Stability Issues and Test Methods for Ink Jet Materials

Thesis at the Department of Image Engineering,
University of Applied Science, Cologne

Testmethoden zur Untersuchung des Stabilitätsverhaltens von Tintenstrahlmaterialien

Diplomarbeit im Fachbereich Photoingenieurwesen
an der Fachhochschule Köln

investigated by
Barbara Vogt
from Oberwesel
Mat. Nr. 11009460

Advisors: Prof. Dr. C. Blendl
Prof. James M. Reilly, Director
Image Permanence Institute, Rochester, NY

Cologne, May 2001

1 Abstract

Title: Stability Issues and Test Methods for Ink Jet Materials

Author: Barbara Vogt

Advisors: Prof. Dr. C. Blendl / Prof. James M. Reilly (Image Permanence Institute, Rochester Institute of Technology, Rochester, NY)

As digital hard copy output has become an alternative to traditional imaging systems (conventional photography), the question about the permanence of this material is raised. There is no standard for color hard copy materials yet, so the tests have to rely on the precedents established by the photo industry. In this study ink jet prints were tested under various conditions to show their complex fading behavior and illustrate the difficulties in providing reliable tests. The results show the different rates and amount of fading, as well as visual color shifts of the chosen dyes and pigments.

Keywords: Color-fading, light-fading, image stability, image permanence, ink jet printing, dye ink, pigmented ink

Date: 21.05.2001

Titel: Testmethoden zur Untersuchung des Stabilitätsverhaltens von Tintenstrahlmaterialien

Autor: Barbara Vogt

Referenten: Prof. Dr. C. Blendl / Prof. James M. Reilly (Image Permanence Institute, Rochester Institute of Technology, Rochester, NY)

Mit der Anerkennung digitaler Druckmedien als Alternative zur traditionellen Photographie stellt sich auch die Frage nach deren Stabilität und Haltbarkeit. Da momentan noch keine standardisierten Testmethoden für diese Materialien zur Verfügung stehen, werden Stabilitätsuntersuchungen nach bestehenden Normen der Photoindustrie durchgeführt. In dieser Arbeit wurden Tintenstrahlausdrucke unter verschiedenen Licht- und Schadstoffeinflüssen auf Ausbleichverhalten sowie visuelle Farbänderungen getestet. Dabei wurden detailliert die komplexen Zusammenhänge der einzelnen Ausbleichparameter untereinander aufgezeigt.

Stichwörter: Licht- und Farbausbleichverhalten, Bildstabilität, Haltbarkeit, Tintenstrahldruck, Farbstofftinten, pigmentierte Tinten

Datum: 21.05.2001

Contents

2 Introduction

In recent years digital hard copy output has increased dramatically as an alternative to traditional imaging systems (conventional photography). At first, the problems of resolution, printing technology, color reproduction and digital capture were in the center of attention. After the print quality of silver-halide images was more or less achieved, questions came up about the permanence of the digital prints compared with that of silver-halide-based chromogenic color prints. Customers simply wanted to know "How long is it going to last?"

In conventional photography, there are a number of standardized accelerated aging tests to compare and predict life expectancy of both the image and the support. The ISO Standard 10977 (it is described in more detailed below) deals with measuring the image stability of color photographic materials and is divided into a dark-stability test and a light-stability test. The standard was first published in 1993. A revised version is now in its draft state and is going to be published soon. As there is no standard for color hard copy materials yet, the tests have to rely on the precedents established by the photo industry. The same ANSI/ISO committee (a group of various manufacturers from the photo industry, ink and paper industry, ink jet technology industry, etc.) that is actually working on the revised version of ISO 10977 has, since 1994, also been working on a new standard for methods for measuring image stability of color hard copy materials. Due to the fast growing number of new output technologies, new ink sets and new media, fast test results are required. Because high-intensity/high-concentration, accelerated aging test can suffer from reciprocity failure, a reliable long-term life prediction under normal display conditions is difficult to make. Further, color hard copy materials can be negatively effected by various factors, like humidity, water and many more, some previously unconsidered. Thus, a wider range of test methods than recommended in the ISO 10977 standard is necessary. The subcommittee split the whole group into smaller task-groups dealing with the following issues:

- Water-fastness
- Humidity-fastness
- Thermal degradation/dark stability
- Indoor light stability
- Outdoor light stability
- Fingerprint test
- Other brittleness and image analysis

A new task-group called "Gas fading" was just added last December due to new problems of ink jet images exposed to airflow observed during the past summer. A specific set of ink jet samples was tested under a high-intensity (50 klx) light source and showed no significant fading over a longer test period (i.e., one month). But customers who used this same material claimed that their prints would turn orange in only a few days:

> "While many people are getting excellent results, many others have reported problems with their prints turning orange, sometimes within 24 hours of being printed." [1]

In tests done by an independent institute, samples were framed and so cut off from any airflow in the environment. The problem was that these test results did not include any fading caused by a possible different source (e.g., air conditioning system). As it turned out, the cyan dye on this particular paper is fairly unstable against any kind of environmental influence (i.e., airflow). This results in a higher fading rate of the cyan dye, causing the printed images to turn orange in a short period of time if not framed.

> "...field reports and data gathered from other sources indicate that this paper has a particular sensitivity to ozone, nitrogen and sulfur oxide, and certain other airborne contaminants which, when concentrations are high enough and the print is not protected from the open atmosphere, may cause rapid fading of the cyan ink; this typically results in the color balance of the print shifting toward red/orange....This type of premature ink fading is NOT caused by exposure to light...." [2]

Thus, this new task-group is trying to address the influence of environmental pollutants as a possible agent causing fading in a print. Since the world is becoming more and more industrialized, degradation in polluted environments is of increasing importance. However, all these problems delay the progress of the new standard.

In the present study various test conditions were chosen to observe different fading behaviors of ink jet prints. Samples, framed and unframed, were exposed to high-intensity light, as well as to airflow. Further, samples were exposed to ozone and nitrogen dioxide to better predict the influence of possible environmental pollutants. A dye-based and a pigmented ink set, each printed on two different papers, were chosen to observe any ink and media interactions and the stability of pigments compared to dyes. The choice of ink jet prints was made because of the medium's popularity in digital photography and its widespread use in nearly every office or home environment.

The purpose of this study is to lead to a better understanding of the complex fading behavior of ink jet prints and to demonstrate the difficulties in providing reliable tests. The analysis of the exposed samples shows how environmental conditions can influence the degradation of ink jet images.

2.1 ISO Standard 10977

ISO Standard 10977 [3] deals with the measurement of the stability of photographic color materials and is divided into two parts: a light and a dark stability test. No physical stability tests of images, supports or binder materials are included.

The tests for predicting long-term stability of color photographic images stored in the dark are based on an adaption of the Arrhenius test method described by Bard and in earlier sources by Arrhenius, Steiger and others. The standard recommends evaluating long-term dark stability by carrying out a series of tests at a particular relative humidity and at least four different temperatures, e.g., 50% RH and 55°-85°C. A relative humidity above 50% RH may give misleading results due to the change in physical or chemical properties in photographic image layers. Two kinds of test methods are available: "sealed-bag" method and "free-hanging" method. The test equipment for the "free-hanging" method must be temperature- and humidity-controlled, while the equipment used for the "sealed-bag" method only must be temperature-controlled.

The light-stability tests are based on a concept that increases the light intensity without changing the spectral distribution of the illuminant, the ambient temperature nor the relative humidity. Thus, a proportional increase in the photochemical reactions that typically occur under normal display conditions without any side effects should be produced.

Five different light-stability tests to simulate common situations are described in the standard:

1. Simulated indoor indirect daylight through window glass 6.0 klx - filtered xenon arc ID65 illuminant
2. Glass-filtered fluorescent room illumination 6.0 klx - “cool white” fluorescent lamps
3. Incandescent tungsten room light 3.0 klx - C.I.E. illuminant A spectral distribution
4. Simulated outdoor sunlight (xenon arc) 100 klx - C.I.E. D65 spectral distribution
5. Intermittent tungsten-halogen lamp slide projection 1000 klx

These are all to operate under specified temperature and humidity conditions for each test. Because color materials can suffer from reciprocity failure, a parallel test, at a lower intensity (e.g., 1 klx) with at least one of the specified indoor illuminant sources, should be done. Another aspect influencing the rate of fading is whether the print is framed (enclosed under a sheet of glass or plastic) or unframed (open to air). This is called “enclosure effect” and described in more detail in Annex E of the standard.

Tests run until the chosen end-point values as measured by densitometry (status A or M as appropriate) are reached:

- 30% change in neutral patches
- 30% change in color patches
- 15% change in color balance of neutral patches
- 0.10 change in d_{min}
- 0.06 change in color balance in d_{min}

> “Note 6: The image-life parameters listed are the critical characteristics that have practical significance for the visual degradation of colour images; however, the numerical end-points given here are only illustrative. The working group that produced this International Standard was not able to specify broadly applicable “acceptable” end-points, because the amount of image change that can be tolerated is subjective and will vary with the product type and specific consumer or institutional requirements. Each user of this International Standard shall select end-points for the listed parameters which, in that user’s judgement, are appropriate for the specific product and intended application...” [3]

The various factors influencing the color perceptions of individual viewers are described in more detail in section 3.4.1.

2.2 Acknowledgments

This thesis was done at the Image Permanence Institute (IPI), and I am very thankful to James M. Reilly for making this possible. I also want to thank Prof. Blendl and Prof. Reilly for acting as my supervisors. Thanks go also to those at IPI who assisted me in carrying out the tests and answered all of my questions. It was a great pleasure to work at this Institute, where I could count on everybody's support. I am especially thankful to Dr. Franziska Frey who not only was my mentor, but also was a good friend.
Further thanks to:
Douglas Nishimura, IPI, Rochester, NY
Edward Zinn, IPI, Rochester, NY
Sarah Arnold, IPI, Rochester, NY
Nyla Schroeder, IPI, Rochester, NY
Karen Santoro, IPI, Rochester, NY
John Arney, RIT, Rochester, NY
Frank Cost, RIT, Rochester, NY
Glenn Miller, RIT, Rochester, NY
Yoshihiko Shibahara, Fuji, Japan
Rita Hoffmann, Ilford AG, Switzerland
Frieder Loebich

Finally I want to thank Christian Loebich for his help and interest in my work, as well as my parents Christel and Sebastian Vogt for their constant support.

3 Fundamentals

3.1 Ink Jet Printing

Ink jet printing can be classified as a masterless digital process. In other words, compared to an conventional process, which uses a physical image carrier or plate (master) to transfer ink to paper, the digital data can be repeatedly converted directly into a printed product [4]. All processes called ink jet share one common factor. To create an image, ink is ejected through very small orifices to form droplets that are directed to a medium. Ink jet printing is a non-impact printing process. Because of the simplicity of this process there is a great variety of applications and technologies on the market today. Scientists have developed a wide range of methods to eject and form droplets. The only restrictions in applying this technology to new or higher-quality digital image solutions are imagination and physical limitations. Due to the fact that no one ink jet process or printhead fabrication has served every sort of requirement, there are many technical differences among the various ink jet methods that are in use.

3.2 Technology Overview

3.2.1 History of Ink Jet Printing

In the 19th century scientists investigated the physics that underlie ink jet technologies. J.A.F Plateau, a Belgian physicist, published "On the recent theories on the circular orifices" in 1856. Lord Raleigh, a English physicist and Noble Prize winner, published a series of foundation papers including "Instability of jets" (1878), "On the instability of cylindrical fluid surfaces" (1892) and "Investigations of capillarity" (1899) [5].

As computer systems advanced more and more in the late 1950s and 1960s the need for high-speed electronic printing methods rose as well. With the rapid growth of electronic information systems, good ways to write electronically stored and generated images were developed. Only a few ink jet products had been introduced to the public by the end of the 1960s: A.B. Dick's Videojet 9600, Casio's first kana calculator printer, and Teletype's Inktronic computer terminal [5, 6].

During the 1970s, work was basically focused on two forms of continuous ink jet (CIJ) and piezoelectrically activated impulse jet. Introduced by IBM in late 1976, the 6640 was the first continuous ink jet system to achieve near-letter-quality 240 dpi. This was the state of the art for ink jet at that time [5, 6]. In 1977 the first continuous ink jet color image printer, developed by Applicon of Burlington, Massachusetts was available on the market. This machine was based on the ink jet work of Professor Hertz of Lund Institute in Sweden [5, 6]. It can be seen as the forerunner to the high resolution IRIS Graphics color proofer introduced in the 1980s. The first drop-on-demand ink jet printer PT-80 based on the piezoelectric principle (Zolant patent), was launched by Siemens also in 1977 [5, 6].

At the beginning of the 1980s, most research was aimed at the development of better print quality, throughput, cost and reliability. CIJ certainly offered enough throughput potential, but the system became very costly to produce once it reached the needed print quality of 300-600 dpi. Piezoelectric drop-on-demand systems were much simpler and inherently more reliable than CIJ systems and only limited by the physical size of the known piezoelectric transducer configuration [5]. The invention of the much smaller thermal ink jet transducers solved the problem of the piezoelectric ink jet printheads. They achieved higher resolutions because it was possible to put a larger number of drop-on-demand jets in a printhead. At the Tokyo Data Show, October 20, 1981, Canon demonstrated its new bubblejet (thermal ink jet) technology. HP launched its ThinkJet computer printer, which was also based on the thermal ink jet process, only two and a half years later. By then, thermal ink jet was established as the ink jet technology of the future for office-quality printing [5].

In the 1990s a real explosion of ink jet products, mainly thermal ink jet, followed. Manufacturers tried to push color in every possible price range. HP extended its DeskJet line and Canon introduced its BJ-10 line of portable printers with a 360 dpi resolution in 1991. With HP launching the DeskJet 1200C and Design Jet (large-format) in May 1993, a major advance in good-quality, plain paper color printing for a reasonable machine investment was provided. The HP 1200C was the first printer using carbon black pigmented ink, which reduced feathering and bleeding of black into other colors [5]. Resolution advanced from 300 dpi at the beginning of the 1990s to 600 dpi or 720 dpi and further to 1200 dpi or 1440 dpi, or even 2880 dpi (Photokina trade fair, September 2000). In the mid-90s the first six-color process using additional diluted magenta and cyan ink to improve color grayscale rendition was introduced to the market. Another method to provide a better highlight tone is to reduce the drop size. Epson launched a series of Stylus color ink jet printers, based on its multilayer activated (MACH) piezoelectric ink jet technology during the 1990s. In 1999 Epson introduced the Stylus 900, offering 1440 x 720 dpi printing by using drops as small as 3 pL. With this capability it equals the world's best lithographic printing [5]. At the DRUPA 2000 trade fair in Düsseldorf, Germany, Epson introduced its first desktop printer Stylus Photo 2000P using pigmented ink.

3.2.2 Printhead Design

There are two main printhead technologies on the market, one that produces drops continuously and one that produces drops on demand. The drop-on-demand printhead design can be categorized into four methods: piezoelectric, thermal, acoustic and electrostatic ink jet (Figure 1).

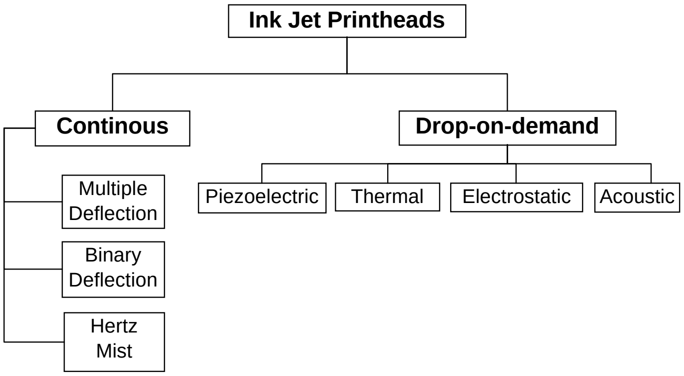


Figure 1: Overview of ink jet printheads

Currently, the thermal ink jet technology dominates the low-end color printer market [5, 6]. Both the electrostatic ink jet and acoustic ink jet methods are still in the development stage, and there are only a few products commercially available.

Continuous Ink Jet Printing
In principle, CIJ printing means that the ink supply is pressurized sufficiently to create a jet. The jet will break up into varying drop sizes based on surface waves produced by a piezoelectric vibrator. Thus, there is a continuous flow of droplets, and the drops have to be deflected, either to the material or to the gutter, to create an image. Usually the deflection force is electrostatic and the ink jet drops are charged as they brake away from the jet stream.

Drop-on-Demand Ink Jet Printing
In all drop-on-demand methods, the ink supply is not sufficiently pressurized to form a jet. The ink is held in a small chamber and forms a meniscus at the orifice. The ink droplet is only produced when it is required to form a dot on the medium. There is no deflection needed and the drops do not need to be charged.

In *piezoelectric ink jet printing* a piezoelectric element is used to squeeze individual drops out of a small chamber by changing its shape. When an electric field is applied to a piezoactivated wall of the chamber, the wall's dimension changes a minute amount, proportional to the applied voltage. Depending on the polarity of the applied voltage, it is either a minute contraction or a minute expansion. In the later case an ink drop is pushed out of the nozzle.

Thermal ink jet printing is based on the concept that when a liquid is vaporized its volume expands tremendously. In a thermal ink jet printhead the ink is heated up by a resistor, and a vapor bubble is formed. The pressure inside the chamber increases due to the growth of the bubble, and a drop is forced through the nozzle. When the heat is suddenly cut off, the drop breaks free and the bubble collapses back onto the heater. At the same moment the pressure decreases and the chamber refills with ink from an ink reservoir and the cycle starts over again.

3.3 Ink Design

The various ink jet applications and printhead designs require different ink formulations. The ink chemistry and formulation not only determine the drop ejection characteristics and the reliability of the printing system but also dictate the quality of the printed image.

3.3.1 Performance Requirement for Inks

In addition to matching the color specifications, the ink should not penetrate so deeply into the medium that it can be seen from the back. Such bleed-through of ink also reduces the image resolution. On the other hand, this property is needed to reduce drying time, smearing and inter-color bleed. Further, the print should be light- and water-fast to meet the users requirements.

To ensure print reliability the ink has to be formulated to allow stable drop formation under either continuous or drop-on-demand operation. The two main properties to control the drop formation are viscosity and surface tension. They have to be addressed differently, depending on the printhead design. A thermal ink jet printhead, for example, requires an ink that is vaporizable, like an aqueous- or water-based ink. Meanwhile, a piezoelectric printhead needs a viscous ink to achieve ink flow through the structure. Further, the ink must be compatible with the various components of the fluid system. This means that the ink should not show any chemical reaction, like corrosion, swelling or adverse interactions with the printhead components, and that can easily be washed off orifices and charge plates. Finally, the ink cannot pose any health or safety problem, nor should it support microbial growth.

The above listed performance requirements [5, 9] give only a brief overview of the desirable physical and chemical properties of ink jet inks. Indeed, the chemical structure of the ink and its interaction with the print media do have a great influence on print quality and image properties.

3.3.2 Ink Formulation

Components added to an ink formulation include: colorant, solvent, solubilizing agent, dispersant, viscosity modifier, pH buffer, biocide, antioxidant and many more. A more detailed description is listed in Appendix B.

3.3.3 Colorants

Chemical Structure of Colorants
In the early days of dye chemistry the correlation between chemical constitution and color of organic compounds was investigated. Graebe and Liebermann recognized in 1868 that all dyes contain a system of conjugated $C = C$ double bonds. Witt postulated in 1876 that a compound is colored due to the presence of particular groups, the chromophores and auxochromes, which must be linked to a system of conjugated double bonds. In 1933 Dilthey and Winzinger divided chromophores into chromophores and antiauxochromes. Later, as physical and organic chemistry developed, it became apparent that auxochromes are electron donors, antiauxochromes are electron acceptors, chromophores are linear or cyclic systems of conjugated double bonds, and the assembly is sometimes called a chromogen. [7, 8]

In the 1920s chemists started to investigate the chemical structures of colorants in regard to their spectra, in particular to the wavelength of the absorption maxima in the visible range. Organic compounds become colored by absorbing electromagnetic radiation in the visible wavelength range (400-700 nm). All molecules have electron-filled and empty orbitals, and the conjugation allows the electrons to be delocalized over the chain/ring system. The energy ($h\nu$) of visible light, and also ultraviolet light (10-400 nm), is absorbed by the colorant molecule and used to promote one of the electrons from its ground state into an orbital of higher energy. Thus, it is the energy gap (ΔE) between the HOMO (highest occupied molecule orbital) and the LUMO (lowest unoccupied molecule orbital) that is critical in determining the color of a pigment or a dye. [7, 8]

The *Einstein-Bohr* frequency condition states that the energy difference (ΔE) between the ground state and a particular excited state is directly proportional to the observed frequency (ν), and, hence, inversely proportional to the wavelength (λ) of the absorbed light:

$$\Delta E = h\nu = \frac{hc}{\lambda} \tag{1}$$

$where\ h = Planck's\ constant\ and\ c = speed\ of\ light$

Shifts from the absorption maxima to longer wavelengths (towards red) are called bathochromic and shorter wavelengths (towards blue) are called hypsochromic and are directly related to the degree of conjugation. Further shifts are produced by the presence of electron donor groups (auxochromes), such as $-NH_2$, $-NMe_2$, $-OH$ and $-OR$, which release electrons into the conjugated system, and electron withdrawing groups (antiauxochromes), such as $-NO_2$ and $-C = O$, which take electrons out of the system [9].

Classification of Colorants

In terms of ink jet, the differentiation of colorants in either dyes or pigments is very important. Dyes are non-planar molecules and they may contain solubilizing groups (e.g., sulfonic acid or carboxylic acid). The dye crystals are less stable due to the fact that their intermolecular forces are weaker than in pigments [10]. Thus, they are easily broken up by a solvent to give solution. Based on the solvent used they can be further classified as water-based or solvent-based dyes.

A pigment, on the other hand, is an aggregation of hundreds or thousands of molecules, depending on the size of the pigment (0.1-1.0 micrometers). Pigments are essentially planar molecules, which usually contain strong hydrogen bonding groups (e.g., amide $-CONHR$ and carbonyl $-C = O$). Further, these molecules' features promote strong intermolecular attractive forces, which lead to a stable crystal with a high lattice energy [10]. Thus, pigments are solid particles and therefore practically insoluble in the applied media. They have to be solubilized by using a dispersant to act as a bridge between the solvent of the ink and the pigment's surface molecules.

Chemists in the 19th century discovered synthetic dyes and pigments that were of organic nature and so opened up the development of a variety of colorants that could be chemically modified. Most organic pigments are closely related to dyes (with respect to their chemical structure). Furthermore, dyes can be formed into pigments by aggregation and binding the dye molecules into particles [7].

Colorants for Ink Jet Inks

The first colorants used for ink jet printing were water-soluble dyes. Pigments were not used, because they could not reach the color gamut of dyes, and they did not perform reliable due to the fact that they are not soluble. However, pigmented inks are now available that perform reliably and have a color gamut approaching that of dyes. Now, the ink manufacturers are trying to improve the permanence requirements of prints, such as light-fastness and water-fastness, mainly in two different ways. Some are continuing to try to control dye aggregation, while others are more focused on producing stable pigment dispersions of smaller particle sizes [5, 7].

Pigments have the advantage of better light-fastness primarily because there are more chromophores in the pigmented particles than in the dye molecules. Light may break apart the chromophores in both the dye and the pigment image, but the pigment image lasts longer because the decomposition of chromophores is less per time. This basically means that all dye molecules (due to their large surface area) are reached by photofading agents, while only the pigment molecules at the surface of the particle (10% of the total) absorb photons [10]. The disadvantage, on the other hand, is that larger particles lead to light scattering on the surface, which reduces color saturation and gives a duller or more matte surface. Because the color gamut depends on chroma and chroma depends on the purity of the reflected light, colorants with a narrow, symmetrical absorption band display the highest chroma. Due to their monomolecular state dyes have the advantage of a narrow absorption band in the visible light spectrum. Aggregation of molecules leads to a broader absorption curve, which results in dullness [10]. Further, the individual dye molecules are so much smaller than the wavelength of light that no light scattering is possible. Pigment particles in the size of 0.2-1.0 microns on the other hand are able to scatter light (0.4-0.7 microns wavelength) [10]. Pigment particles can also cause nozzle clogging and crusting problems as well.

Thus, the chemistry of forming a stable, uniform dispersion of solid particles in a liquid is more difficult than in dye chemistry. The development of pigment-based inks is a greater technical challenge than that of dye-based inks. The achievement of a particle dispersion stable enough to compete with dye solutions was the key to pigmented ink, in the beginning used mainly in outdoor applications, i.e., advertising, due to its better durability.

Because of the possibility of modifying the chemistry of a dye to match that of the medium coating, dyes have greater versatility, and they are still mostly applied in indoor use, i.e., desktop printers in home or office environments.

Examples of currently used dyes and pigments are included in Appendix C.

3.4 Color Science

3.4.1 Basic Concept of Color

Color vision is based on a variety of physical, chemical physiological and psychological processes [11].

An object appears colored due to its ability to absorb visible light (400-700 nm). The part that is not absorbed can be reflected or transmitted. The light that is emitted from a light source and the reflected or transmitted light from the object reaches the retina in the human eye, where the photosensitive cells, the rods and the cones are located. There, the light with wavelengths between 400 nm and 700 nm initiates a photochemical reaction, and subsequently a series of light-independent reactions in the visual pigment take place. Then, through the transfer of the information from the eye to the brain where further image processing takes place, this process results in visual perception.

Metameric Color

The color from an object seen by the human eye depends on the wavelengths that reach the retina. This depends on the color of the object as well as the emitted light spectrum of the illuminator used. Because the human eye is not able to separate different spectra of the incoming light, it has difficulty comparing color under different light sources (e.g., fluorescent light, daylight). The effect of color matches changing their apparent color under different light sources is called metamerism [11]. This effect is quite important in terms of color reproduction and color measurement. There has to be a standard definition (i.e., standard light source) in order to compare and match colors on different output devices. Although the human eye has a great variety of physical receptors, a standard observer is needed nonetheless (see section 3.4.3.).

Color Perception

Color is a three-dimensional phenomenon, which is best described with the terminology of hue, chroma (saturation) and lightness (value). All of the three factors influence how the human eye sees color. Further, some of the variables that influence color perception include the light source (as explained above) and the surrounding colors, as well as the personal sensitivity of the eye and the mood of the viewer, which are more subjective parameters. Because these physiological factors influence the viewer's judgment of a color image, they determine the rate of accepted fading in a color image as well [12].

The eye is more sensitive to color shifts than to reduction in saturation, a 10% change in contrast is usually not noticed, while the same change in a color shift is noticeable to the viewer. The eye can detect even smaller changes in memorized colors (i.e., skin tone or sky) as well as in lower densities. Due to the different sensitivity of the receptors, achromatic aberration in the purple shades are more disturbing than in yellow shades. Further, if there is still an original reference in the faded image (i.e., the image was partly covered while fading and so partly protected) small changes are detected (i.e., 10% contrast reduction). Uniform fading of all three colors up to 30% can still be accepted by a viewer, if there is no comparison. All these different factors influence the predictive life expectancy of an image and the end-points chosen by the standards committee.

3.4.2 Color Theory

In basic color theory it is understood that there are three additive primary colors (red, green and blue) and three subtractive primary colors (yellow, magenta, cyan). The three additive primaries represent the broad band of light energy. Additive theory is mainly used in display systems (e.g., monitors). The primary subtractive colors receive their name from the fact that each color absorbs one-third of the white light spectrum. These primaries are used in printing, because they subtract color from the white sheet of paper. Printed images are produced by subtracting different degrees of the red, green and blue light reflected by the white sheet of paper. The three "process" inks (subtractive theory) act as transparent filters for the red, green and blue light.

The additive and subtractive primaries are called complementary colors because of the paired relationship in which each subtractive color absorbs its complementary one-third of the light spectrum. So, on white paper cyan ink absorbs the red light, green and blue light are reflected, and we see the color cyan. To see the color blue, cyan and magenta ink need to be printed on the white paper. The cyan ink absorbs the red light, the magenta ink absorbs the green light and only the last third of the spectrum, blue light, is left to reach the retina.

In theory, every color can be reproduced by mixing those three subtractive primary colors. A perfect ink can absorb 100% of its complementary color of light and reflect 100% of the two remaining colors of light. However, there is no such colorant in real life. Colorants normally absorb some colors of light they should reflect (e.g., yellow dye absorbs a small amount of green light). This is a well known fact, that led to the use of a fourth color, black. Black ink also helps reproduce detail and increases contrast [11].

3.4.3 Color Measurement

Because the human eye can distinguish about ten million different colors, the identification and exact definition of a specific color is complicated. The three basic components: sources of light, object illuminated by them, and observer determine how the human eye sees color. Color measuring, therefore, has to be based on a well defined system.

CIE Color System
In 1931, the International Commission de l'Eclairage (CIE) recommended a method to obtain parameters that quantify the color of a sample as seen under a standard source of illumination by a standard observer. The most commonly used illuminant is designated D65, which represents the spectral power distribution of average daylight with a color temperature of 6500°K. Also two standard observers, a 2° and a 10° observer are defined. This means that the colored area subtends an angle of vision of either 2° or 10°. The spectral response of the observer's eye is characterized by the three color-matching functions (red $\overline{r}(\lambda)$, green $\overline{g}(\lambda)$ and blue $\overline{b}(\lambda)$) [13].

Densitometry
Densitometers measure various degrees of density by using CIE standards. Density can be defined as the light-absorbing property of a substrate and can be measured for either reflecting material such as paper or transmitting material such as film. As described in the ANSI/ISO 5-3 standard, status A densitometry specifies the condition for transparencies and reflection prints, and status M is specified for negatives. The measured density also depends on the geometry of the incident light and that of the existent light. These geometric conditions are described in the ANSI/ISO 5-2 standard.
Density is mathematically defined with the following equation:

$$D_T = log_{10}\frac{1}{\%T} \qquad D_R = log_{10}\frac{1}{\%R} \tag{2}$$

$$where\ T = transmitance,\ and\ R = reflectance$$

The optical density of an image measured by a densitometer depends on the combined effect of the printed colors (CMYK) and is called integral density. If information about the individual contributions of the dyes is needed, the analytical density is to be measured, by using a spectrophotometer. (Figure 2)

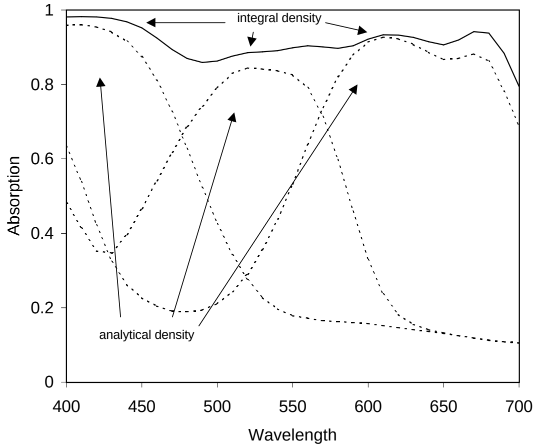


Figure 2: Integral and analytical density

Furthermore, a densitometer uses three filters (bandwidth 30-60 nm) to read its complementary color (Figure 3) [14]. Because these filter curves are optimized for photographic material, they do not match the absorption maxima of the dyes or pigments used in ink jet printing. The exact amount of the present dye or pigment is not measurable with those filters (Figure 4). Still, densitometers are essential quality-control tools for printers today. Their measured data contain enough information about the present dyes to give an adequate overview about the printed image, and in term of image-fading tests predictable tendencies of the fading behavior. However, there are currently many discussions going on concerning the recommended measurement practice for the light-fading test.

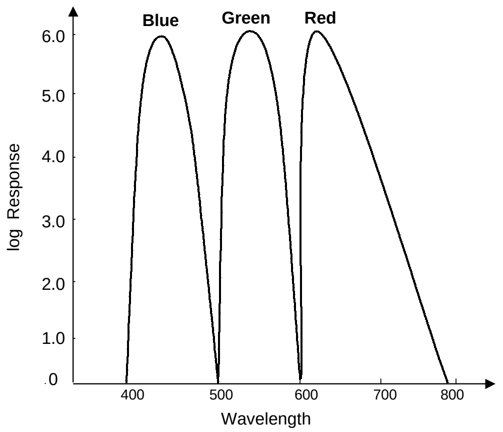


Figure 3: Red, Green, and Blue response functions for status A densitometry

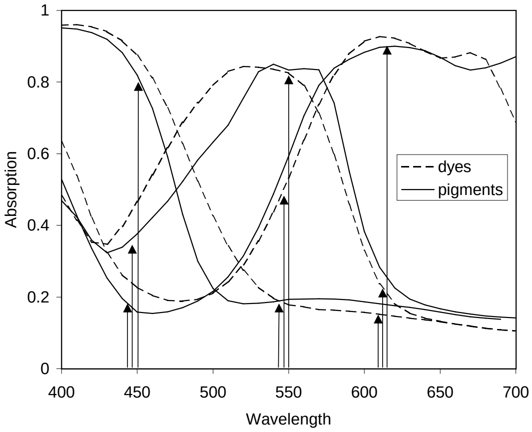


Figure 4: The arrows indicate the absorption maxima measured by the used filters

Spectrophotometry

The spectrophotometer is used to measure the spectral characteristics of light-reflecting and light-transmitting materials over the whole visible spectrum. Those spectral measurements require a diffraction grating or prism that disperses a light beam into its component colors of wavelength. By using an optical network of lenses and slits, a narrow bandwidth of color (10 nm or less) can be isolated. The various isolated wavelengths of light being transmitted or reflected from a surface are measured and their intensity is plotted along the entire visible portion of the electromagnetic spectrum (spectrophotometric curves). It is the most sensitive of the color measurement systems and its use increases more and more as it is linked with software to control color on display and output devices.

3.5 Media Design

The advent of digital color printing has opened up many new areas for ink jet including wide-format, graphic arts and textiles, which until recently were dominated by the traditional print technologies. Due to the variety of applications served by ink jet printing, there is also a huge range of media types including high-gloss films, canvas, vinyl, and textiles and also a wide range of coated and plain papers available. In terms of digital photography, ink jet printing has allowed photographic images to be printed on virtually any material that is capable of absorbing the ink and that can be fed through the printer.

Nevertheless, paper was the traditional substrate for impact printing, and it was the first choice for non-impact printing as well. Due to the fact that ink jet printing is very paper-sensitive, the paper needs to be optimized for ink acceptance to achieve higher-quality and more permanent prints. Paper needs at least an internal and a surface sizing in order to render adequate results. Further, paper can be coated with special ink receptive coatings to increase the print quality and provide photo-quality prints.

3.5.1 Ink and Media Interaction

The traditional physical and chemical treatments applied to paper were not adequate to assure ink jet print quality. To enhance the quality it was necessary to investigate the interactions that occur when ink jet ink is printed on paper. The key interactions take place when the ink hits the surface of the substrate. By modifying the structure of the colorant as well as the surface of the medium, prints with better image quality and a higher durability result [15].

There are a number of factors to consider when a colorant interacts with a substrate. Depending on the relatively complex chemical structure of both, different modes of interactions (i.e., covalent bonding, electrostatic or ionic interactions, $\pi - \pi$ interactions, hydrogen bonding, hydrophobic interactions, dipole-dipole interactions and Van der Waals force) take place [15]. Further, the energy for binding colorant to the medium has a significant influence on the fastness properties of the print. To get the highest quality images for specific ink jet applications, the choice of the medium and its matching colorant must be made very carefully.

3.5.2 Print Quality

The printer and printhead in combination with color management software play an important role in determining image quality, but the ink and medium are the two components that have the greatest influence on image properties. Thanks to such advances as smaller ink drops and the use of up to seven ink colors, the image quality of ink jet printing has begun to approach that of silver-halide photography.

For an optimum print density and good color saturation, the ink layer should remain at or near the surface after drying. The best materials hold much of the ink in the upper ten micrometers [5]. With the colorant fixed to the surface, however, it is directly exposed to light and pollution, and therefor it is vulnerable to decomposition of the dye. The light-fastness of the dyes can be improved by protecting them with surface coating or a polymer layer.

3.5.3 Ink Jet Papers

Plain Paper
This is the paper typically used in photocopy machines and electrophotographic printers in the office environment. This so-called office bond paper is made in very large volumes by mills worldwide and is the lowest cost paper available that satisfies ordinary electronic printing applications. Plain paper consists mainly of cellulose fibers and is not recommended for liquid ink jet printing because the ink wicks along these fiber structures. This decreases the sharpness of the image. Surface sizing is added to modify the characteristic of the paper by sealing the surface fibers. Common surface sizers are starches and gelatin. Latex and a variety of combinations of synthetic substances also can be used. Further, pigments such as calcium carbonate ($CaCO_3$) or titanium dioxide (TiO_2) can be added as external sizing to decrease ink wicking and also make the paper whiter [16].

If the medium cannot absorb the ink quickly enough, then the printer throughput must be constrained to a few pages or a dryer subsystem must be added to reach a satisfactory image quality [5]. However, this drying hardware is usually avoided because of its cost and impact on printer size. If the ink absorption characteristic of a medium can be improved via a coating then drying hardware is unnecessary.

Coated Media
Particularly for color ink jet printing, there has been considerable growth in the development of coated media to achieve photo quality images. Coated media can contain inorganic oxides such as alumina, silica, clay, titanium dioxide, calcium carbonate, etc., and also polymers such as polyvinylpyrrolidone (PVP), polyvinylalcohol (PVOH), gelatin, carboxylmethylcellulose and polyvinylacetate [15]. The receiver layers of the coated papers interact much more effectively with the colorant. These interactions greatly increase the binding energies for the colorant and lead to high chroma prints with no color-to-color bleed; they also improve water-fastness in most cases.

So-called matte-coated papers are basically coated with silicium or aluminium oxides and do not have a polymer layer (Figure 5). They are less anisotropic than uncoated paper, have high optical density, have a large color gamut, have good water-fastness and appear matte to the viewer [17].

Polymer-coated ink jet media show a homogeneous surface, excellent optical density, a large color gamut and a very high gloss [17] (Figure 6). The disadvantages of these water-swellable polymers or binders (receiver layers) are slow ink drying, loss of gloss after printing, curling both before and after printing and low water-fastness. The poor water-fastness occurs due to the use of a quick-swelling polymer, which essentially means a highly water-soluble polymer.

These polymers are typically gelatin, PVOH, PVP or combinations of these polymer systems and coated mainly on two kinds of media [18]. The first category is the resin-coated media where the paper substrate (rawbase) is coated with polyethylene (PE) on both sides and the receiver layers are applied to the primed surface of TiO_2-filled PE (frontside). This resin-coated paper is well known from conventional photography. The second group of media is classified as glossy paper media. There is no barrier layer as in the resin-coated media; instead there is a layer of barium sulfate (baryta) or clay in a crosslinked gelatin binder directly applied to the rawbase. Baryta-coated photo media have a high reflectivity and brightness and produce a very smooth surface, which is ideal for coating receiver layers. The baryta layer offers some additional ink absorption capacity; therefore, there can be problems with drying time and issues with cockle and curl. These baryta-coated papers were introduced to the conventional photography over one hundred years ago. The clay-coated papers tend to be not quite as good as the baryta-coated papers for brightness and gloss, but they still provide a good glossy photo paper. As long as the rawbase has a relatively smooth surface the receiver layers can be coated directly on it. The result is a reasonably good-quality photo medium.

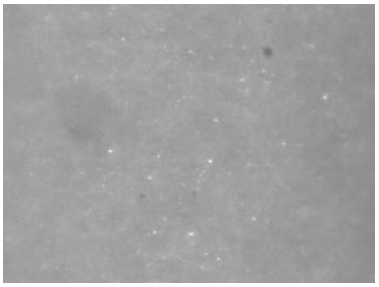


Figure 5: 50% magnification of a matte paper

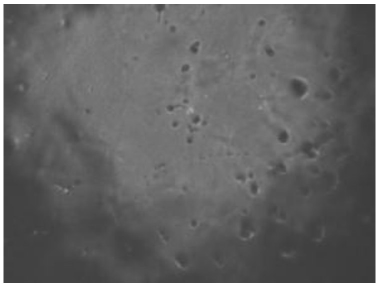


Figure 6: 50% magnification of a polymer coated paper

As the speed of printers has increased, fast-drying micro- or nanoporous media have been developed. In contrast to polymer coated media, the image-receiving layers of these papers do not need to swell in order to absorb ink, so that this medium avoids all of the disadvantages of swelling paper. An inorganic oxide such as aluminia or silica is used by this technology, which results in an instantly dry printing medium. The ink is absorbed into the micro- or nanocapillaries created by the alumina or silica particles [18] (Figure 7). Those systems can also be coated on both the resin coated and glossy paper substrates. Since such a receiver layer is fragile, a polymer binder is needed to keep the layer from cracking. A non-swelling polymer was found to satisfy the requirements and also increase the water resistance [19].

The micro- or nanoporous medium shows a homogeneous surface, excellent optical density, a large color gamut, good water-fastness and glossy appearance [17]. Pigmented inks can have problems penetrating these surface structures. They mainly reside on the surface, which leads to poor ink spread, loss of print gloss and smudging of the image when touched [6, 18]. The development of a pigment-compatible glossy photo paper is a different technical challenge.

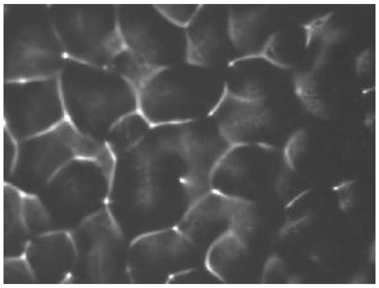


Figure 7: 50% magnification of a microporous paper

The conclusion of Aidan Lavery from Felix Schoeller Digital Imaging in his paper about "Photomedia for Ink Jet Printing" presented at the NIP 16 (International Conference on Digital Printing Technologies) in October 2000 in Vancouver was:

> "The development of the receiver layers matched to the future systems offers the best opportunity for achieving the ultimate goal of silver-halide quality using an ink jet printer." [18]

3.6 Issues in Ink Jet Image Stability

After the print quality of silver-halide images was more or less achieved by the ink jet technology, questions came up about the permanence of the digital prints compared with that of silver-halide-based chromogenic color prints. This led to developments of enhanced stability of inks and media, and also addressed the issue of image stability in ink jet printing. Images produced by ink jet technology can be affected by light, water, humidity and many other factors, some previously unconsidered. The most studied and well-known issues are light- and water-fastness; some of the newer ones are humidity- and ozone-fastness.

3.6.1 Light-Fastness

In general, dyes resist fading in a vacuum. In contact with the atmosphere, the media and other compounds in the ink, they will fade to varying degrees. The understanding of the controlling mechanisms is somewhat limited due to the fact that there is no single, well-defined mechanism explaining the photodegration. More often there is a whole group of mechanisms that have to be understood in order to improve light-fastness.

Photo-oxidation and Photo-reduction
On absorbing a photon, the dye is excited to a higher singlet state (S_1). Then it can return either to the ground state (S_0) directly, resulting in fluorescence or, by "inter system crossing" (ISC), to the triplet state (T_1), resulting in phosphorescence (Figure 8) [20].

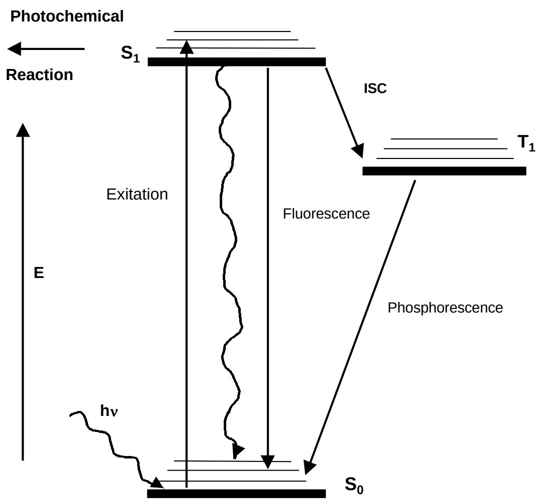


Figure 8: Chromophore excitation by a photon of light

Because UV radiation has more energy than the light of the visible spectrum it forces more excited singlet states. Visible light gets absorbed by the dye as well, this is why we can see the color of the dye. When the dye is photo-exited (D^*) it can undergo a photochemical reaction leading to degradation.

Most colorants undergo oxidative fading in the presence of light, moisture and oxygen. Either the photoexcited dye can react with water and the hydrogen peroxide, formed in a second step from oxygen, and the hydrogen radical destroys the dye, or the dye can react with oxygen leading to singlet oxygen which also destroys the dye direct or indirect [21].

Photo-oxidation:

$$\begin{array}{lll} D + h\nu & \longrightarrow & D^* \\ D^* + H_2O & \longrightarrow & \cdot DOH + H\cdot \\ H\cdot + O_2 & \longrightarrow & HOO\cdot \end{array}$$

$$\begin{array}{lll} D + h\nu & \longrightarrow & D^* \\ D^* + O_2 & \longrightarrow & D + O_2^* \\ O_2^* + H_2O & \longrightarrow & HO\cdot + HOO\cdot \end{array}$$

Another possible photochemical reaction which destroys the dye's molecule into a colorless product is the reductive mechanism. Either the dye picks up a hydrogen or an electron transfer takes place [21].

Photo-reduction:

$$\begin{array}{lll} D + h\nu & \longrightarrow & D^* \\ D^* + RH & \longrightarrow & \cdot D^- + RH^+ \\ D^* + RH & \longrightarrow & \cdot DH + R\cdot \end{array}$$

The photostability can be increased by reducing the lifetime of the dye in its excited single state, i.e by adding a substituent (antioxidant) or changing the dye's molecular structure (auxiliary groups) [20].

The mechanism of decomposition of azo dyes (i.e., magenta dyes) has been investigated by a number of researchers. The oxidative fading of an azo dye has been attributed to the attack of singlet oxygen on its hydrazone tautomer. This initial reaction produces an unstable peroxide which rapidly decomposes into a colorless molecule. While this reaction is promoted by singlet oxygen sensitizers (e.g., other dyes), singlet oxygen quenchers such as 1,4-diaszabicyclo[2,2,2]-octane (DABCO) and nickel-dibutyldithiocarbamate (NBC) suppress the fading [9, 22].

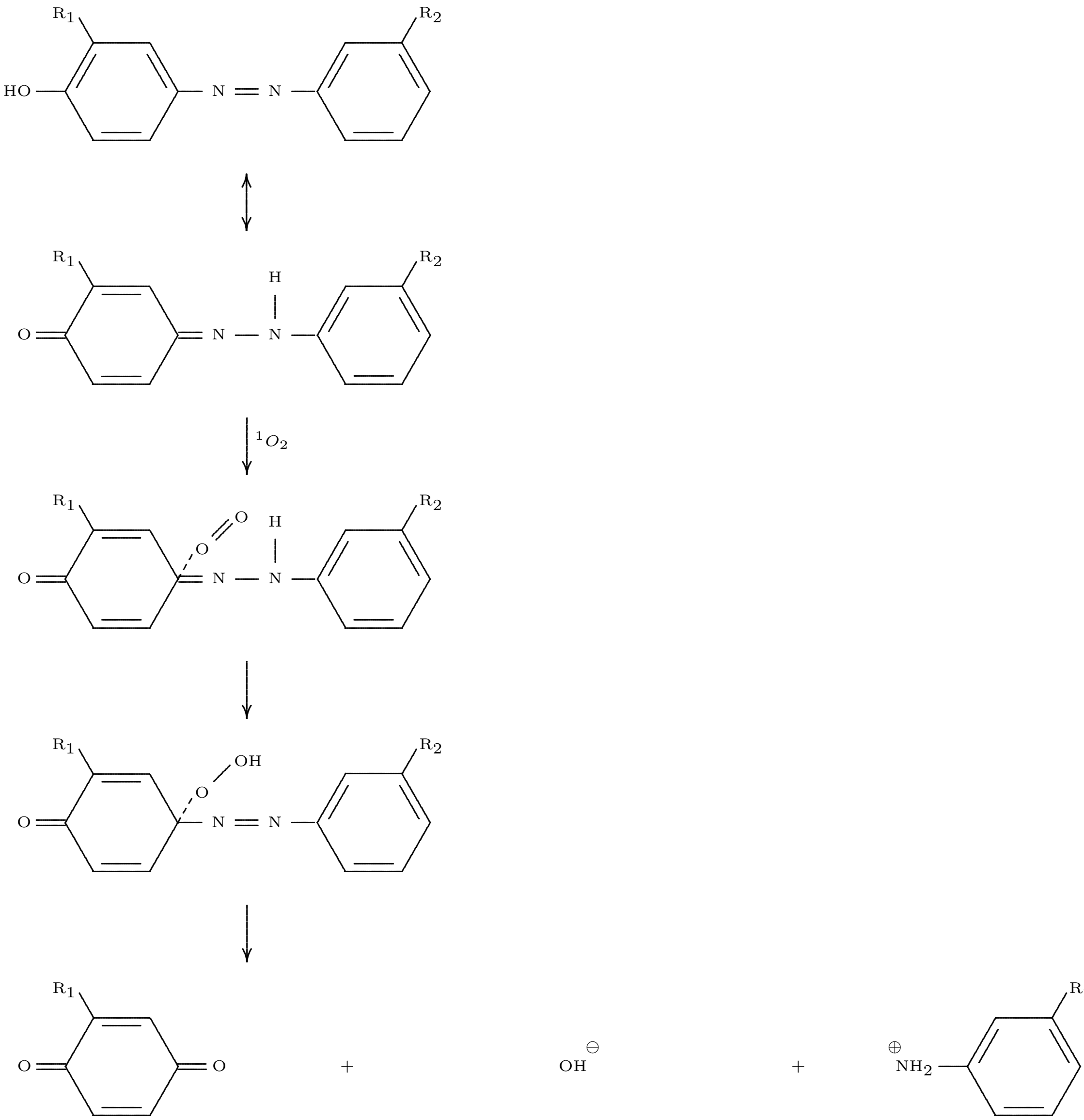


Figure 9: Oxidation mechanism for azo dyes

The reductive fading mechanism of an azo dye under anaerobic conditions is based on the addition of a hydrogen donor, like alcohols, amines, ketones, carboxylic acids, ethers and esters. This reaction is greatly accelerated when either the hydrogen donor or the dye is photo- excited [9, 22].

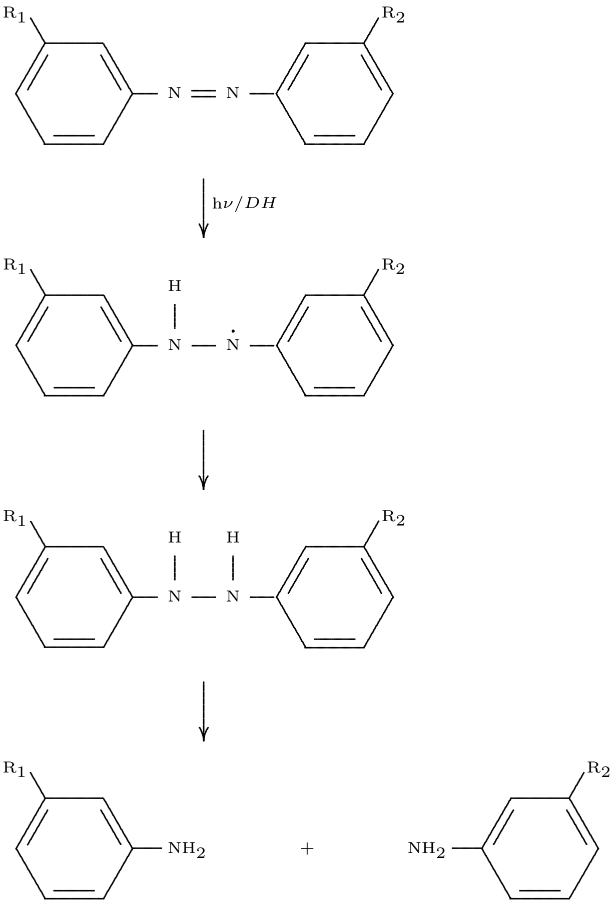


Figure 10: Reduction mechanism for azo dyes

Photocatalysis

As mentioned above, excited dyes can produce singlet oxygen resulting in oxidative fading. Catalytic fading happens when one dye can transfer its absorbed energy to another dye at a lower energy level and increases the other dye's radiative exposure and its fading. The dyes have to be mixed on the image for catalytic fading to take place. In ink jet, for example, it is possible to observe catalytic fading of magenta dyes by the presence of cyan dyes, i.e., in a blue hue where the cyan and magenta dots are overlapping [23].

Dye Aggregation and Pigments

By investigating the light stability of ink jet images it has been found that dye aggregates (formation of micelles [22]) are more resistant to fading than their monomolecular state.

The positive effect that aggregation can have on light-fastness has been attributed to several factors [24]. For example, these larger aggregates diminish the attack by radicals due to the surface area per unit mass of the available dye. Since light is absorbed within the surface layers of the larger aggregates, as the outer layer is degraded, reactants diffuse more slowly through it to reach the reservoir of unreacted dye in the interior. Another factor is that the lifetime of the dye's excited state is possibly shorter in the aggregated state, which allows it less time to react [9]. These arguments explain the reduction of fading rate over time in aggregated dyes. They are the same arguments used to explain the better light-fastness of pigments over dyes. Organic pigments are known to achieve their light-fastness due to their particle-forming properties. However, if they are fine enough to meet the requirements of modern printers, such as passing through the nozzle and matching the color gamut of dyes, they begin to lose their inherently better light stability due to the reduced stability of smaller particle sizes.

Dye aggregation can be induced in several ways; for example, it can be induced by reducing the dye's solubility via a co-solvent. A less basic pH and the addition of salts also lead to aggregation. Overall, the two most important variables to control aggregation are relative dye concentration and solvent concentration in the drying dot in the image layer. The decrease of dye concentration and/or increase of solvent concentration leads to fewer dye molecules in a dot, where they are no longer able to build aggregates of larger particle size. The use of diluted ink, i.e., in a six-ink system to improve the highlights of an image, reduces the light-fastness of low and medium densities up to a factor of two [23].

Effect of Additives

The additives used in an ink formulation can influence the light stability. For example, optical brighteners, mainly used in paper based substrates to make the paper appear whiter, can have a great influence on the photo-fading mechanism. Basically these brighteners are designed to absorb photons of one energy (usually UV light) and emit a photon of a lower energy in the visible spectrum. Now, as the dye comes into contact with the brightener it has the opportunity to absorb energy, not from a photon but from an optical brightener molecule excited by a photon [25]. These energy transfer mechanisms are well known and can function as an additional center where a photochemical reaction begins and cascades.

Other substances are added to protect the chromophores and enhance light stability. Depending on the photo-fading mechanism, reducing agents or antioxidants could be added [9]. Further, it should be kept in mind, that the components chosen to stabilize one colorant may well destabilize others.

3.6.2 Water-Fastness

Due to the widespread use of water-soluble ink, water-fastness can be a major issue for water-based dyes. These dyes are needed to achieve maximum freedom in formulating the ink to perform reliably in the printer, but once on paper they should not re-dissolve or disperse on contact with water.

Avecia, an ink supplier in Manchester, UK, has used two successful approaches. One is based on pH and the other on a zwitterionic-type mechanism [26]. Not only the ink vendors but also the media manufactures tried to solve the water-fastness problems with ink jet prints. The development of the fast-drying micro- or nanoporous papers, as described in section 3.5.3., were a great step towards water-resistant prints.

3.6.3 Humidity-Fastness

The term "humidity-fastness" describes the durability of an image under conditions of high humidity at sometimes higher than normal temperature. These conditions can lead to dye de-aggregation and to dye diffusion (bleeding) through the medium. These effects should be kept in mind when looking at accelerated light-fading tests. The high irradiance tends to dry out the test samples, which often helps to preserve them. But dry environmental conditions cannot be assumed for all locations where prints will be displayed; often they are much cooler and more humid. Test results by Ilford show that density changes are typically 1.5-3 times higher under humid conditions, than under dry conditions [27]. However, the separation of these two effects (humidity and light) in accelerated fading experiments is very difficult. Another issue where humidity has a great influence is dark storage print life. ISO Standard 10977 recommends primarily testing at a humidity of 50% ± 3% at different temperatures for color photographic materials.

For ink jet prints, humidity levels that are higher than 50% are of greater concern for dark stability. Test results from the measurement of humidity effects on ink jet prints kept in the dark were given by Kodak at the NIP 16 Conference in Vancouver [28]. The observed changes, like lateral ink diffusion (dye smear or blur), density changes (increase or decrease) and color balance changes (hue shifts) were measured. It was found that a relative humidity level of 60% is enough to cause significant changes in the image quality of the test target. At an increase of humidity above 60% the amount of time eliciting these changes decreased.

3.6.4 Ozone-Fastness and Other Pollutants

Ozone has been suggested as a reason for fading of ink jet prints, but it has not yet been proven. There is a hypothesis that exposure to an ambient level of ozone over time can cause significant fading of ink jet prints. The impact of high levels of ozone in accelerated testing is easy to see, but the fact is that these high concentrations of ozone regularly force chemical reactions that can result in dye fading. However, no one has yet demonstrated that the level of ozone present in normal air at ground level is unambiguously an agent that causes significant degradation. On the other hand, it is well known that airflow (e.g., air conditioning systems) causes fading in ink jet images [1, 2]. As other pollutants, such as NO_x and SO_2, are obvious possibilities as well, it has not yet been proved which one really is the culprit.

The effect of environmental pollution on the aging stability of papers as archival materials has been addressed in several investigations [29, 30]. The studies have been focused mainly on the interaction between paper and SO_2 or NO_2, since the impact of ozone (as a bleaching agent) on paper degradation has attracted less interest in the field of paper conservation. It has been found that NO_2 and SO_2 or a mixture of NO_2/SO_2 causes yellowness to varying degrees on tested papers.

Since there is no standard test method for determining paper deterioration, the Paper and Paper Products Committee of the American Society for Testing and Materials (ASTM) started a research program with the purpose of developing the needed test methods. Five laboratories joined to do the research on temperature, light and atmospheric pollutant gases, as the means to accelerate aging. The scope of the project assigned to IPI was to develop an atmospheric pollution aging test [31].

4 Test Methods

In the present study various test conditions were chosen to observe different fading behaviors of ink jet prints. Samples, framed and unframed, were exposed to high-intensity light, as well as to airflow. Further, samples were exposed to ozone and nitrogen dioxide to better predict the influence of possible environmental pollutants. A dye-based and a pigmented ink set, each printed on two different papers, were chosen to observe any ink and media interactions and the stability of pigments compared to dyes. The purpose of this study is to lead to a better understanding of the complex fading behavior of ink jet prints and to demonstrate the difficulties in providing reliable tests.

4.1 Light-Stability Test

The accelerated high-intensity light-fading test was done in a light-fading unit at IPI. Cool-white fluorescent tubes in a unit as described below were used as a light source. The test ran 10 weeks (dye samples) and 14 weeks (pigment samples) at 50 klx, at an ambient temperature of 20°C ± 2°C and a relative humidity of 45% ± 5%. Sample readings were done every week.

Studies and testing in home environments, done in the United States, have shown that the average amount of light an image is exposed to in real life is about 215 lx. Temperature and humidity are at an average about 21°C and 50% RH [32, 33]. By using high-intensity lights, the accelerated light-stability tests can be complicated by the so-called reciprocity law. The reciprocity law simply states that the amount of photochemical changes is constant for any constant exposure (intensity x time). For light-fading experiments, this law says that the same degree of fading should occur with ten times the intensity in one-tenth the time. However, there are color photographic materials as well as ink jet materials that do not follow this law and fail. The magnitude of reciprocity failure is influenced by the display condition in real time, i.e., humidity, temperature or oxygen, and can result in faster or slower fading of colorants than predicted.

A recent study, with high and low-intensity light exposures of ink jet materials, showed that the fade rate is about two (non-porous media) to three (porous media) times faster on average under the lower exposure conditions [34]. Thus, accelerated light-stability tests are valid at the specified test conditions, but they might not reliably predict the behavior of the tested material in long-term display under normal conditions. Due to this fact, a low-intensity test (e.g., 1 klx for at least four months) is recommended [3] to determine if a material has a tendency to exhibit reciprocity failures.

No low-intensity test was done in this study, because of the limited test time.

4.1.1 Apparatus

The IPI high-intensity fluorescent unit [35] uses forty-two, GE F72T12CW 1500W cool-white (4100°K) outdoor fluorescent tubes. These lamps are divided into groups of three giving 14 separate circuits and on/off switches, which make it easier to pinpoint bad lamps. A transformer powers each circuit. The lamps are mounted vertically in the lamp frame with 21 lamps on each side of the fixture. They are placed as close together as possible to minimize “cold spots” at the sample plane. Samples are mounted in two panels on either side of the lamp frame. The panels are fitted with aluminum channels that receive the samples. Light intensity can be adjusted by moving the sample panels in or out as needed, and it is possible to maintain any intensity level between 50 klx and 100 klx. In the current configuration, thirty-two, 20 x 25 cm samples at 50 klx can be tested (Figure 11).

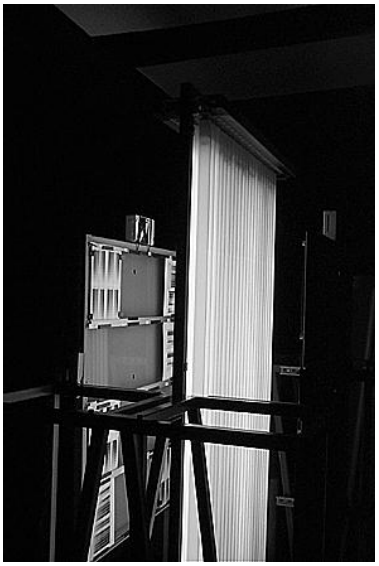


Figure 11: Light-fading unit at IPI

To provide a humidity- and temperature-controlled environment and to cool down the tubes, the unit stands in a separate room with an air conditioning system. An air stream of about 1.3 m/s, at 18°C and 55% RH is continuously passed across the tubes and the surface of the test samples to produce a white backing temperature of 20°C ± 2°C and 45% ± 5%RH.

4.1.2 Test Conditions Control (Room)

To monitor the temperature and humidity in the light-fading room, a datalogger called Preservation Environment Monitor (PEM) developed by IPI was used. The PEM was mounted on top of the sample racks, below the air conditioning slits. The data were read out using a PC-card and were imported with software called "Climate Notebook", which was also developed by IPI. To look at the data and to print out a chart, the Engineer's View, which is the most technical view provided by the software, including all the data points of the temperature and humidity measurement, was used and is shown in Appendix D.

Exposure control was done by a Minolta Illuminance Meter, Model T-1M, reading klx. A frequent control of the exposure (intensity x time) is essential because the exposure is not even over the sample rack. Due to the construction of the unit, samples located in the middle part of the rack get a higher exposure than those located on the edges. This necessitates the rotation of the samples to ensure an even exposure for all samples.

The weekly lux readings were used to create the following "sample rotation plan" what ensures that each sample gets the same exposure: The lux measurement was taken when the samples were out for reading. A sheet of grey plastic covered the back of each sample rack (and it has nine holes per sheet in the size of the detector from the lux measurement device). It was important to do the lux reading consistently to keep the deviation as small as possible. There is an expected average deviation of ± 10%, because of variability in the measurement and the device handling. The measured data were used to create a “sample rotation plan” in Microsoft Excel. Excel sorts the measured data in an ascending list and puts the highest and the lowest measured spots together in a pair, then puts the next highest and the next lowest together, and so on. In the end, every sample in a pair has the same average amount of light because the samples have been rotated.

This intensity measurement is also used to control the aging of the tubes. When the samples are getting a lower exposure than 50 klx, tubes have to be replaced. Normally they should be replaced after 2000 hours of operation (ISO Standard 10977), which equals 12 weeks. The tubes in IPI’s unit are checked on a weekly basis, and replaced if needed, and to ensure that they are not more than 12 weeks old.

Another aspect of tube aging is the UV fading. To control this, a dual channel optometer (model 380 A) from UDT Instruments was used. The detector is calibrated from 200-400 nm in 10 nm steps and the display is in mW. The reading was done every week, after the lux measurement. No significant changes in the UV spectrum over the test period were observed.

4.1.3 Target Specifications

Each target contains ten steps of varying densities from 10-100 dot percentage of each of the following colors:

- Black (containing cyan, magenta, yellow and black)
- Pure Cyan
- Pure Magenta
- Pure Yellow
- Red (containing yellow and magenta only)
- Green (containing yellow and cyan only)
- Blue (containing cyan and magenta only)

Each step is approximately 1 cm square. An area of approximately 1 cm square is left blank so that a d_{min} reading can be taken (paper density). The end-size of the target is 8 x 11 cm. The target was created in *Adobe*© *Illustrator*© 8.0 in CMYK modus and saved as an EPS file (Figure 12).

Figure 12: Test target

4.1.4 Samples

The targets were printed on two different desktop printers on two different papers. One printer is an Epson PM-820 (Stylus Photo 1270) with a six-ink system using dye-based ink. The other one is an Epson MC-2000 (Stylus Photo 2000P) also with a six-ink system, using pigmented ink. The two papers are PM matte paper (Epson Matte Paper Heavyweight) and MC photo paper (Epson Premium Glossy Photo Paper) a microporous paper, specially developed for pigmented ink.
The combinations are:

1. Epson PM-820
    (a) PM matte paper
    (b) MC photo paper
2. Epson MC-2000
    (a) PM matte paper
    (b) MC photo paper

Due to the fact that every printer driver has its own implemented color management or color adjustment that always tries to optimize the print, it is difficult to print pure color patches. In the driver software, the window "no color adjustment" has to be chosen. There are problems with printing pure colors at all with a few of the newer printers. Further, the software must allow the choice of the right modus (CMYK in this case); also any color adjustments provided by the software itself must be switched off. *Adobe*$^©$ *Photoshop*$^©$ 6.0, for example can not be used, due to this fact; only the previous versions can be used. Thus, to control the printed target, it is recommended that a magnifying glass or a microscope be used to view especially the pure color patches. Figure 13 and 14 are showing a magnification of pure yellow patches as an example.

The samples were provided by Yoshihiko Shibahara from Fuji Photo Film Co., Ashigara Research Laboratories. They were printed using *Photoshop*$^©$ 4.0 (CMYK modus) and "no color adjustment" in the driver software. The papers used were PM matte paper, KA4250PM, Lot No 00000022M, 0.23 mm, and the MC photo paper, KA420MSH, Lot No BOEF23140, 0.27 mm, purchased in fall 2000.

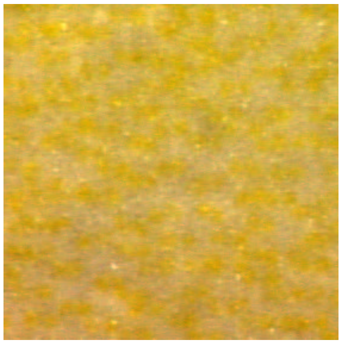


Figure 13: Pure Yellow patch, okay, only yellow dots

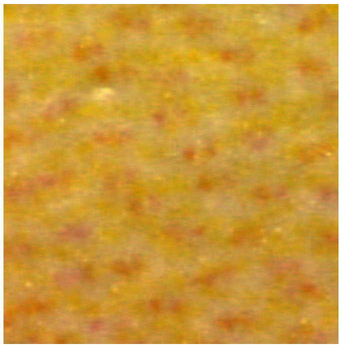


Figure 14: Pure Yellow patch, contaminated with red dots

4.1.5 Sample Handling

The samples were mounted on white 20 x 25 cm cardboard with photocorners, which makes it easier to take them out for the readings. Two targets per sample, mounted on different cardboards to avoid significant exposure differences, were exposed for each test. Three different test conditions were used. Altogether, 24 targets mounted on six cardboards were exposed. Also, a set of targets were kept in the dark, under the same ambient conditions and monitored for any changes during the test period.

4.1.6 Test Conditions

1. 50 klx light: 2 x 4 Samples were exposed for 10 or 14 weeks to 50 klx fluorescent light and the normal airflow in the light-fading room. These are the normal test conditions used by IPI.
2. Glass filtered: 2 x 4 Samples were filtered with window glass and were exposed for 10 or 14 weeks to 50 klx fluorescent light. There was no airflow and UV light hitting the samples. There was no way to separate these two effects from each other, e.g., blocking the airflow without cutting of the UV light or vice versa, because the unit was packed with customer testings, which did not leave room for any modifications. The spectral energy distribution of the tubes as well as the transmission of the window glass meet the standard requirements.
3. Airflow: 2 x 4 Samples were exposed for 10 or 14 weeks only to the normal airflow in the light-fading room and to approximately 150 lx roomlight (fluorescent light), because the samples were put on the "back" of the unit (Figure 15). Due to the fact that a special apparatus would have been needed, no real dark fading test under the same airflow was done.

The temperature and humidity conditions were monitored over the test period and are shown in Appendix D.

Figure 15: Position of the airflow samples

4.1.7 Measurement

The measurement of optical density as well as the reflectance spectrum of the samples was done once a week with the SpectroScan from GretagMacbeth. Due to the fact that the SpectroScan does not have any display, readings were carried out by using a specific software called SpectoChartLight in an Excel data sheet. The test target has to be positioned on the electrostatic surface. After the last position is inserted, an absolute white calibration of the Spectrolino is performed automatically, and the automatic data reading procedure is started (Figure 16).
The general settings for the reading are:

- Measuring geometry: annular optics 45°/0°, measuring diaphragm diameter 4 mm
- Light source: tungsten lamp, gas-filled, type A light
- Physical filtering: no filter
- Densitometry: ANSI/ISO status A
- Spectral measurement: by holographic defraction grating, from 380 nm to 730 nm at 10 nm intervals

Figure 16: SpectroScan

The given equipment accordance is:
as norm 0.3 ΔE CIE on average by 12 BCRA ceramics and as maximum shift 0.8 ΔE CIE by 12 BCRA ceramics. [36] The short-term repeatability is 0.02 ΔE CIE (standard shift from ten measurements at ten second intervals on white).

4.1.8 Analysis

To analyze all the measured data, the software Excel was used. No calculation of image stability parameters as recommended in the standard was done. The analysis was more focused on looking at the whole behavior of the colorant, i.e., density changes over all step wedges to observe different fading rates in D_{min} (diluted ink) to D_{max} (concentrated ink). For the whole analysis only the raw data were used. No interpolation was done between two step wedges to get $D_{1.0}$ (ISO Standard 10977). Also, no d_{min} (paper density) correction was done, as no significant yellowing occurred. Density data were plotted in a graph showing the density changes from one color in all patches from D_{min} to D_{max} over a specific time period. The integral optical density (OD) of the initial readings were written on the x-axis, while the integral OD readings of the faded patches were written on the y-axis (Figure 17). In some cases the percentage change in density, using a single patch over time was calculated and graphed as well (Figure 18).

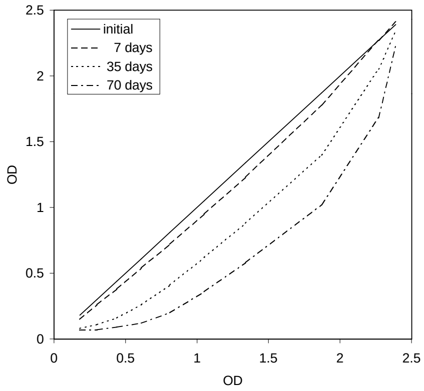


Figure 17: Integral optical densities (OD) over a specific time period

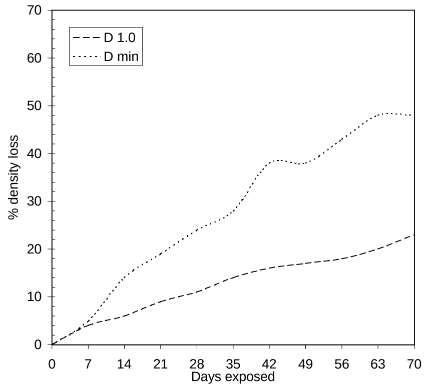


Figure 18: Percentage density loss over time for a specific patch

In addition, spectral data were analyzed by plotting them in a graph showing the absorption of the different colorants in various patches over the whole visual spectrum (400-700 nm) at different time periods. This way, it was easy to observe changes in the absorption maxima while fading occurred, which can result in color shifts. The spectral readings were used only for visual analysis. No further calculation of ΔE values was done, because they are not part of the standard yet.

4.2 Pollution Test

Accelerated pollution tests using ozone and nitrogen dioxide were added to the light-fading test. As there is neither a standard for ink jet stability tests, nor a standard test method for determining paper deterioration, the testing was done based on an atmospheric pollution aging test developed by IPI. The tests ran 18 days at an ambient temperature of 25°C and a relative humidity of 50% and concentrations of 10 ppm ozone and 10 ppm nitrogen dioxide, respectively. In addition the two dye-based samples ran four days at an ozone concentration of 1 ppm. Sample readings were done after 1, 2, 3, 4, 7, 14 and 18 days.

Studies have shown that atmospheric pollutant gases, such as NO_2, SO_2 and O_3, vary widely, not only with the population (i.e., growing numbers of cars), the geographical locations (i.e., industry), but also with the time of the day (i.e., rush hour) and of the year (i.e., winter/summer). The average O_3 and NO_2 level is typically 0.01 to 0.03 ppm (by volume) over a whole day. It is also well known, that indoor concentrations of ozone are smaller than outdoor concentrations, due to the high reactivity of ozone with all kinds of surfaces, (i.e., textiles on walls and floors). Like the high-intensity light-stability tests, the accelerated pollution test can also fail the reciprocity law. In this case, the reciprocity failure occurs due to the high concentration of gases which can force chemical reactions; this might not happen under normal conditions (e.g., changes in d_{min} [yellowing] do not follow the reciprocity law) [31].

4.2.1 Apparatus

The Image Permanence Institute had previously constructed two large pollution chambers [31] which were provided with temperature (24°-90°C) and relative humidity (10-90% RH) control (Figure 19). The operating conditions are set and monitored from a PC computer via software with two ANAFAZE 8LS controllers. Oxides of nitrogen are supplied from storage tanks while ozone is generated on demand using a high-voltage discharge. The gas concentration in the chambers is controlled by an operator and is monitored daily. This reading is used to adjust the amount of gas introduced into the chamber. The gas monitors used were all made by Monitor Labs, Inc. The ozone monitor is a model 8810 UV photometric ozone analyzer. Nitrogen dioxide is measured by a model 8840 chemiluminescent nitrogen oxides analyzer. The monitoring equipment is mounted on an outside instrumentation rack and is calibrated by a Monitor Labs 8500 calibrator. Readings have a precision of approximately ± 1%. In order to withstand the corrosive atmospheres, the inner walls are constructed of 12 mm PVDF (polyvinylidene fluoride). PVDF is an inert fluoropolymer that is highly resistant to oxidative and acidic environment. There are some stainless steel components inside the chambers (rack and airflow control panels) which can be replaced, if necessary. All intake and exhaust tubing for the pollutant gases as well as wiring insulation are PTFE (polytetrafluoroethylene). To avoid stratification and interactions between papers, there is a very high airflow, with air entering the chamber from a perforated plate in the rear panel at a velocity of 2 m/s. Approximately 5% of the air is exhausted, so that there is no buildup of degradation products, and the gas concentration is monitored and kept at a constant level.

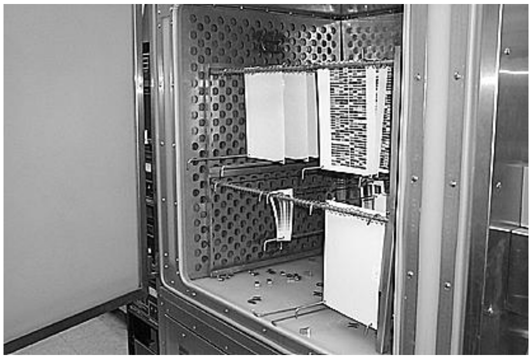


Figure 19: Pollution chamber at IPI

4.2.2 Samples/Target Specification

The same samples with the same target specification as for the light-fading tests were used.

4.2.3 Sample Handling

All paper samples were threaded through two stainless steel rods (at top and bottom) and suspended on a rack. This prevents paper movement due to the high airflow. Two targets of each sample were exposed for each test.

4.2.4 Test Conditions

1. 10 ppm O_3: 2 x 4 samples were exposed 18 days, at a concentration of 10 ppm.
2. 10 ppm NO_2: 2 x 4 samples were exposed 18 days, at a concentration of 10 ppm.
3. 1 ppm O_3: 2 x 2 samples (only dye-based) were exposed four days, at a concentration of 1 ppm

Both chambers were set to 50% RH and 25°C, since these conditions are most typical of practice, and monitored daily.

4.2.5 Measurement

For the measurement of the samples, the same SpectroScan with the same settings as for the light-fading tests was used.

4.2.6 Analysis

The measured data were analyzed the same way as the light-fading data were analyzed.

5 Analysis & Discussion

In this study two different ink sets on two different papers were tested. A dye-based ink and a pigmented ink were chosen and environmental influences on the stability of these colorants were compared. They were printed on two different media (a matte and a glossy photo paper) to observe any ink/media interactions. Various light and airflow conditions were used in the tests; the airflow condition was included because of a problem observed recently with a particular glossy photo paper (microporous paper) when exposed to airflow [1, 2]. To better investigate this problem a test was added to observe the effect of environmental pollutants, such as ozone and nitrogen dioxide, on the stability of ink jet prints.

Due to limitations of time and available apparatus it was not possible to do a separate test for each condition that can influence the speed and the amount of fading of an ink jet image (i.e., light, humidity, temperature, airflow, ozone). The test results show the behavior of the samples exposed to 50 klx light (unfiltered and glass-filtered) and to airflow (150 lx light). However, the humidity in the 50 klx light samples was lower than in the airflow samples because of the high irradiance, which tends to dry out the samples. As humidity increases, the fading rate of ink jet prints increases as well (as mentioned in section 3.6.3.). Therefore, this effect was added to the effect of the airflow samples; it was impossible to separate the two.

Similar problems occurred in analyzing the samples (unfiltered and glass-filtered) exposed to 50 klx light, because the UV-light and the airflow were cut off at the same time. UV light is known to have more energy than visible light, but it was difficult to tell how much fading was caused by UV light, how much by the light of the visual spectrum (VIS light), and how much by airflow. However, by looking at all samples aged by the three test conditions it could be determined, more or less, which fading was caused by UV light and which was caused by airflow. The highest fading rate of the dye-based samples occurred always with 50 klx light (Condition 1). If the next highest fading rate was caused by the glass-filtered condition (Condition 2) or the airflow condition (Condition 3), then the stability or unstability of the colorant against airflow or UV light could more or less be determined.

Further, it was not possible to completely separate the effect of pollutant gases (i.e., O_3 and NO_2) and airflow on the fading rate of the samples. This is because of the high airflow used in the pollution chamber (to avoid stratification of the chamber atmosphere and interactions between the samples) and because of the possible presence of pollutants in the environment that could not be measured (for example, ozone in the light-fading room). A table with an overview of the results is presented at the end of each chapter.

5.1 Dye-based samples

5.1.1 Density analysis

The density data were used to look at the rate of fading over all patches over time. To interpret the different behavior of each dye under the different test conditions, they are graphed as explained under 3.1.8. The goal was to observe how the rate of fading was influenced by the various factors, as the three dyes (cyan, magenta and yellow) show different stabilities against UV light, VIS light, airflow, ozone and NO_2.

Cyan

The cyan dye turned out to be the most stable of the three dyes in the VIS light when exposed to 50 klx light behind glass (filtered). It was the least stable when exposed to 50 klx light (unfiltered), airflow, ozone and NO_2. Figures 20 and 21 show examples of the cyan dye in a pure patch, printed on glossy photo paper.

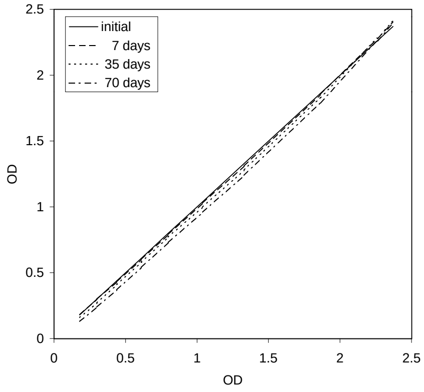


Figure 20: Cyan dye exposed to 50 klx light (glass-filtered)

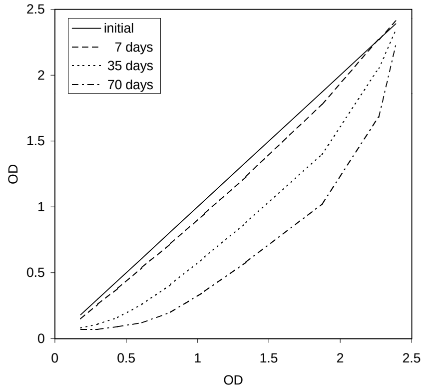


Figure 21: Cyan dye exposed to 50 klx light

Magenta

The magenta dye was the least stable in the VIS light and was unstable in UV light as well. In terms of airflow, ozone and NO_2, magenta turned out to be fairly stable. Only in high concentration of 10 ppm O_3 did fading occur. Figures 22 and 23 show examples of the magenta dye in a pure patch, printed on glossy photo paper.

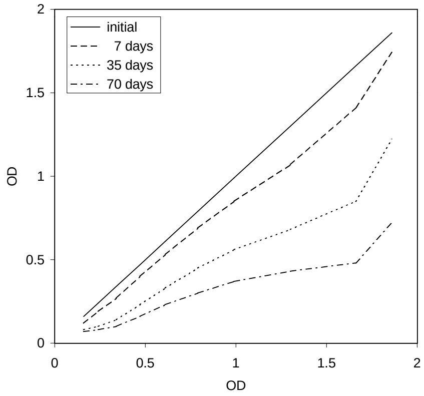


Figure 22: Magenta dye exposed to 50 klx light

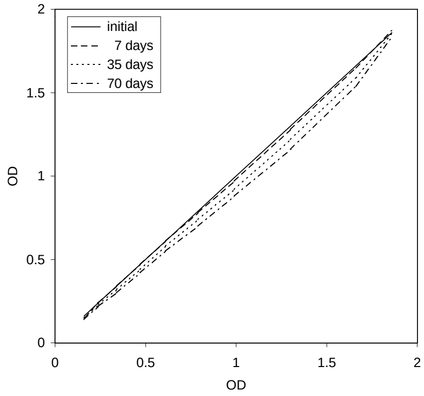


Figure 23: Magenta dye exposed to airflow

Yellow

The yellow dye was nearly as unstable as the magenta dye in both VIS and UV light. It did not show any significant fading in airflow, and only high concentrations of O_3 and NO_2 led to density decrease. Figures 24 and 25 show examples of the yellow dye in a pure patch, printed on glossy photo paper.

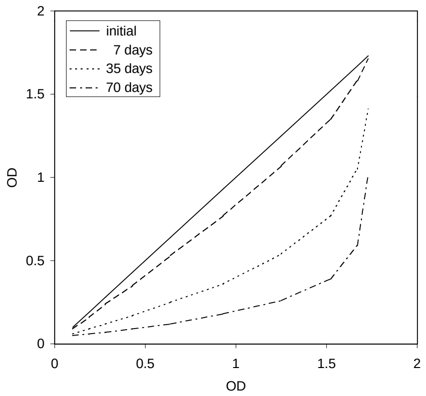


Figure 24: Yellow dye exposed to 50 klx light

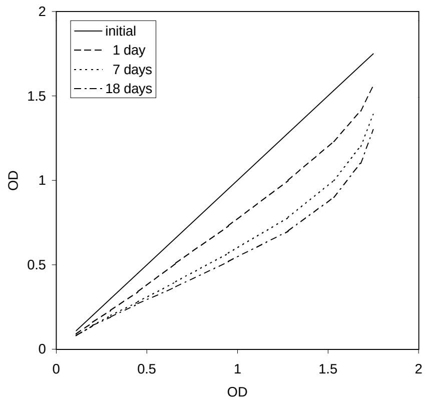


Figure 25: Yellow dye exposed to 10 ppm NO_2

Catalytic Fading and Aggregation

Almost no catalytic fading (section 3.6.1.) in the mixed patches was observed, except in a few cases. The cyan dye showed catalytic fading on glossy photo paper under the glass-filtered (Figure 26) and airflow conditions in all patches. The magenta dye showed catalytic fading as well, mainly in the blue patch in the presence of the cyan dye when printed on glossy photo paper and exposed to airflow (Figure 27).

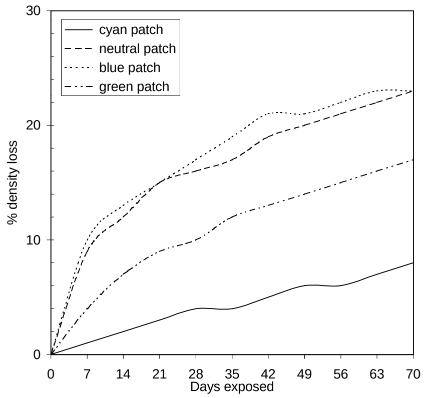


Figure 26: Cyan dye exposed to 50 klx light (glass-filtered)

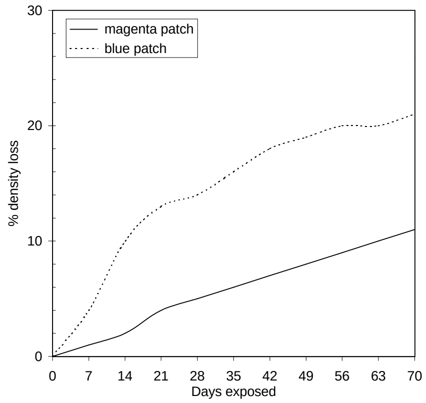


Figure 27: Magenta dye exposed to airflow

Another phenomenon occurring in all light-exposed neutral patches was that the D_{max} fading rate increased, while in all other cases the D_{max} patch was the most stable and only faded to a small degree. The overall better stability of the higher densities ($D_{1.0}$ and especially D_{max}) over the lower densities (D_{min} to $D_{0.6}$) when exposed to light was due to the use of concentrated ink. A diluted magenta and cyan ink is used to print the low-density patches. The use of diluted and concentrated ink influences the dye aggregation, and so the stability of the dye, as mentioned in section 3.6.1. However this does not explain the higher fading rate of the D_{max} in only the neutral patches, exposed to light (Figure 28). Because this happened neither in the D_{max} in other patches, nor in the neutral patches exposed to airflow (Figure 29), ozone and NO_2, this phenomenon seems to be a light reaction related to the presence of the black dye.

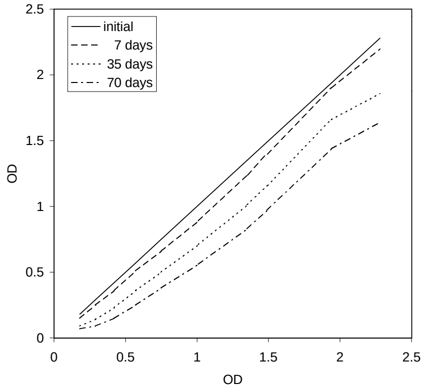


Figure 28: Neutral patch exposed to 50 klx light

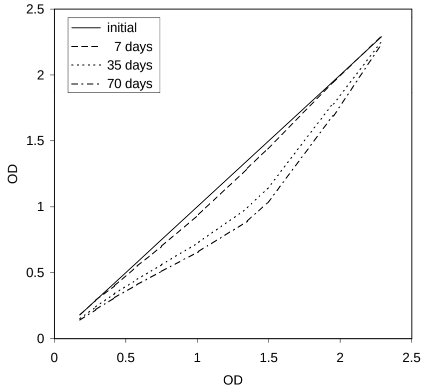


Figure 29: Neutral patch exposed to airflow

Ink/Media Interaction

The dyes printed on glossy photo paper and on matte paper show similar trends in the behavior and tendency to fade. The surface structure of matte paper, which allows the ink to penetrate more deeply into the medium, stabilizes the dyes to a certain degree. Thus, the samples printed on matte paper showed an overall lower fading rate over time. The surface structure had less influence on the samples positioned behind glass, because the airflow was cut off. All the exposed samples that were also exposed to airflow showed a significant fade rate, up to three times (cyan dye) faster on the glossy photo paper (Figure 30). This can be explained by the structure of the glossy photo paper which is a so-called microporous paper. Because the ink is kept near the surface, the dyes are less protected against environmental influences and this results in more severe and faster degradation of the dyes. The stabilizing effect of the matte paper does not seem to count for the neutral patch (a combination of cyan, magenta, yellow and black dyes), because the fade rate of the D_{max} in the neutral patch exposed to light, as mentioned above, was about 10% higher on matte paper than on glossy photo paper (Figure 31).

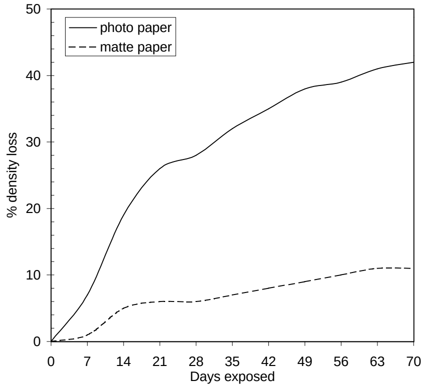


Figure 30: Cyan dye ($D_{1.0}$) exposed to 50 klx light

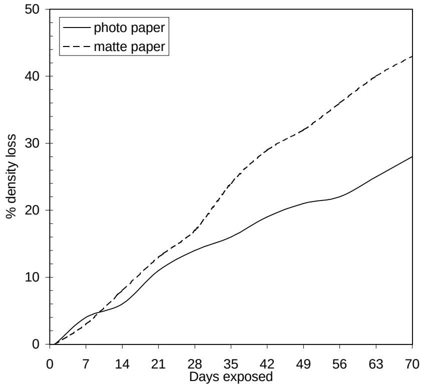


Figure 31: Neutral (D_{max}) exposed to 50 klx light

Conclusion

The dye-based samples on glossy photo paper show the highest fading rate overall. The dyes turned out to be fairly unstable, especially under the 50 klx light condition. After only one week of exposure a density loss of up to 25% (magenta dye) in the low densities was noticeable. The influence of the media on the stability of the dye could be seen best with the cyan dye. While the cyan dye was fairly stable against VIS light on both papers (glass-filtered samples), the dye was very unstable against airflow on glossy photo paper. There does not necessarily have to be a pollutant like ozone present to decompose the cyan dye. This was also true for the magenta dye although it had a lower fading rate. The yellow dye was fairly stable against both effects.

The cyan samples exposed to airflow (150 lx) in the light fading room showed significantly more fading after 35 days (real time) than the samples exposed for one day to 1 ppm O_3, which equals forty days at an average of 0.025 ppm O_3 (Figure 32). The cyan dye printed on glossy photo paper reached nearly the same rate of fading after fourteen days of airflow and two days in 1 ppm O_3 (Figure 33). The humidity in both cases was nearly the same because the samples exposed to airflow were not heated up and so not dried out by a high irradiance. The light fading room was set to 55% RH and the pollution chambers to 50% RH. However, it is not possible to determine the exact rate of fading caused by ambient air or by ozone due to the unknown concentration of ozone in the ambient air and the possibility of reciprocity failure in the accelerated pollution test. However, it was definitely shown that a high airflow (e.g., from air conditioning systems) without measurable concentration of pollutants can cause a significant rate of fading in an ink jet image.

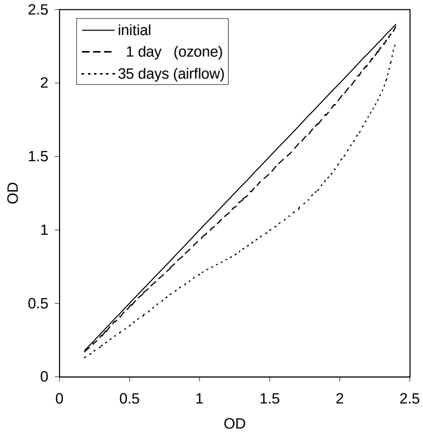


Figure 32: Cyan dye exposed to airflow and 1 ppm O_3

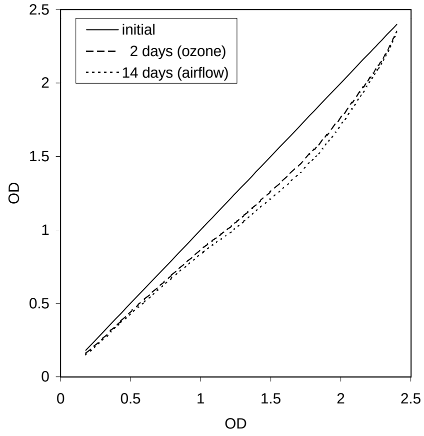


Figure 33: Cyan dye exposed to airflow and 1 ppm O_3

The papers themselves were stable against high concentrations of pollutants or light, as no yellowing in the d_{min} (paper density) was noticeable.

Further, the so-called filtration effect was observed in some cases. The rate of fading will be about 1.5 to 2 times slower for glass-framed samples than for samples without glass [34]. The high-density patches of the yellow dye (Figure 34), as well as the diluted magenta (Figure 35), both on glossy photo paper, showed some increased fading if not framed. Because cyan is so unstable in the presence of airflow, it is not easy to tell if the better stability behind glass is due to the blocking of UV light or of airflow.

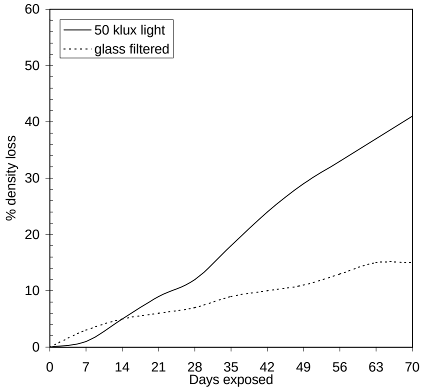


Figure 34: Yellow dye, D_{max} patch

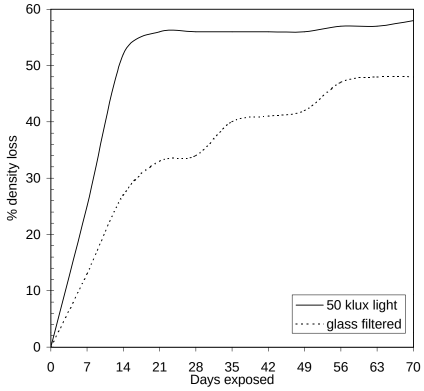


Figure 35: Magenta dye, D_{min} patch

Another aspect influencing the dye stability is the use of diluted ink. As mentioned in section 3.6.1., diluted inks tend to fade up to two times faster than the concentrated inks. When exposed to light the cyan and magenta dye showed a fading rate up to two times higher in the low densities than in the high densities (Figures 36 and 37). This does not occur under the non-light test conditions. The tendency of the diluted dyes to fade faster than the concentrated ones occurs on both papers at the same rate.

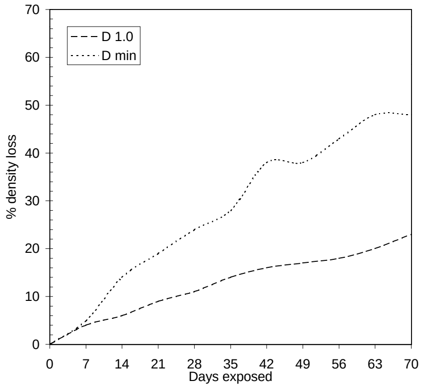


Figure 36: Cyan dye exposed to 50 klx light

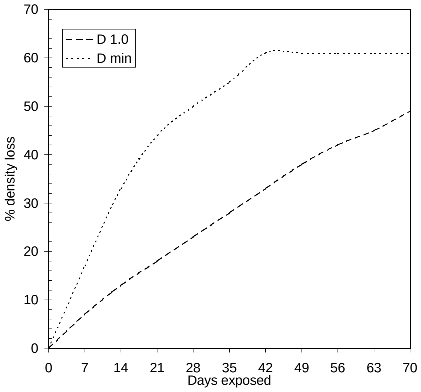


Figure 37: Magenta dye exposed to 50 klx light

The analysis of the measured density data shows more or less the expected results as written in different published papers on studies of the stability of ink jet materials.

The table shows a summary of the stability of the three dyes on glossy photo paper. In general were the dyes more stable on (approximately at a factor of two) on matte paper.

Colorant	*Light*	*Filtered*	*Airflow*	*Ozone*	NO_2
Cyan dye	very unstable	rel. stable	unstable	very unstable	unstable
Magenta dye	very unstable	unstable	rel. stable	unstable	rel. stable
Yellow dye	very unstable	unstable	stable	rel. stable	unstable

Key of evaluation:

- very stable: no fading, fading rate below 4%
- stable: nearly no fading, fading rate below 10 %
- relatively stable: slow fading rate, max. 20% after eight weeks
- unstable: approx. 10% fading rate after the first week of exposure, max. up to 40-50%
- very unstable: over 15% fading rate after the first week of exposure, max. up to 60-70%

5.1.2 Spectrum analysis

The samples were read with a spectrophotometer, making it possible to get an overview on the fading behavior over the whole spectrum. An additional advantage of this approach was not to be limited to the filters used in densitometers, because they are not ideal for the inks used in ink jet printing. An absorption spectrum can show if the dye is only degrading and losing its ability to absorb light at special wavelengths or if a new product with different absorption characteristics (i.e., a new maximum) is created. Changes in an absorption maximum of a pure dye normally result in color shift. Further shifts occur in mixed color patches due to the different fading rates of the single dyes.

Cyan
On glossy photo paper exposed to light the cyan dye showed a light shift in the absorption maxima (approximately 10 nm) while fading. Further, the fading of the cyan dye led to a loss in the absorption (580-700 nm), which is noticeable as the cyan patches turning slightly yellow (Figure 38). This behavior occurs while exposed to 50 klx light, airflow and 1 ppm O_3 and the "670 nm bump" faded even more at 10 ppm NO_2. As cyan is fairly stable behind glass, only slight changes were observed in the absorption spectrum, following the same tendencies as described above. On matte paper exposed to light, the cyan dye showed the same behavior as on glossy photo paper and turned slightly yellow. No significant changes are observed in the glass-filtered and airflow samples. Exposed to NO_2, the cyan patch turned greenish, due to the increasing absorption in the 430-470 nm area (Figure 39).

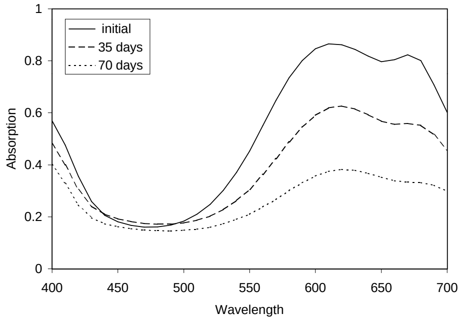


Figure 38: Cyan patch (5) exposed to 50 klx light

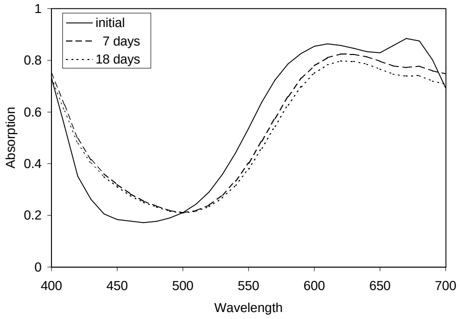


Figure 39: Cyan patch (5) exposed to 10 ppm NO_2

Magenta
The absorption maxima of the magenta dye decreased while fading and the absorption in the short (400-450 nm) spectrum, and in the longer (620-700 nm) spectrum increased by a small amount. This resulted in an overall loss of magenta with no visible color shift. This was observed on both papers under all test conditions, with magenta being fairly stable against airflow and pollutants (Figures 40 and 41).

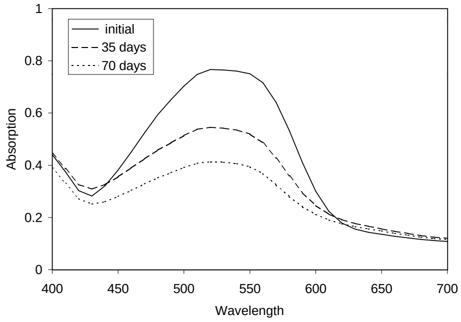


Figure 40: Magenta patch (5) exposed to 50 klx light

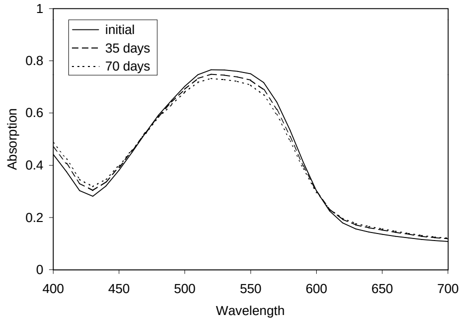


Figure 41: Magenta patch (5) exposed to airflow

Yellow

In the absorption spectrum of the yellow dye the shape of the curve (430-510 nm) flattens while fading; this is noticeable as a slightly muddy-looking yellow patch. This fading behavior mainly occurred on both papers, when exposed to light as well as when exposed to 10 ppm NO_2 (Figures 42 and 43). There is no change at all in the patches exposed to airflow or ozone.

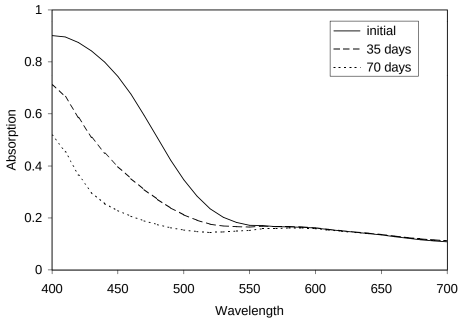


Figure 42: Yellow patch (5) exposed to 50 klx light

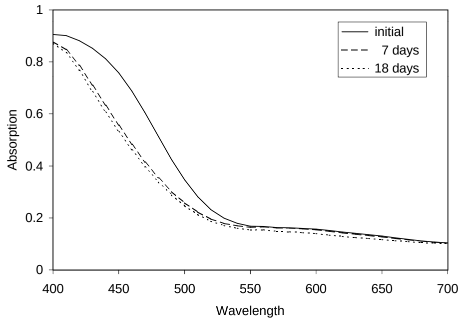


Figure 43: Yellow patch (5) exposed to 10 ppm NO_2

Red

Because red is a combination of magenta and yellow, the absorption spectrum depends on the behavior of these two dyes. On both papers under all test conditions except under the influence of NO_2 the magenta dye faded faster than the yellow dye, which resulted in a red patch turning yellow (Figure 44). Exposed to NO_2 the yellow dye faded faster, so that the red patch turned magenta (Figure 45).

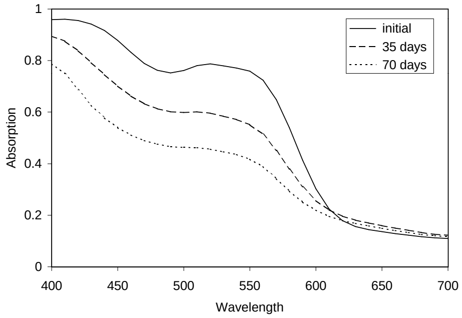


Figure 44: Red patch (5) exposed to 50 klx light

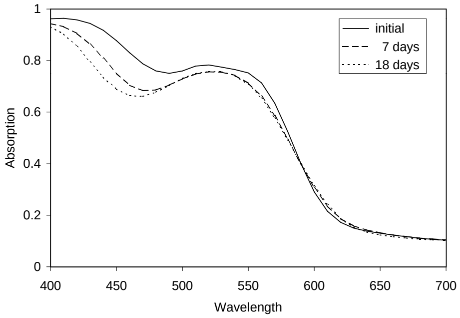


Figure 45: Red patch (5) exposed to 10 ppm NO_2

Green

Because green is a combination of cyan and yellow, the spectral behavior of these two dyes can be observed in the green patch as well. The cyan turned slightly yellow, and the yellow turned muddy; therefore the green patch became yellow, muddy-looking green. These color changes were mainly observed in the light-exposed samples (Figure 46). Due to the fairly good stability of the yellow dye against airflow and pollutants, the green patch turned slightly yellow under these test conditions. Printed on matte paper and exposed to 50 klx light (both glass-filtered and unfiltered), as well as glass-filtered on glossy photo paper, the lower densities in the green patch turned slightly blue. This is due to the relatively good stability of the cyan dye behind glass and on matte paper. Thus, in these three cases the yellow dye faded faster than the cyan dye which resulted in a slightly blue-looking green patch (Figure 47).

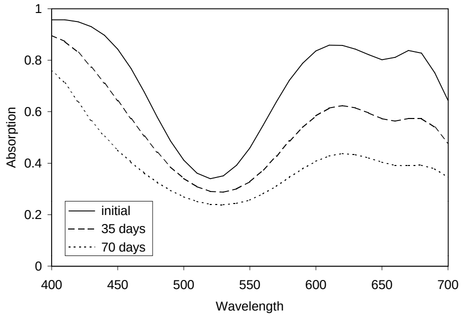


Figure 46: Green patch (5) exposed to 50 klx light

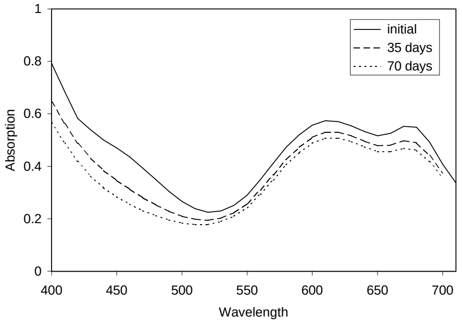


Figure 47: Green patch (5) exposed to 50 klx light (glass-filtered)

Blue

The blue patches are a combination of magenta and cyan dyes. On glossy photo paper the cyan dye showed a higher fading rate when exposed to 50 klx light, airflow, 10 ppm NO_2 and 1 ppm O_3 than the magenta dye (Figure 48). This was noticeable as a reddish-looking blue patch. It occurred less when exposed to ozone and more when exposed to NO_2 ("670 nm bump" faded most). Behind glass and also printed on matte paper, the cyan dye was more stable than the magenta dye, so the blue patches turned slightly greenish in the low densities (Figure 49). If exposed to NO_2 the blue patch turned reddish on both the matte and the glossy photo papers. These color shifts were observed mainly in the low-density patches.

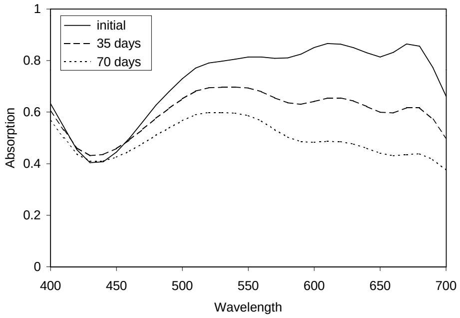


Figure 48: Blue patch (5) exposed to 50 klx light

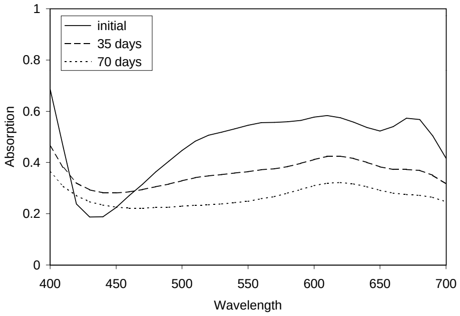


Figure 49: Blue patch (2) exposed to 50 klx light (matte paper)

Neutral

The black patches, a combination of cyan, magenta, yellow and black, were not neutral grey right from the beginning; they showed a green color shift on both papers. Printed on glossy photo paper and exposed to 50 klx light, the low-density patches turned slightly red due to the higher fading rate of the cyan dye (Figure 50), while the higher-density patches turned even more greenish. A fact that was very visible in the samples but not easy to observe in the absorption spectrum. Also under the glass-filtered condition and on matte paper and exposed to light, the low density patches look even more greenish after fading (Figure 51). The magenta faded more. Exposed to NO_2, the patches turned slightly magenta on both papers, due to the higher fading rates of yellow and cyan dyes (Figure 52). As cyan and magenta tended to fade more under airflow including ozone, the patches showed a yellowish "warmer" color after fading under these test conditions (Figure 53). This was also observed on both papers. Printed on matte paper and exposed to light, the D_{max} showed a totally different behavior; it turned brown, while the other patches turned even more greenish.

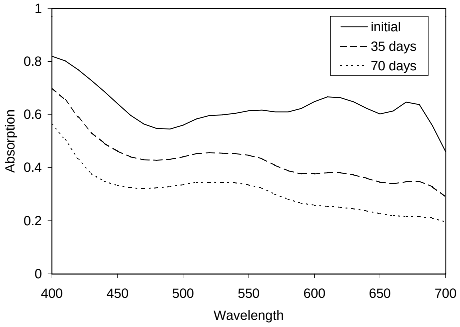


Figure 50: Neutral patch (3) exposed to 50 klx light

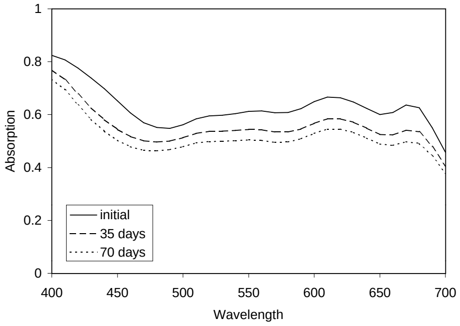


Figure 51: Neutral patch (3) exposed to 50 klx light (glass-filtered)

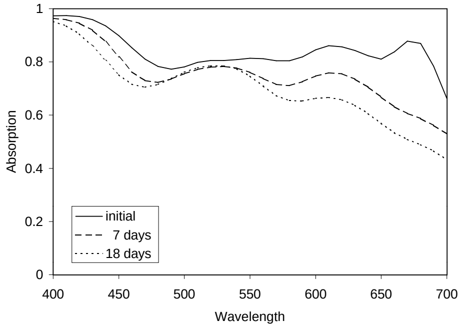


Figure 52: Neutral patch (5) exposed to 10 ppm NO_2

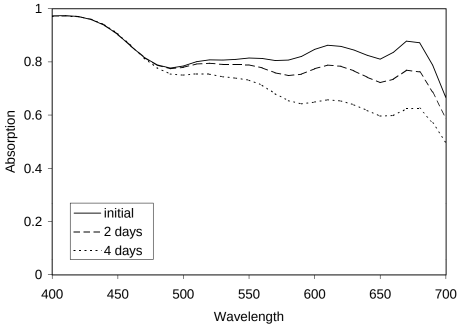


Figure 53: Neutral patch (5) exposed to 1 ppm O_3

Conclusion

Visual examination of the absorption spectra of the dyes showed, no "new" maxima, due to a "new" product as a result of a chemical degradation while fading. Only slight increases of absorption mainly in the magenta dye spectrum were seen. However, color shifts in pure or mixed patches are easy to predict in an absorption spectrum. The fading behavior of the single dyes can be recognized in the mixed patches as well. As mentioned above, different density patches of one color showed different color shifts. The greatest color shift was seen in the neutral patches printed on glossy photo paper, where the high densities turned even more greenish, while the low densities turned slightly red. This effect is known as "crossed curves" in photographic color materials. This crossed curves effect makes it necessary to look at more than one density patch to make a reliable prediction about how an image might look like after fading. With the density data, the color balance changes as recommended in the ISO Standard 10977 can be calculated. These percent numbers predict a color shift as well, but only in one patch ($D_{1.0}$). A color shift occurring in low or high density patches will not be observed by this method.

The table shows a summary of the color shifts observed in each color patch. The first row includes the color shifts that occurred on glossy photo paper and the second row includes those that occurred on matte paper.

Colorant	*Light*	*Filtered*	*Airflow*	*Ozone*	NO_2
Cyan patch	yellowish yellowish		yellowish	yellowish	yellowish greenish
Magenta patch					
Yellow patch	muddy muddy	muddy muddy			muddy muddy
Red patch	yellowish yellowish	yellowish yellowish	yellowish yellowish	yellowish yellowish	magenta magenta
Green patch	muddy, yellowish bluish	bluish bluish	yellowish bluish	yellowish bluish	yellowish bluish
Blue patch	reddish greenish	greenish greenish	reddish greenish	reddish greenish	reddish reddish
Neutral patch	reddish greenish	greenish greenish	yellowish yellowish	yellowish yellowish	magenta magenta

5.2 Pigment-based samples

5.2.1 Density analysis

The density analysis used for the dyes was used for the pigmented inks as well.

Cyan
The cyan pigment was stable when exposed to glass-filtered light (VIS light), as well as when exposed to NO_2 (Figures 54 and 55). It showed some fading under the 50 klx light and 10 ppm O_3; it showed even less under the airflow condition. The pigment was more stable on matte paper than on glossy photo paper.

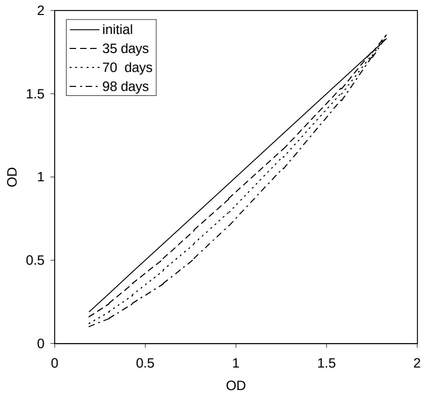


Figure 54: Cyan pigment exposed to 50 klx light

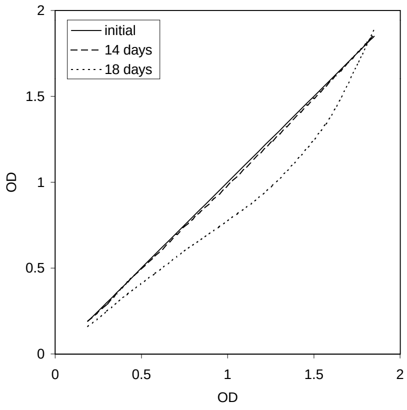


Figure 55: Cyan pigment exposed to 10 ppm O_3

Magenta
The magenta pigment showed the highest rate of fading when exposed to 50 klx light and 10 ppm O_3 (Figures 56 and 57). Under the glass-filtered and airflow conditions it faded only to a small amount on the glossy photo paper and even less on matte paper in the middle densities. It does not show any fading at all when exposed to NO_2.

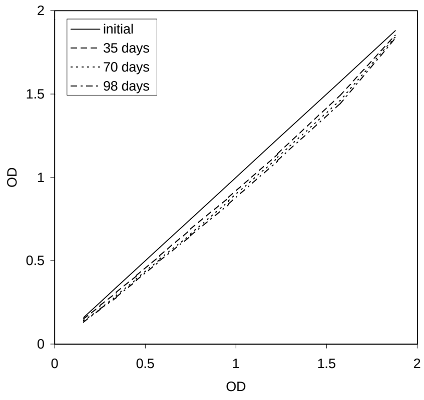


Figure 56: Magenta pigment exposed to 50 klx light

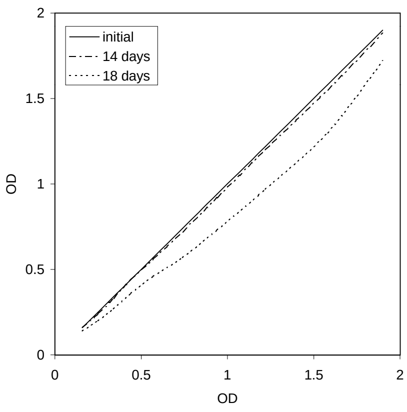


Figure 57: Magenta pigment exposed to 10 ppm O_3

Yellow
The yellow pigment turned out to be the most stable. It faded when exposed to 50 klx light (Figure 58); the $D_{0.3-0.5}$ patches in particular showed a significantly higher rate of fading when printed on matte paper (Figure 59). Other densities were more stable on the matte paper. Exposed to 10 ppm O_3 the yellow pigment printed on glossy photo paper showed a small rate of fading; on matte paper it did not show any fading at all.

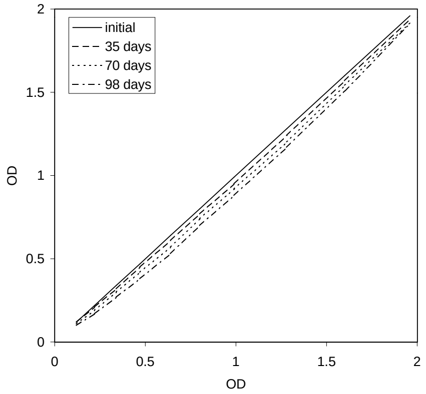


Figure 58: Yellow pigment exposed to 50 klx light (photo paper)

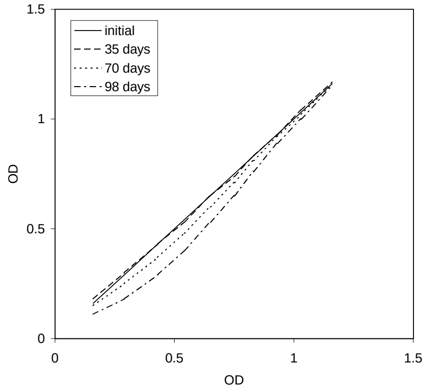


Figure 59: Yellow pigment exposed to 50 klx light (matte paper)

Catalytic Fading and Aggregation
No catalytic fading was observed in the mixed patches of the pigmented ink. There was also no catalytic fading in the neutral patches, when they included black ink. In fact, if fading did occur, the lower densities showed fading rates up to two times higher than those of the higher densities on both papers when exposed to the light conditions (Figures 60 and 61). Even so pigments are generally more light-stable than dyes, if they are used in diluted inks they show de-aggregation behavior and become less light-stable.

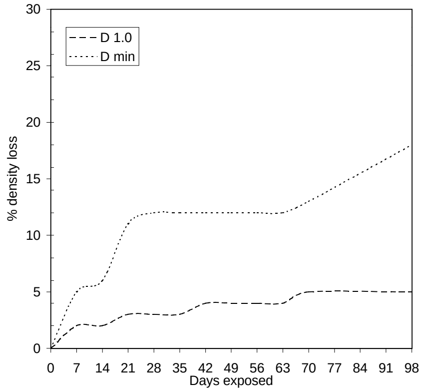


Figure 60: Magenta pigment exposed to 50 klx light

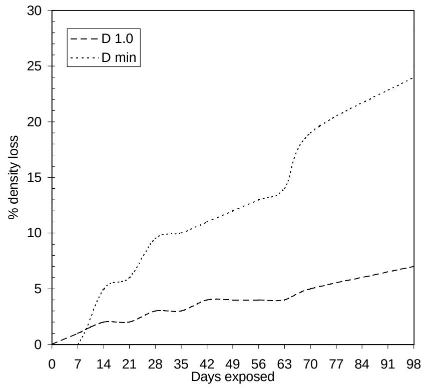


Figure 61: Cyan pigment exposed to 50 klx light

Ink/Media Interaction

Since there was little fading, there were few ink/media interactions to observe. But all pigments printed on matte paper showed an overall better stability than those printed on glossy photo paper. Only the diluted magenta and the low yellow densities showed the same or even a higher fading rate on matte paper than on the glossy photo paper (Figures 62 and 63). When exposed to ozone, the samples on photo paper showed degradation after 18 days, while the samples on matte paper showed degradation after the first day.

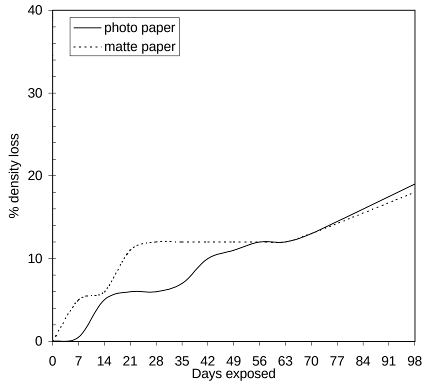


Figure 62: Magenta pigment exposed to 50 klx light

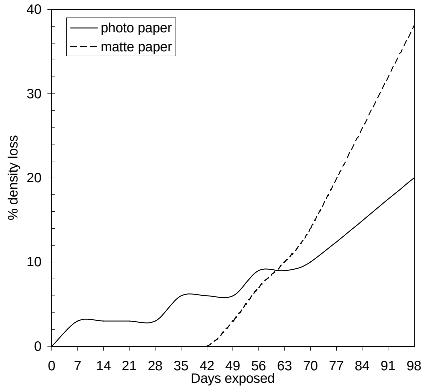


Figure 63: Yellow pigment exposed to 50 klx light

Conclusion

In general, the pigmented ink was much more stable than the dye ink. However when fading occurred, the pigments showed the same fading behavior as the dyes. Cyan, for example, turned out to be unstable when exposed to VIS light, airflow and ozone both as a dye and as a pigment. The magenta dye faded most when exposed to light, and so did the magenta pigment. Both the yellow dye and pigment were fairly stable when exposed to airflow and pollutants. The highest rate of fading was observed in the diluted cyan when exposed to 50 klx light. It was the only one to reach 30% density loss.

The table shows a summary of the stability of the three pigments on glossy photo paper.

Colorant	*Light*	*Filtered*	*Airflow*	*Ozone*	NO_2
Cyan pigment	unstable	very stable	rel. stable	rel. stable	stable
Magenta pigment	rel. stable	stable	stable	rel. stable	stable
Yellow pigment	rel. stable	very stable	very stable	very stable	stable

Explanation: The used key of evaluation is shown on page 42.

5.2.2 Spectrum analysis

The visual spectrum analysis used for the dyes was used for the pigmented inks as well.

Cyan

While exposed to 50 klx light, the fading of the cyan pigment led to a loss in the 580-700 nm absorption, which resulted in a slightly yellowish-looking cyan patch (Figure 64). Further, when exposed to ozone the absorption in 400-510 nm increased, while the absorption in 580-700 nm decreased; this led to an overall loss of cyan with no visible color shift (Figure 65).

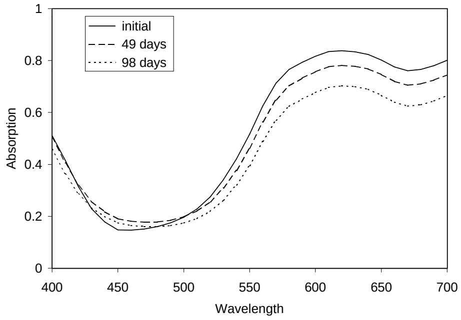


Figure 64: Cyan patch (5) exposed to 50 klx light

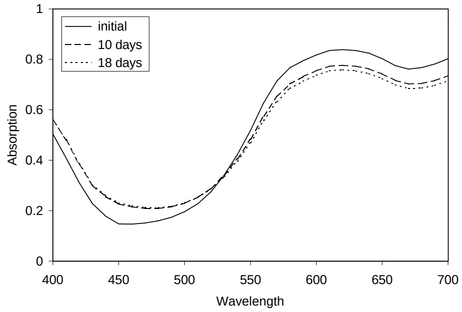


Figure 65: Cyan patch (5) exposed to 10 ppm O_3

Magenta

The absorption maxima of the magenta pigment decreased while fading and the absorption in the short (400-450 nm) spectrum and in the longer (620-700 nm) spectrum, increased by a small amount (Figure 66). This resulted in an overall loss of magenta with no visible color shift. This was observed in every case where fading occurred.

Yellow

The yellow pigment faded hardly at all, so no visible color shifts are observed. Only some decrease in the 400-500 nm absorption was seen (Figure 67).

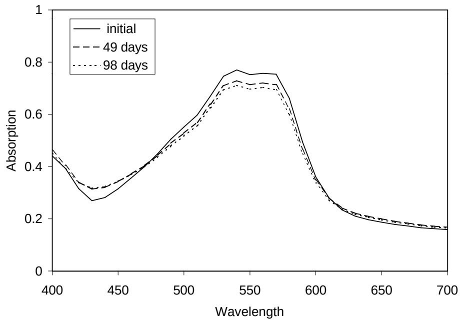


Figure 66: Magenta patch (5) exposed to 50 klx light

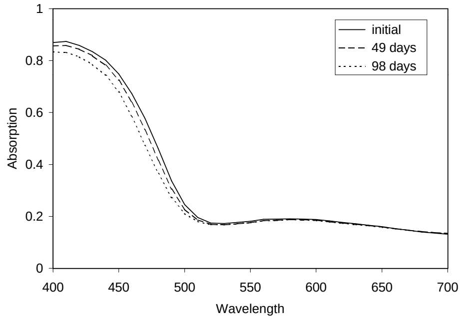


Figure 67: Yellow patch (5) exposed to 50 klx light

Red

Because red is a combination of magenta and yellow, the absorption spectrum depends on the behavior of these two pigments. Due to the stability of the yellow pigment, only the magenta pigment showed any fading at all (while exposed to ozone), which led to a slightly yellow-looking patch (Figure 68).

Green

Because green is a combination of cyan and yellow, any color shifts are related to the behavior of these pigments. Again, the yellow pigment was the most stable, and so only the cyan pigment showed some fading when exposed to 50 klx light and ozone. This resulted in a yellowish-looking green patch (Figure 69).

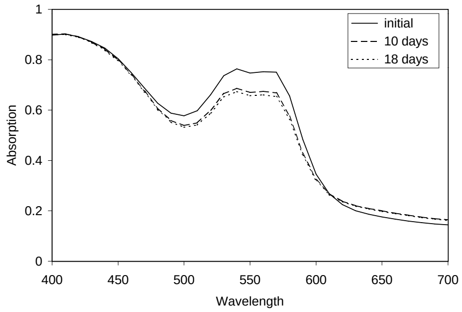


Figure 68: Red patch (5) exposed to 10 ppm O_3

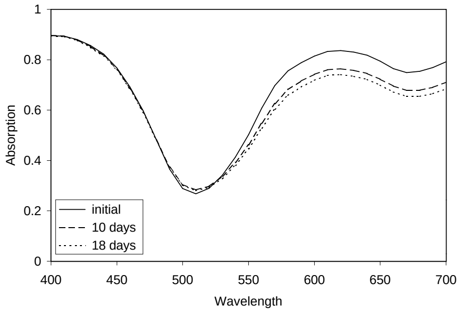


Figure 69: Green patch (5) exposed to 10 ppm O_3

Blue

The blue patch only showed some decrease in the 500-700 nm absorption (cyan and magenta pigment) as well as some increase in the 400-490 nm absorption when exposed to 50 klux light and ozone (Figure 70). These changes led to an overall color loss in the blue patch without any visible color shift.

Neutral

As in the dye patches, the black patches, made up of cyan, magenta, yellow and black pigments, were not neutral grey right from the beginning. They show a green color shift on both papers. Any further color shift was observed only when the neutral patch was printed on glossy photo paper and exposed to 50 klx light and ozone (Figure 71). Due to the higher fading rate of the cyan pigment, the low density patches turned slightly reddish.

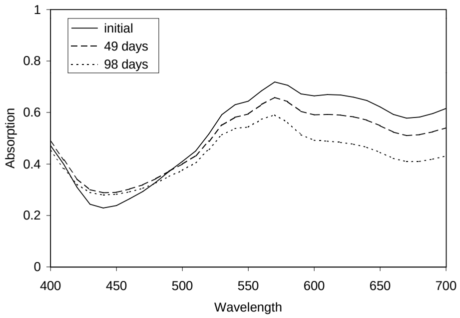


Figure 70: Blue patch (3) exposed to 50 klx light

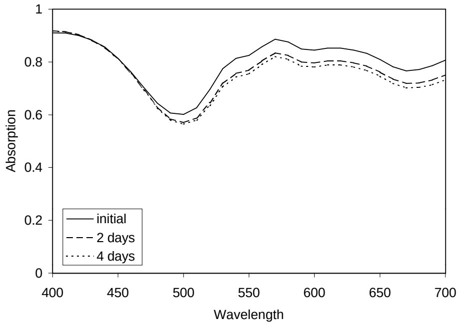


Figure 71: Neutral patch (5) exposed to 10 ppm O_3

Conclusion

Very little fading occurred in the pigmented samples. Only small color shifts were observed. These color shifts occurred only when the pigments were printed on glossy photo paper. Samples printed on matte paper did not show any color changes at all. If the patches did show changes, they were always in the same direction as those of the dye samples (i.e., cyan turning yellowish). This shows the similarity between the molecular structures of dyes' and pigments.

The table shows a summary of the color shifts observed in each color patch on glossy photo paper.

Colorant	*Light*	*Filtered*	*Airflow*	*Ozone*	NO_2
Cyan patch	yellowish				
Magenta patch					
Yellow patch					
Red patch	yellowish			yellowish	
Green patch	yellowish			yellowish	
Blue patch					
Neutral patch	reddish			reddish	

6 Summary and Outlook

The purpose of this study is to provide a better understanding of the complex fading behavior of ink jet prints, as well as to demonstrate the difficulties in creating reliable tests. The analysis of the exposed samples shows how environmental conditions can influence the degradation of ink jet images.

It was not possible to separate each effect that can influence the fading of ink jet images in these tests. The various test conditions demonstrate the complexity of the possible influencing factors. Each dye and also each pigment showed different fading behaviors in the various conditions. The observed changes included the rate and amount of fading as well as visual color shifts.

To provide reliable tests, the operating conditions have to be set and monitored. These conditions need to be controlled in order to correctly analyze and interpret the test results. All these controlled conditions complicate the tests and make them rather complex. In some cases it is not possible to measure and control every influencing effect that will make it difficult to interpret the results. In addition, measurement procedures have to be specified and closely followed.

Further problems can occur when printing the test targets, because some printers do not allow the user to change the color adjustments. Therefore, it might not be possible to print pure color patches. Thus, no changes in the pure dyes or pigments, without any influence by another dye or pigment, can be observed.

Also, the test target should include steps of varying densities, because of the different fading occurring in the lower and higher density patches. This effect makes it necessary to look at more than one patch. To get even more information about the fading behavior of dyes or pigments, a spectrophotometer instead of a densitometer can be used which gives an overview over the whole spectrum.

All those issues have to be kept in mind when doing fading tests of ink jet images. In a research environment where inks and media are being optimized, the tests have to be even more controlled and the analysis needs to be even more complex.

For consumer testing the analysis, or at least the results, should be less complicated, because the consumer just wants to know how long the ink jet print is going to last.

Without any controlled and standardized test methods, test results are not reliable. To compare various inks, media and ink/media combinations all over the world, a controlled, standardized and reproducible test is necessary. However, all these problems delay the progress of the new standard for methods for measuring image stability for color hardcopy.

A References

References

[1] Meyer B.: *I've got the Epson Blues, Because My Photos Don't*
http://home.cox.rr.com/meyerfamily/epson/epson.html#2000 (September 2000), p. 1

[2] Wilhelm Imaging Research, Inc.: *Inks and Media for Desktop Inkjet Printers, Years of Print Display Before Noticeable Fading Occures*
www.wilhelm-research.com, file: wir_desktop 06_20_00.pdf (June 2000), p. 3

[3] ISO Standard No. 10977: *Photography - Processed photographic colour films and paper prints - Methods for measuring image stability*
(published 1993)

[4] Cost F.: *Pocket Guide to Digital Printing*
Delmar Publisher Inc., ITP (1997), p. 80

[5] Stephen F. Pond, Ph.D.: *Inkjet Technology and Product Development Strategies*
Torry Pines Research (2000)

[6] Hue P.Le: *Progress and Trends in Ink-jet Printing Technology*
IS&T Journal of Image Science and Technology, Volume 42, Number 1 (Janurary/February 1998), p. 49-62

[7] Zollinger H.: *Color Chemistry*
VCH Verlagsgesellschaft (1991), p 1-49, 104

[8] Meier H.: *Die Photochemie der Organischen Farbstoffe*
Springer Verlag (1963), p. 7

[9] Wnek J.W.: *The Role of Pigment Dispersion in the Performance of Ink-Jet Inks*
IS&T NIP16: International Conference on Digital Printing Technologies, T18 Tutorial Notes (October 2000)

[10] Gregory P.: *Dyes Versus Pigments: The Truth*
IS&T Recent Progress in Ink Jet Technologies (1996), p. 276-278

[11] Schildgen T.E.: *Pocket Guide to Color*
Delmar Publisher Inc., ITP (1998), p. 2-54

[12] Tuite R.J.: *Image Stability in Color Photography*
IS&T Journal of Applied Photographic Engineering, Volume 5, Number 4 (Fall 1979), p. 200-207

[13] Hunt R.W.G.: *Measuring Color*
Ellis Horwood (1991), second edition, p. 50

[14] Stroeble L., Campton J., Current I., Zakia R.: *Photographic Materials and Processes*
Focal Press (1986), p. 252

[15] Lavery A., Provost J.: *Color-Media Interactions in Ink Jet Printing*
IS&T Recent Progress in Ink Jet Technologies II (1996), p. 400-405

[16] Jee D., Fass W., Winslow A.: *Engineering an Ink Jet Paper - What's involved?*
IS&T Recent Progress in Ink Jet Technologies (1996), p. 247-253

[17] Lyne O., Yuasa M.: *Paper and Printing: Overview of Paper Making, Paper Properties and Performance in Electrophotograhic and Ink Jet Printing*
IS&T NIP16: International Conference on Digital Printing Technologies, T5 Tutorial Notes, (October 2000)

[18] Lavery A.: *Photomedia for Ink Jet Printing*
IS&T NIP16: International Conference on Digital Printing Technologies (October 2000), p. 216-220

[19] Kasahara K.: *A New Quick-Drying, High-Water-Resistant Glossy Ink Jet Paper*
IS&T NIP16: International Conference on Digital Printing Technologies (October 2000), p. 150-152

[20] Lavery A., Provost J., Sherwin A., Watkinson J.: *The Influence of Media on the Lightfastness of Ink-Jet Prints*
IS&T NIP14: International Conference on Digital Printing Technologies (October 1998), p. 123-128

[21] Frey, Franziska S.: *Untersuchung des Stabilitätsverhaltens von Fotografischen Farbmaterialien*
Dissertation ETH Nr.10509, Zürich (1994), p. 41

[22] Freeman H.S., Peterson A.T.: *Physico-Chemical Principles of Color Chemistry*
Advances in Color Chemistry Series, Volume 4, Blackie A&P (1996), p. 84, 196-253

[23] Schuettel S., Hofmann R.: *The Influence of Diluted Inks and Drying on the Lightfastness of Dye Based Ink-Jet Prints*
IS&T NIP15: International Conference on Digital Printing Technologies (October 1999), p. 120-123

[24] Steiger R., Brugger P-A.: *Photochemical Studies on the Lightfastness of Ink-Jet Systems*
IS&T NIP14: International Conference on Digital Printing Technologies (October 1998), p. 114-117

[25] Lee C., Urlaub J., Bagwell A.S., MacDonald J.G., Nohr R.S.: *Properties of Inks Containing Novel Lightfastness Additives*
IS&T Recent Progress in Ink Jet Technologies II (1996), p. 444-446

[26] Wight P.: *Issues in Ink Jet Stability*
IS&T NIP16: International Conference on Digital Printing Technologies (October 2000), p. 86-89

[27] Fryberg M., Hofmann R.: *Influence of Dye Structure on Permanence*
IS&T NIP16: International Conference on Digital Printing Technologies (October 2000), p. 95-98

[28] Hill P., Suitor K., Artz P.: *Measurement of Humidity Effects on the Dark Keeping Properties of Inkjet Photographic Prints*
IS&T NIP16: International Conference on Digital Printing Technologies (October 2000), p. 70-73

[29] Havermans J.B.G.A. *Environmental Influences of the Deterioration of Paper*
Barjestke, Meeuwese (1995)

[30] Johansson A., Kolseth P., Lindqvist O.: *Uptake of Air Pollutants by Paper*
Restauro, Vol. 21, No. 3 (2000), p. 117-185

[31] Reilly J.M., Zinn E., Adelstein P.: *Atmospheric Pollutant Aging Test Method Development*
Final Report to American Society for Testing Materials
Image Permanence Institute, RIT (June 2000)

[32] Anderson S.I., Anderson R.J.: *A Study of Lighting Conditions Associated with Print Display in Homes*
IS&T Journal of Imaging Technology, Volume 17, Number 3 (June/July 1991), p. 127-132

[33] Anderson S., Larson G.: *A Study of Environmental Conditions Associated with Customer Keeping of Photographic Prints*
IS&T Journal of Imaging Technology, Volume 13, Number 2 (April 1987), p. 49-54

[34] Bugner D.E., Suminski C.: *Filtration and Reciprocity Effects on the Fade Rate of Inkjet Photographic Prints*
IS&T NIP16: International Conference on Digital Printing Technologies (October 2000), p. 90-94

[35] Zinn E., Nishimura D.W., Reilly J.M.: *High-Intensity Fluorescent Light-Fading Tests for Digital Output Materials*
IS&T NIP15: International Conference on Digital Printing Technologies (October 1999), p. 416-420

[36] McLaren, K.: *The Colour Science of Dyes and Pigments*
Bristol, England, Boston, Mass, :Hilger (1986), p.126

[37] Kang H.R.: *Water-Based Ink-Jet. I. Formulation*
IS&T Journal of Image Science, Volume 35, Number 3 (May/June 1991), p. 179-187

B Ink Formulation

The typical components of an ink formulation are listed below: [5, 9]

Colorant
Normally a dye or pigment
Usually 2-8% of the total weight by ink (wt%)

Solvent
Primary ink vehicle that dissolves or suspends the colorant
Typical solvents are: water, alcohols and methyl ethyl ketone
Usually 35-80 wt%

Surfactant, Penetrant
Added to lower the surface tension of the ink and to promote penetration (wetting) into the substrate
Tergitol 15-S-5, a secondary alcohol ethoxylate made by Union Carbide, is used as surfactant, and isopropyl alcohol is used as penetrant, for example
Usually 0.1-2.0 wt% surfactant, and 1-5 wt% penetrant

Solubilizing Agent
Added to promote dye solubility in the primary solvent. This is also called co-solvent and is used to increase the loading of the dye, which enhances the ink's optical density. Further it should hold the dye in solution in case of increasing concentration due to nozzle evaporation, for example.
N-methyl pyrrolidone is used as agent, for example
Usually 2-5 wt%

Dispersant
Added to assists the colloidal suspension of a pigment
Derussol carbon black made by Degussa, is used as dispersant, for example
Usually 3-8 wt%

Humectant
Added to inhibit evaporation
Glycols are typical for aqueous ink.
Usually 10-30 wt%

Viscosity Modifier
Added to raise the ink viscosity, often a humectant like glycols
Usually 1-3 wt%

pH Buffer
A pH adjustment toward the basic side is typically used. This improves ink-metal compatibility (i.e., less corrosion of the printer's metal parts) [37]. Further pH changes influence color shifts.
Triethylamine are used as buffer, for example
Usually 0.1-1.0 wt%

Chelating agent
Added to complex metal ions to prevent scale buildup where ink may evaporate.

A typical material is EDTA (Ethyldiaminetetra-acetic acid)
Usually 0.1-0.5 wt%

Biocide
Added to kill bacterial and other organisms
1,2 Benzisothiazolin-3-one, available by Zeneca under PROXEL GXL, for example
Usually 0.1-0.3 wt%

UV-Blocker, Antioxidant, Free Radical Inhibitor
Added to promote light-fastness, or to prevent degradation of long-chain dye molecules
Usually 1-5 wt%

Not all of these components are used in an ink formulation, and also some inks have other ingredients that are not listed above.

C Colorants for Ink Jet Inks

For example the first black ink, Food Black 2 with four sulfonic groups, had good solubility but poor water-fastness. By replacing some of the sulfonic groups with carboxylic ones, the second generation of black dye was made less water-soluble so that it would aggregate upon contact with acid paper. The next step was to metallize the dye, which improves light-fastness. Due to their electron withdrawing effect, metal atoms like Cu and Ni stabilize the dye molecule. Today, carbon black, a pigmented ink, is used as an effective replacement for black dyes in many applications. [9]

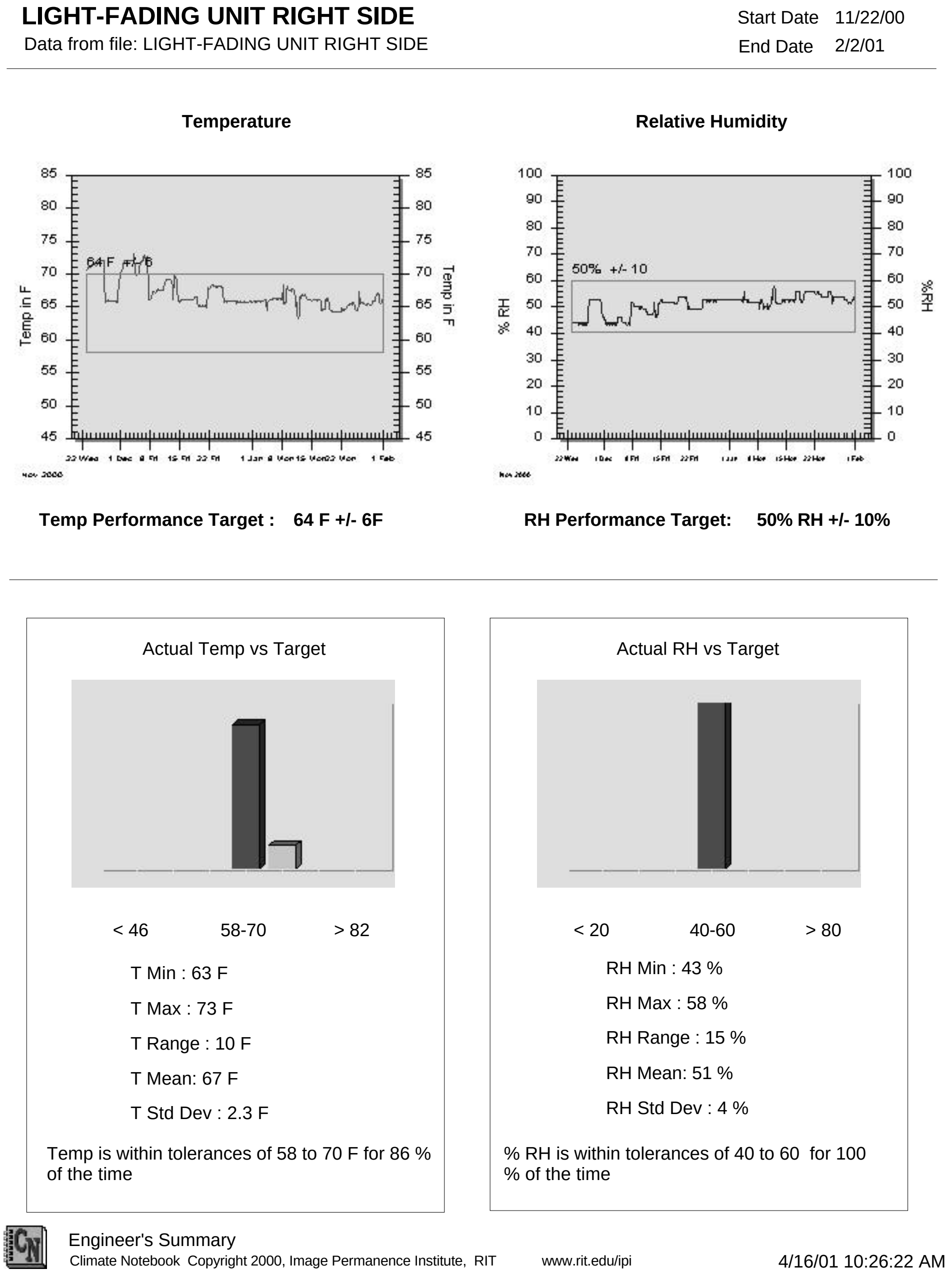
The first generation of cyan dyes (e.g., Acid blue 9) were based on the triphenylmethane structure. Later they were replaced by the more light-fast copper phthalocyanines, such as CI Direct Blue. The first copper phthalocyanine was made in pigment form and later was transformed into a water-soluble dye by incorporating sulfonic groups. [9, 7]

The first generation of magenta dyes were xanthene, such as CI Acid Red 37, but they have been replaced, also because of their poor light-fastness, by H-acid dyes, such as CI Reactive Red 180. Light stability can be further improved by metallizing the dye as done in the CI Reactive Red 23 dye. Typical magenta pigments are quinacridones, such as CI Pigment Red 122 and naphthol AS pigments such as CI Pigment Red 184. [9]

Typical yellow dyes are CI Direct Yellow 86, CI Direct Yellow 132, CI Acid Yellow 23 and CI Acid 17. Representative yellow pigments are monoazo yellow (CI Pigment Yellow 74), benzimidazolone yellow (CI Pigment Yellow 154), and diarylide yellow (CI Pigment Yellow 13). [5, 9]

CI stands for Color Index and is used as a classification of colorants according to their end use. The Color Index, issued by the Society of Dyers and Colourants, Bradford, and the American Association of Textile Chemists and Colorists, includes commercial names and suppliers of any dye currently in use, as well as information about their chemical structure.

D Temperature and Humidity Control



LIGHT-FADING UNIT RIGHT SIDE

Data from file: LIGHT-FADING UNIT RIGHT SIDE

Start Date 11/22/00
End Date 2/2/01

Temperature

Relative Humidity

Temp Performance Target : 64 F +/- 6F

RH Performance Target: 50% RH +/- 10%

Actual Temp vs Target

< 46 58-70 > 82

T Min : 63 F
T Max : 73 F
T Range : 10 F
T Mean: 67 F
T Std Dev : 2.3 F

Temp is within tolerances of 58 to 70 F for 86 % of the time

Actual RH vs Target

< 20 40-60 > 80

RH Min : 43 %
RH Max : 58 %
RH Range : 15 %
RH Mean: 51 %
RH Std Dev : 4 %

% RH is within tolerances of 40 to 60 for 100 % of the time

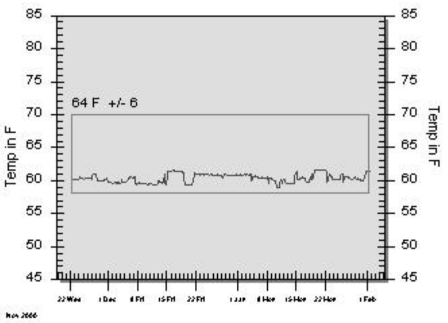
Engineer's Summary
Climate Notebook Copyright 2000, Image Permanence Institute, RIT www.rit.edu/ipi 4/16/01 10:26:22 AM

LIGHT-FADING UNIT LEFT SIDE

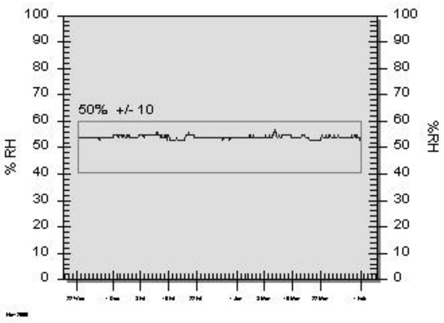
Data from file: LIGHT-FADING UNIT LEFT SIDE

Start Date 11/22/00
End Date 2/2/01

Temperature



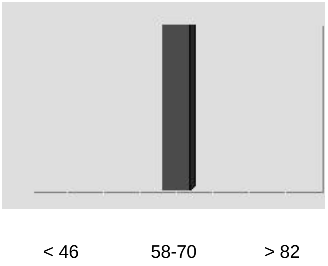
Relative Humidity



Temp Performance Target : 64 F +/- 6F

RH Performance Target: 50% RH +/- 10%

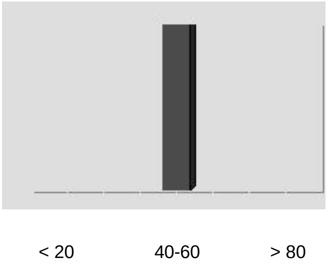
Actual Temp vs Target



T Min : 59 F
T Max : 62 F
T Range : 3 F
T Mean: 60 F
T Std Dev : 0.6 F

Temp is within tolerances of 58 to 70 F for 100 % of the time

Actual RH vs Target



RH Min : 52 %
RH Max : 57 %
RH Range : 5 %
RH Mean: 54 %
RH Std Dev : 1 %

% RH is within tolerances of 40 to 60 for 100 % of the time

Engineer's Summary

4/16/01 10:27:49 AM