uncovered in a constant temperature-constant humidity chamber kept at 60°C, 70°C and 80°C with 60% humidity. Each patch was evaluated by measuring changes in the initial density of 1.0 and changes in the unprinted white area of the recording media itself.

4) Plasticizer-fastness: One factor that determines the permanence of images on ink jet recording media is plasticizer-fastness. The effect here is when plasticizer in the plastic files used to store ink jet recording media seeps out from the file and reacts with the media, causing it in some cases to yellow.

Plasticizer-fastness was evaluated by placing the recording media in a plastic file, leaving it for two weeks in a constant-temperature chamber kept at 70°C, and then measuring the change in color (delta E) on the unprinted white area (i.e. yellowing) using CIELAB colorimetry. This same test was conducted on other commercially available glossy photo papers for comparison.

5) Lightfastness (Indoor light stability): Lightfastness was evaluated in accelerated testing by continuous illumination using an accelerated fluorescent light tester under two different conditions with the assumption that the media will be in rooms with fluorescent lighting. The test conditions are given below.

Table 2. Test Conditions of Lightfastness

	Test 1	Test 2
Light source	fluorescent lamp	
Lighting intensity	70,000 lux	10,000 lux
Temperature	24 °C	
Humidity	55%RH	
Glass frame	mount	

The acceleration factor under the preceding conditions is hypothetically about 300 times in test 1 and about 40 times in test 2 according to our calculations which assume the accumulated illumination for one day in an ordinary office or home is about 450 lux for 12 hours.

In order to eliminate the effects of factors other than light (i.e. moisture on the sample surface and fluctuating wind and gas effects in the chamber), the test was conducted with the sample protected by 2 mm thick soda-lime glass (simulation assumes the photo is in a glass frame). A 2 mm gap was also inserted so the glass is not in direct contact with sample.

Evaluation samples were prepared by printing patches of composite black and pure colors (yellow, magenta and cyan) with a reflection density of about 1.0 at 24 °C with 55% humidity, and then leaving them to dry between 24 and 48 hours to eliminate any residual solvent.

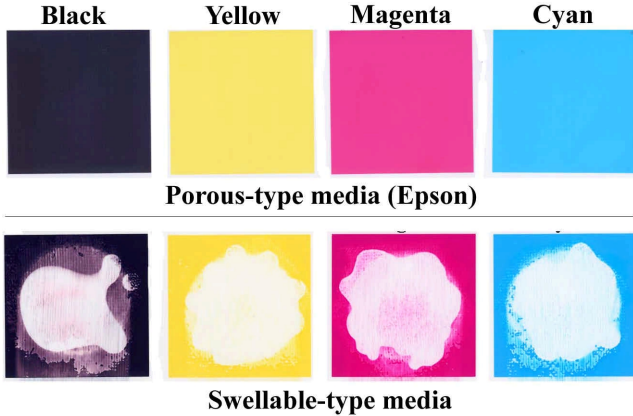
Following accelerated fluorescent light testing, the samples were set aside at 24°C with 55% humidity for 24 hours, the retained density for yellow, magenta, cyan and composite black were measured, and the relationship between accumulated illumination (luxxhour) and retained density were plotted on a graph.

A new media that was developed to improve lightfastness was also tested for comparison.

6) Gasfastness: Because dye inks on highly porous recording media are exposed to atmospheric gases, oxidizing and reducing gases in the atmosphere may degrade and fade colors. This makes gasfastness a top priority with dye inks. Gasfastness was tested by exposing color patches with a optical density of 1.0 for 24, 48 and 72 hours in oxidizing gas and reducing gas exposure apparatus. The gases selected for the test were O₃, SO₂, and NO₂ at concentrations of 0.5, 5 and 10 ppm, respectively. Each gas was tested under environmental conditions maintained at 24°C with 60% humidity. The amount of discoloration on composite black with an initial O.D. of 1.0 due to the gases was evaluated by measuring the change in color (delta E) by CIELAB colorimetry. In addition, the ink sets with the purpose of improving ozone fastness and media used in the lightfastness experiments were evaluated according to the same ozone experimental conditions to confirm the improvements in the fastness.

Results

1) Waterfastness: The Pictures below show the results of the waterfastness test. We know from these results that colors showed no signs of bleeding for the ink and recording media combination evaluated in the present study, while colors from another brand printer and recording media combination show bleeding at an unacceptable level. It is clear from these results that Epson has optimized its colorants and fixers to achieve waterfastness that poses no problems from a practical standpoint even with dye inks.



Picture. Test result of the Waterfastness. The pictures above the single line are on porous-type Epson premium glossy paper. The pictures below single line are on swellable-type media.

2) Humidityfastness: Figure 1 shows the results of humidityfastness testing. The horizontal axis shows the exposure time and the vertical axis shows the delta E for each color.

Water-based inks are generally used in ink jet printing. Therefore the water-soluble organic solvent with a high boiling point and low volatility that is used to prevent silting leaves a residue that make inks extremely susceptible to bleeding under high-temperature conditions. Even in evaluations under the harsh, high - temperature, high-

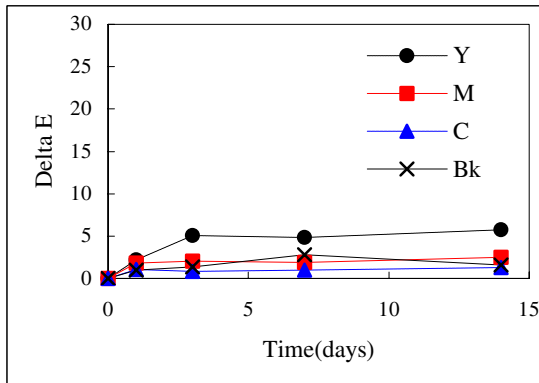


Figure 1. Test result of the Humidityfastness at 40°C×85%RH.

humidity environmental conditions (40°C at 85%RH) however, the below results showed virtually no change in color as well as excellent image permanence.

3) Thermal degradation (dark stability): The following shows the evaluation results for thermal degradation. Figure 2 shows results calculating the life of discoloration (Dmin change) of unprinted white area from the Arrhenius Plot. It is clear from plotted results of Dmin change up to 0.1 that the Arrhenius Plot was a linear progression at 80°, 70° and 60°C. The results also tell us that the life of color calculated at 24 °C with 60%RH is around 350 years, and that the photo output recording media evaluated in the present study exhibits excellent long-term permanence when stored in a dark place.

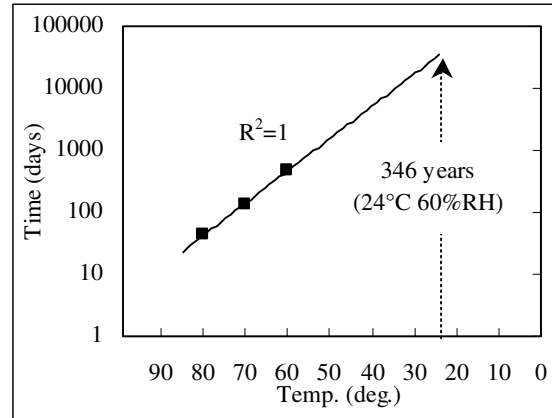


Figure 2. Arrhenius Plot of Dmin change at 60°, 70° and 80°C×60%RH.

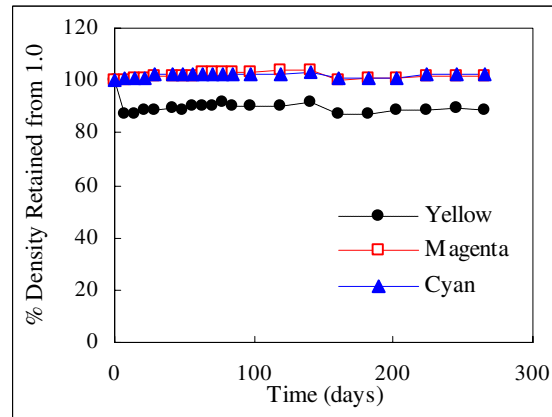


Figure 3. The Thermal Degradation at 70°C×60%.

Figure 3 shows the results of discoloration evaluations at three levels between 60°C and 80°C that were conducted for 266 days at 70°C with 60% RH since accelerated testing below 60°C showed too small a change to make the Arrhenius Plot. The test showed virtually no change in cyan and magenta and a 10% drop in yellow, but this is where levels stabilized.

It can be inferred from these results that the recorded images can be stored for long periods of time in dark locations like photo albums.

4) Plasticizer-fastness: Figure 4 shows the degree of yellowing caused by plasticizers on recording media made by Epson as well as on commercially available glossy photo paper. Unlike the commercially available products, yellowing was kept to a minimum and the effects of plasticizers caused by storage in plastic files were virtually non-existent on recording media made by Epson.

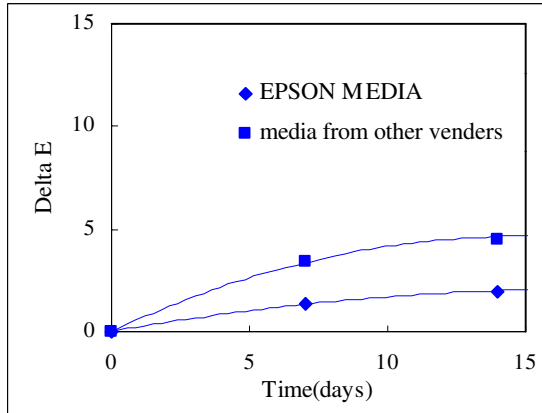


Figure 4. The Plasticizer-fastness of EPSON Premium Glossy Photo Paper at 70 °C.

5) Lightfastness: Figs. 5(a), 5(b) show the results from Test 1 (accelerated testing at 70,000 lux) and Test 2 (accelerated testing at 10,000 lux). The vertical axis shows the retained density with respect to initial density following accelerated fluorescent light testing, while the horizontal axis shows the number of years calculated on the assumption that the image will be exposed to light for 12 hours at an accumulated illumination volume of 450 lux per day.

When the results of the two tests were compared, the accelerated testing at 10,000 lux showed slightly faster degradation than accelerated testing at 70,000 lux.

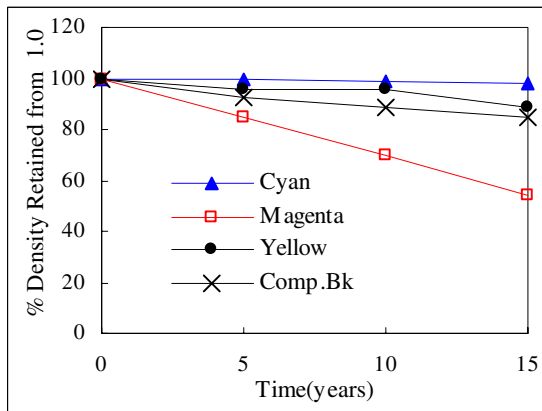


Figure 5(a). The Lightfastness of prints using PGPP. The test was maintained at 70 Klux x 24°C x 55%RH

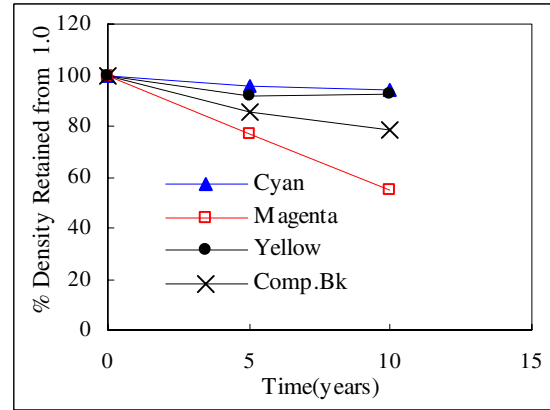


Figure 5(b). The Lightfastness of prints using PGPP. The test was maintained at 10 Klux x 24°C x 55%RH.

Figs. 6(a), 6(b) show the results of evaluations on newly developed media that were to test improvements to lightfastness.

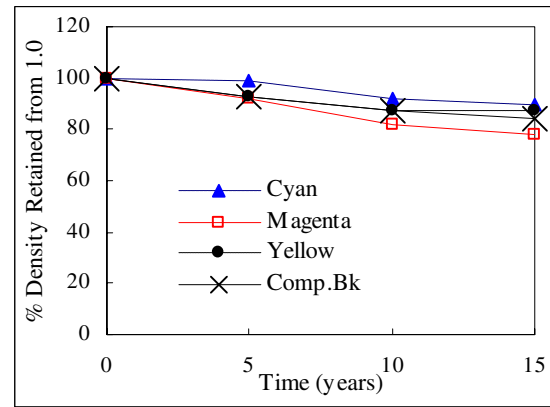


Figure 6(a). The Lightfastness of prints using PGPP-N. The test was maintained at 70 Klux x 24°C x 55%RH.

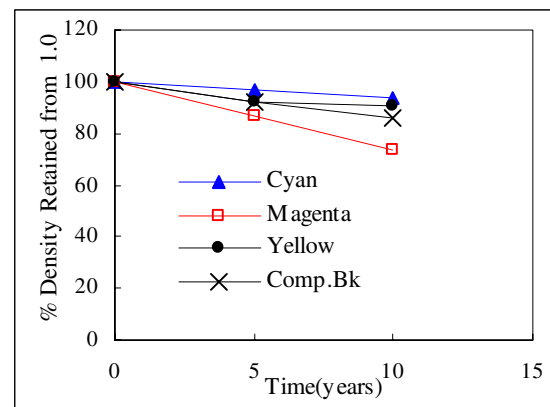


Figure 6(b). The Lightfastness of prints using PGPP-N. The test was maintained at 10 Klux x 24°C x 55%RH.

It is clear from Figure 6 that lightfastness was further improved by improving the recording media, but a comparison of Figs. 6(a) and 6(b) also shows that degradation was slightly faster with accelerated testing at 10,000 lux than with accelerated testing at 70,000 lux. The lightfastness study needs more in-depth demonstration of acceleration characteristics (i.e. at less than 10,000 lux) under these same environmental conditions.

6) Gasfastness: Figure 7 shows the relationship between the amount of exposure (ppm x hours) to delta E for composite black in single gas testing with ozone, NO₂ and SO₂. It is clear from Fig. 7 that O₃ caused the most fading, and that NO₂ and SO₂ had virtually no effect.

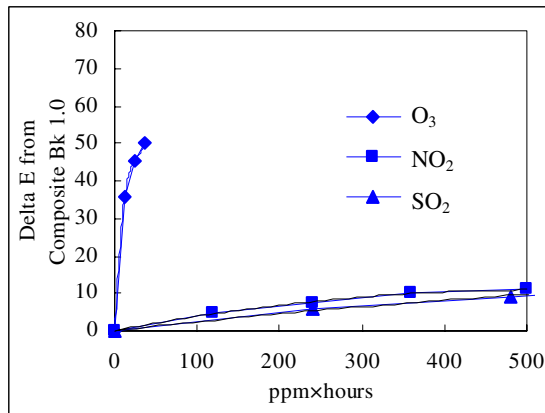


Figure 7. Test results of the Gasfastness at 24°C x 60%RH.

Figure 8 shows ozone test results comparing the effects before and after improvements using the ink set that was improved to resist fading caused by ozone and the media with much-improved lightfastness (same media used in the lightfastness test). It is clear from the figure that ozonefastness was markedly improved.

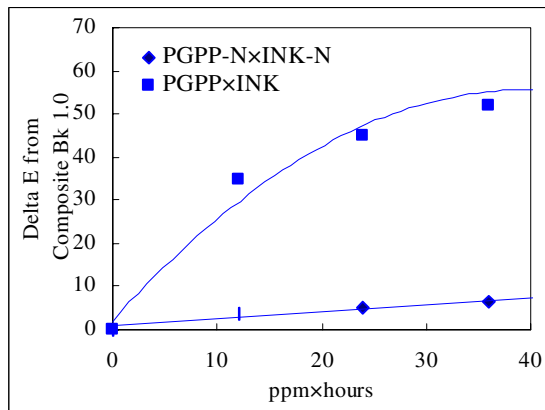


Figure 8. The Gasfastness of delta E on composite Bk before and after improvement.

Conclusions

The critical factors that determine the permanence of ink jet recorded images are listed below.

- 1) Water
- 2) Humidity
- 3) Thermal
- 4) Plasticizer
- 5) Light
- 6) Atmospheric gases

When image permanence performance was evaluated in these areas using a combination of dye inks available today and porous-type photo recording media, the results showed excellent image permanence using that combination particularly in terms of the effects of water, humidity, temperature and plasticizers.

It was also found that the recording media approach brought much-improved lightfastness, which had been a problem in the past.

Meanwhile, it was clear that NO₂ and SO₂ had less effect on gasfastness, which posed problems in the past with highly porous recording media, and that the combination of more advanced media and inks significantly improved discoloration due to ozone.

References

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Biography

Hiroyuki Onishi is a manager in the Printer Development Division of SEIKO EPSON CORPORATION. He received his B.E. in chemical engineering from Kanazawa University, Japan in 1986.

Mr. Onishi worked on the development and design of ink jet recording ink for five years and is currently working on the development of ink jet recording media.

His primary responsibilities are improving the performance of ink jet recording media for dye-based and pigment-based inks, developing matching technology for ink jet ink and ink jet media combinations, and establishing evaluation technology for permanent ink jet print images.