Ink Jet Inks and Substrates - Novel Approaches for Their Physical and Optical Properties Characterization

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INK JET INKS AND SUBSTRATES – NOVEL APPROACHES
FOR THEIR PHYSICAL AND OPTICAL PROPERTIES
CHARACTERIZATION

by

Veronika Lovell

A Dissertation
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Doctor of Philosophy
Department of Paper Engineering, Chemical Engineering, and Imaging
Dr. Paul D. Fleming, III, Advisor

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Undoubtedly, within the last couple of decades, the progress in non impact printing technologies has grown to an enormous level. In order to keep the development of this non impact printing method to grow even more, technicians, researchers and educators must continue in conducting investigation and provoking new ideas and questions that will lead to new outcomes and expansion of ink jet printing.

In this work, a broader area that comprises deep look into the ink jet ink and substrate performance, their physical properties and optical properties when printed is discussed in great details. Innovative techniques, novel materials and novel recommendations are presented here in order to enhance the progress in the area of ink jet technology in near future.

The output should be evaluated in terms of overall printer capability, not only in terms of a substrate quality (price, grade, optical and physical properties), the type of ink set, and the basic level of color reproduction (density, Lab values). All these should be taken into consideration together with other very important factors, such as the length of time required for colors to stabilize, the image permanence of the printout, and the ink levels in terms of color gamut.
The work includes a comprehensive study of ink and substrate combinations, the interaction between them, and integration of novel techniques, two and three dimensional color gamut projections and gamut volume values, into color output characterization. Using this method it is possible to demonstrate how properties of a substrate correlate with the final output presentation. The aforementioned approach can be also used as an image permanence evaluation technique, in preference to the change in densities and L’ab’ values of miniature charts. Definitely, the gamut volume can be utilized as a sophisticated device, which enables to control the final color output of the printing job.
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Veronika Lovell
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INTRODUCTION

Phil Owen, European Editor for the American Association of Textile Chemists and Colorists, asked a very interesting question in his 2001 review:\(^{1}\) “Can digital printing make the huge step from being a useful and versatile tool for sampling, proofing, and customization jobs to becoming a serious production method?”

This question is becoming even more popular nowadays, when we see all the recent progress in chemistry, technologies and materials that are being developed more and more rapidly. Owen’s answer to his question stated in his review supports today’s ink jet technology stage: “However, the commitment to digital printing now shown by many important suppliers of machines, chemicals, and software suggests that they are confident that ink jets will have an increasing future role.” Undoubtedly, within the last couple of decades, the progress in non impact printing technologies has grown to an enormous level.

In order to keep the development of this non impact printing method to grow even more, technicians, researchers and educators must continue in conducting investigation and provoking new ideas and questions that will lead to new outcomes and expansion of ink jet printing.

In this work, a broader area that comprises the ink jet inks, substrates and digital reproduction of prints is discussed. It presents a broad view into the ink jet ink and substrate performance, the physical properties and optical properties of printed patterns, the interaction between ink and substrates, as well as an integration of gamut volumes into color output characterization.
More specifically, the work is divided into two main parts. The first part, Literature Review part, will help understand the terms and methods used in the process and also explain definitions and basics of the theories that were utilized to support steps of the work. The second part articles that have been published in journals or reviewed are presented. The work included in these papers has been also presented at different conferences and published in proceedings.

The first paper discusses the role of pigmented inks versus dye based inks and their color and lightfastness performance when used in ink jet printing process. “Color and Lightfastness Performance of Different Epson Ink Sets” by Veronika Chovancova, Paul D. Fleming III, Paul Howell and Adam Rasmusson was published in Journal of Imaging Science and Technology in 2005. Partial and preliminary results to this work were presented at International Conference on Digital Printing Technologies in Salt Lake City in 2004 and also published in Hilltop Review, Journal of Graduate Research at Western Michigan University in 2005.

The next topic talks about production of novel hot melt inks for creation of three dimensional structures. The formulation of hot melt inks with the addition of special chemicals - blowing agents was carried out in order for the raised image to attain the required height and firmness, and thus be used in printing Braille characters. The article titled “Novel Phase Change Inks for Printing 3D Structures” by Veronika Chovancova-Lovell, Alexandra Pekarovicova and Paul D. Fleming III has been submitted to the Journal of Imaging Science and Technology and was accepted with revisions.
Supporting materials on this subject have been presented at NIP21/DF05 International Conferences in Baltimore, 2005 and TAGA Technical Conference in Toronto, 2005.

The third article titled “Color Gamut – New Tool in Pressroom?” was prepared as a part of invited presentation, which was given at 2006 TAPPI Coating and Graphic Arts Conference in Atlanta. The panel discussion was led by five different people from academia and industry. In the work the issue of combination of substrates and inks is discussed. Different substrates have been considered in order to demonstrate how the substrate properties do or don’t affect the overall final presentation of the prints in terms of color gamut volume. The final output should be evaluated in terms of overall printer capability, not only in terms of a substrate quality, the type of ink set, and the basic level of color reproduction. The results show that there is no evident correlation between the physical and/or optical properties of the certain choice of the substrates and the amount of colors that can be produced on such substrates. It was proposed that the color gamut volume, which enables characterization of a wide range of media, can be used as a new tool in the pressroom. The article, which has been submitted to TAPPI Journal, also deals with this comprehensive ink jet technology study.

The choice of proper substrate and coating, ink jet inks, and a form of UV protection for printouts is discussed in the last part of this work. Substrates with special ink jet with and without optical brightening agents were chosen for the evaluation. Preliminary discussion on ink performance and substrate properties interaction has been conducted at the TAPPI 2006.
Coating and Graphic Arts Conference in Atlanta this year. More detailed work, "Effect of Optical Brightening Agents and UV Protective Coating on Print Stability of Fine Art Substrates for Ink Jet", will be published and presented at the IS&T NIP22 International Conference in Denver this year.

The paper with more comprehensive results including the water penetration characteristics of the substrates and inclusion of a look into color abilities of the Epson's newest generation, K3, pigmented inks will be submitted to the Journal of Imaging Science and Technology.

The topics mentioned above are discussed in greater details in the following chapters.
LITERATURE REVIEW

Inkjet Printing Process

History of Ink Jet

The first description of a mechanism by which a stream of ink or liquid breaks up into droplets was described by Lord Rayleigh in 1878. Inkjet technology development started in the early 1960s. In 1951, Siemens patented the first practical Rayleigh mechanism ink jet device.\textsuperscript{11,12,13}

The continuous inkjet printer technology was developed later by IBM in the 1970s. The continuous inkjet technology basis is to deflect and control a continuous inkjet droplet stream direction onto the printed media or into a gutter for recirculation by applying an electric field to previously charged inkjet droplets.\textsuperscript{14,15}

The drop-on-demand inkjet printer technology was led to the market in 1977 when Siemens introduced the PT-80 serial character printer. This approach is based on the application of voltage pulses, ink drops are ejected by a pressure wave created by the mechanical motion of the piezoelectric ceramic. The drop-on-demand printer ejects ink droplets only when they are needed to print on the media. This reduces the complications with drop charging and deflection hardware, as well as the irregularity of the ink recirculation systems required for the continuous ink jet technology.\textsuperscript{12}

Later, in 1979, Endo and Hara of Canon developed the bubble jet printer technology, a drop-on-demand inkjet printing method where ink drops were ejected from the nozzle by the fast growth of an ink vapor bubble...
on the top surface of a small heater. At the same time, Hewlett-Packard independently developed a similar inkjet printing technology and named it thermal inkjet.

Inkjet printer models with higher printing resolution and color capability became available with very affordable prices. Since the late 1980s, because of their low cost, small size, quietness, and particularly their color capability, the thermal inkjet or bubble jet printers became the viable alternative for home users and small businesses. The down side is that although inkjet printers are generally cheaper to buy than lasers, they are far more expensive to maintain.

A characteristic of all modern ink jet systems lies in their utilization of micromanufacture of electronic, thermoelectric and electroacoustic elements. These techniques were developed elsewhere in the electronics industry. They found applications in the construction of ink jet elements, which require extremely small size and close spacing of elements. The ink jet print mechanism is an example of a MEMS (Micro Electrical Mechanical System) device.

Imaging System – Ink Jet

Inkjet printing is one of the most common non impact (NIP) technology used for digital printing systems and is currently the fastest growing printing process. Inkjet is used to personalize mass mailings for advertising, and promotions. A large and growing consumer market for ink jet was established in packaging, publication, and specialty areas. It is used anywhere that a small piece of information needs to be added – after...
conventional impact printing. Inkjet printers have established their fastest growth in wide format digital color printing, outdoors graphics, banners, signs, and/or posters.

The ink jet process is a computer to print technology in which ink is sprayed from nozzles, no image carrier is needed. The data of the digital print job are transferred directly to control the imaging unit. The ink transfers to the paper via nozzles, mostly directly or in some applications indirectly depending on the technology used. Therefore, the functional units, imaging system, image carrier, and inking unit are combined into a single module and they transfer the ink directly onto the paper.\textsuperscript{18}

In principle, ink jet does not require an intermediate carrier for the image. In the ink jet process the ink can be transferred directly onto the paper. There are two broad ink jet technologies: Continuous Ink Jet and Drop on Demand. Within each of these there are other variations as shown in the Figure 1.\textsuperscript{19}
The continuous ink jet technology generates a constant stream of small ink droplets, which are charged according to the image and controlled electronically. The charged droplets are deflected by a subsequent electric field, while the uncharged ones flow onto the paper. Continuous ink jet printing usually feeds only a small proportion of the stream of droplets to the substrate. With continuous ink jet generally only a small part of the drop volume covering the sheet in accordance with the print information is applied to the substrate. The large part is fed back into the system.

In the drop on demand ink jet technology, a droplet is only produced if it is required by the image. The most important “drop on demand” technologies are thermal ink jet and piezo ink jet printing. Thermal ink jet, or bubble jet, generates the drops by the heating and localized vaporization of the liquid in a jet chamber. With piezo ink jet the ink drop is formed and
catapulted out of the nozzle by mechanically deforming the jet chamber, an action resulting from an electronic signal and the piezoelectric properties of the chamber wall.\textsuperscript{18}

**Inks for Ink Jet**

The ink used for ink jet printing is usually liquid. Exceptions are hot-melt inks that liquefy by heating. The ink is sprayed onto the substrate where it solidifies after cooling. The hot melt inks will be discussed in greater details later on.

Almost all the types of ink jet ink can comprise dyes or pigments as colorants and an ink carrier, e.g., water or solvents. The type of ink to be used is also substantially determined by the properties of the substrate, the surrounding conditions of the print substrate, e.g. light, wear, weather resistance, and the drying process required during printing with different printing systems. If liquid inks are used, the drying process occurs through evaporation and absorption. The evaporation process can be accelerated by the application of heat or UV drying unit.\textsuperscript{18}

Both types of colorants contain hydroxy or amino substituents which have delocalized pi-electrons conjugated from 2pz orbitals. These electrons can interact to form a charge transfer band in the visible portion of the electromagnetic spectrum and thus create a color.\textsuperscript{20} A dye is a colorant which is dissolved in the carrier medium. A pigment is a colorant that is insoluble in the carrier medium, but is dispersed or suspended in the form of small particles, often stabilized against flocculation and settling by the use of dispersing agents. The carrier medium can be a liquid or a solid at room
temperature in both cases. Commonly used carrier media include water, mixtures of water and organic co-solvents and high boiling organic solvents, such as hydrocarbons, esters, ketones, etc.\textsuperscript{21}

**Dye Based Inks**

Dyes are non-planar molecules some containing solubilizing groups, e.g. carboxylic or sulfonic acid. The intermolecular forces are weaker than in pigments with the result that the crystals are less stable and are easily broken up by solvents to give solutions.\textsuperscript{20}

Although dye based aqueous ink systems are enthusiastically employed, dyes also possess several disadvantages. For example, when exposed to significant amount of moisture or water they can dissolve and run since dyes in nature are water soluble. Also, images may further smear or rub off when scratched, polished or touched by a finger. They usually have poorer water and lightfastness, and thermal stability than pigment based inks but this topic becomes more and more questionable. An example of a blue dye used in ink formulas is shown in Figure 2.

![Chemical Structure of Brilliant Blue RS Dye](image)

**Figure 2. Chemical Structure of Brilliant Blue RS Dye.**
Pigment Based Inks

Pigments are planar insoluble molecules that contain strong hydrogen-bonding groups such as amide and carbonyl. These molecular features make possible strong intermolecular attractive forces leading to stable crystals having high lattice energies which are difficult to disrupt by solvents.

The use of colored pigments in the industry has gained wide acceptance in a number of applications. Generally, the particle size of available colored pigments has hindered efforts to improve products containing colored pigments. Pigments generally are more resistant to oxidation, and have higher thermal stability. Examples of such pigments include carbon black, titanium dioxide white, cobalt blue (CoO—Al: O₃), phthalocyanine blue, phthalocyanine green, and chrome yellow (PbCrO₄).²²

![Chemical Structure of Phthalocyanine Blue Pigment.](image)

Figure 3. Chemical Structure of Phthalocyanine Blue Pigment.

In an effort to improve color and other print qualities, the drop mass
and the nozzle diameter of ink jet print heads has been reduced. To accommodate smaller drop mass and nozzle diameters and simultaneously maintain chroma and performance, pigment based inks require pigment dispersions with improved stability.\textsuperscript{23}

Currently, the satisfactory way to make colored pigments having small particle sizes has been with the use of dispersants, such as surfactants and polymeric resins. Otherwise, the colored pigments will agglomerate and thus lose their small particle size. Not to forget, redispersion rather than redissolvability must be achieved to have good system start-up. Also, because pigments exist as discrete particles in ink, pigments have a strong light scattering effect. As a result, pigmented inks have a lower chroma as compared to dye based inks. Several methods have been used in an attempt to improve the chroma, dispersability, and performance of pigment based inks. For example, additives such as optical brighteners and fluorescent whiteners have been added to the ink formulation. Dyes can also be added to pigment based inks in the form of a dyed pigment, polymeric dyes, a polymer resin with an oil soluble dye, or a complex product of dye and polymer. Methods to improve the chroma, dispersability, and performance of pigment based inks may solve some of these problems, but at the same time, other physical qualities of the ink can be sacrificed.

The ink used and its interaction with the substrate determine the thickness of the ink layer on the paper and thereby the quality of the printed image, especially in multicolor printing. The thickness of the deposited liquid ink layer is approximately 0.5 µm. For UV ink and hot-melt ink, the ink layer
thickness ranges between 10 and 15 \( \mu m \). This may cause three dimensional structures that can affect the visual impression.\(^{18} \)

CIE Color System

CIE Chromaticity Values

To make these values easier to work with, the CIE specified a system of virtual primary values, called CIE XYZ tristimulus values. These are referred to as CIE coordinates \( X, Y \) and \( Z \), with \( X \) corresponding to a red tristimulus value, \( Y \) to an green, and \( Z \) to an blue value. The spectral values associated with these standard tristimulus values are referred to as standard spectral values, and the color values calculated on this basis are called standard color values. Tristimulus values of a measured color are calculated by multiplying, for each wavelength interval used, the spectral power distribution of the light source \( P \), the spectral sensitivity of the standard observer \( \bar{x}, \bar{y}, \) or \( \bar{z} \), and the spectral reflectance curve of the measured sample \( R \) as follows.\(^{24} \)

\[
X = k \int P R \bar{x} \quad Y = k \int P R \bar{y} \quad Z = k \int P R \bar{z}
\]

where:

- \( k \) - a constant, which is a function of the power distribution
- \( P \) - spectral power distribution of light source
- \( R \) - spectral reflectance of object
- \( \bar{x}, \bar{y}, \) and \( \bar{z} \) - standard observer functions,

The standard spectral values allow for the deduction of a number of
special characteristics. An ideal white features the standard spectral values $X=Y=Z=100$, with brightness characterized directly by the imaginary standard spectral value $Y$. The primary color of green light (546 nm), chosen by the CIE to define the standard observer, corresponds with overall human visual response to all color or lightness. Therefore, the $Y$ value indicates not only a sample's green response but also its luminance or lightness value.$^{25,26,27,28}$

CIE Chromaticity Diagram

CIE $xyz$ chromaticity values provide a method of graphically plotting the colorimetric values of a sample in three-dimensional color space.

$$x = \frac{X}{X+Y+Z}, \quad y = \frac{Y}{X+Y+Z}, \quad z = \frac{Z}{X+Y+Z}$$

(2)

where:

$X$, $Y$, and $Z$ are the tristimulus values of the red, green, and blue responses, respectively (source x object x observer)

![CIE Chromaticity Diagram](image)

Figure 4. CIE Chromaticity Diagram.
The resulting representation is known as the CIE 1931 Chromaticity diagram, or "horseshoe" (Figure 4). The axes of this color space are similar to the HSL color space. Chromaticity coordinates x, y and z (hue and chroma) are a simple transformation of tristimulus values that can be represented on a two-dimensional graph. The third dimension is tristimulus Y (luminosity), which represent how bright the color is.29

CIE xyY color values are straight calculations from XYZ tristimulus values and according to this, it is possible to plot all achievable colors. All other color spaces (e.g. RGB, CMYK,) are subsets of the CIE 1931 color space and the full range of these color spaces can be represented in the context of the CIE 1931 xyY model. However, The XYZ color space is a device-independent, repeatable standard. The CIEXYZ color system is specified as an important reference color space under standard illuminant D50 at a viewing angle of 2 degrees.

CIE Lab Color Model

A practical limitation of the CIE chromaticity diagram is that it does not provide a perceptually uniform color space. The distance between two or more colors in xyY space does not necessarily correspond with the colors' visual similarity or difference. Apart from systematic allocation of the CIE chromaticity diagram, other concepts for the creation of equidistant color system and distance formulas were developed, known as the Compensation Color Theory by Hering.30

The two uniform color spaces accepted by the CIE are called CIE L’a’b’
& CIE L’u’v’, both accepted in 1976. The former is mostly used for flat reflective color, whereas the latter is used for color displays. These are mathematical transformations of the XYZ color space where the Euclidean distance between two colors is proportional to the perceived difference between both. CIE L’a’b’ is almost certainly the most accepted and significant color space based on Compensation Color Theory. The CIELAB color distance formula was used mainly to standardize different LAB models developed in the past. The coordinates L’, a’ and b’ can be calculated from the standard color values XYZ as shown in following formula.

\[
L^* = 116\left(\frac{Y}{Y_n}\right) - 16; \quad a^* = 500\left[f\left(\frac{X}{X_n}\right) - f\left(\frac{Y}{Y_n}\right)\right]; \quad b^* = 200\left[f\left(\frac{Y}{Y_n}\right) - f\left(\frac{Z}{Z_n}\right)\right]
\]

(3)

where:

X, Y, and Z are the tristimulus values of red, green and blue responses

Xn, Yn, Zn – tristimulus values of illuminant and

\[
f(x) = x^{(1/3)}, \quad x > (6/29)^3 = 0.008856... = (29/6)^2x/3 + 16/116, \quad x < (6/29)^3
\]

In the new model, the color differences, which people perceive to be equispaced, really do correspond to those distances when measured colorimetrically. The a axis extends from green (-a) to red (+a) and the b axis from blue (-b) to yellow (+b). The brightness (L) increases from the bottom to the top of the three-dimensional model (Figure 5).
Color Difference - Delta E

CIELAB color values are often used in quality control, such as for comparing the differences in a reproduction and original. The numerical value specifying the distance between two colors in a color space system is generally indicated as Delta E (ΔE). ΔE is calculated using the distance formula to determine the distance in color space from one color to another within one color space (Equation 4).

\[
\Delta E = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2}
\]  

where:

\[L^*, a^*, b^*\] - CIELAB coordinates of reference color

Figure 5. CIELAB Color Space.
\[ L'_2, a'_2, b'_2 \] - CIELAB coordinates of comparison color

Some color management system vendors prefer not to use CIELAB values for device characterization, because it is not perfectly uniform. Some manufacturers use CIE XYZ tristimulus values along with their own proprietary appearance models to compute color profiles.

When working with colorimetrically controlled reproduction systems (Color Management System), it is much easier for the untrained user to describe and edit CIELAB data in its LCH representation. Chroma \( C \) and hue angle \( h \) are calculated from values \( a' \) and \( b' \) as shown in formulas.\(^{33}\)

\[ C_{ab} = \sqrt{(a')^2 + (b')^2} \quad (5) \]

\[ h_{ab} = \arctan \left( \frac{b'}{a'} \right) \quad (6) \]

Color Management

International Color Consortium (ICC)

Color management has been with us since the early '90s, and as it turned out, Apple underestimated the complexity of the assignment as well as the degree of sophistication and productivity needed by prepress and printing experts. Not long after the original ColorSync was distributed, Apple and seven other vendors decided to work together on updating the concept and the software and established the ColorSync Profile Consortium. Members including Adobe, Agfa, and Kodak, considered that the new standards should go beyond the Apple Macintosh platform, and as a result, Microsoft,
and Silicon Graphics joined what was soon to be renamed the International Color Consortium (ICC), which now has much more members.

The new standards were consequently designed to allow color consistency between all devices, applications and platforms involved in the printing process. The ICC device profiles are usually text documents that should be workable at any platform, not only the one on which the profile was created.

**Color Management System (CMS)**

The CMS provides the contribution to many fields of the imaging industry, which works with graphic images displayed on monitors. These include prepress services, advertising agencies, graphic design studios and, recently on World Wide Web pages, where users expect what-you-see-is-what-you-get (WYSIWYG) color production. Whether using an RGB or CMYK workflow, aligning scanners, monitors and printing devices will promote predictable color results every time digital images and documents are scanned, viewed, or created.

The goal of color management is to coordinate the color spaces of all devices involved to allow a data interchange, which will guarantee a true color reproduction of images and graphics throughout the process. The color management system can be also defined as a system that uses profiles for input and output devices to transform device dependent values (RGB, CMYK) into device independent values (XYZ, L\'a\'b\'). This could be named as a central profile connection space (PCS). Device characterization information
is stored in profiles; an input profile provides a mapping between input RGB data and the PCS, and an output profile provides a mapping between the PCS and output RGB/CMYK values. Only if the profiles represent a good characterization of the device can the system work well.\textsuperscript{27,36,37} Obviously, the quality of the color profiles has a direct impact on the entire color management process. It is always important to have a quality measure for ICC profiles because this indicates how well a device has been characterized and therefore how accurate the color is likely to be in a color managed workflow.

A complete CMS consists of three main parts: a tool measures actual colors and stores results as numbers; software that creates systematic profiles of colors and results from various devices and converts the colors into a standard format; and color matching software that translates the color profiles from input to output. In general, the intelligence of the color management system is stored in the color profiles. This is where the system defines how colors that are theoretically not reproducible, can nonetheless be output by a printing system in such a way that the human eye will perceive them as an authentic reproduction of the original. Obviously, the quality of the color profiles has a direct impact on the entire color management process. The actual color conversion technology of the default CMM (Color Management Model) is based on simple but fast mathematical operations.\textsuperscript{38,39}

\textbf{ANSI IT8. 7/3 Chart}

ANSI (American National Standards Institute) is a U.S. member of the
International Standards Organizations (ISO) that develops voluntary standards for business and industry. IT8 is a set of standards developed by the ANSI committee governing color communications and control specifications. IT8 standards cover RGB, CMYK, scanning targets, and multi vendor calibration.

An IT8.7/3 target (Figure 6), also known as ISO 12642 target, is a printed reflection target that can be used to obtain the color gamut achievable by the fingerprint test. Many devices exist today that will even automate the process of reading and interpreting the target generating a color profile of the achievable color gamut for each fingerprint test. These color profiles are governed by the ICC (International Color Consortium). They can be attached to color halftone files thus optimizing the color balance of the printed halftone itself for a particular fingerprint.40

Color profiles have helped to attain consistency within the printing process by permitting predictable color reproductions. It is very important to understand that a separate profile is created from each fingerprint. Failure to utilize the appropriate profile may result in unpredictable print. If used correctly, ICC color profiles can be a powerful tool aiding all types of printers.41
profiling tools have meanwhile updated their products to handle the ECI 2002 CMYK target.

Figure 7. a. ECI 2002V CMYK Target, b. ECI 2002R CMYK Target.

Color Gamut

As mentioned above, color can be represented as a point in a three dimensional coordinate system, e.g. CIELab Color Model. A color gamut is a delimited region in color space, containing colors that are physically realizable by a given device or that are present in a given image.

In order to obtain high quality color reproductions between all the devices in production chain, some type of color gamut mapping must occur. In order to perform gamut mapping in a visually effective manner a description of a device's color gamut needs to be obtained.

The set of all colors which can be produced by a printing system is that system's color gamut. If all of the colors in a color gamut were plotted in a three dimensional coordinate system they would form a color solid. The
volume of the solid would be proportional to the effective number of colors in
the gamut.\textsuperscript{46}

Often the color gamut is displayed as a full 3-dimensional space
because critical data are generally lost in the 2D representation, which may
lead to incorrect interpretations of the results. Many software packages are
commercially available that use the gamut’s full profile data to display 2D
and 3D chromaticity plots (Figure 8) together with all the statistics (Figure 9).
The gamuts are always generated from measuring a large set of printed color
patches that were created to define the gamuts profile.

Figure 8. 3D Gamut Plot.

From these data, various algorithms allow one to define the surface of
the gamut allowing for numerical calculation of the gamut volume.\textsuperscript{49}
Figure 9. Gamut Volume Statistics.

Color gamut mapping is an integral part of color management and has become a very important research tool. It is used for the quantitative comparison of the effects of colorants, media, and other variables that affect device’s behavior. Typically, the color gamut is a tool used in color management systems that allows device-independent representation of the image or the reproduction device, input and output. Input device’s gamut, usually obtained from scanner or digital camera and displayed on the screen in RGB mode, and output device’s gamut, printer or press operating in CMYK, can be characterized in terms of gamut boundaries representations and the diversity of all the devices in the production chain can be observed. Based on the information obtained from gamut observations, the gamut clipping occurs when the range of colors of an input device is out off the gamut of the output one and thus impossible to reproduce. Very often, the
color gamut is used in comparison of different devices or ink sets and their performance. The characterization of substrates based on differences in gamut boundaries and volume is a new way the color gamut can be incorporated in the printing production. It was proposed that without changing any printing process and ink characteristics, the variety of substrates can be studied and information about their performance under the same conditions consequently collected. Also, this novel approach can be used in the way ink sets' lightfastness is evaluated. Instead of measuring the differences in densities and L*a*b* values of small amount of patches before and after the tests, which is the standard procedure for colorimetric lightfastness evaluation, the changes expressed in gamut volume loss and 2D and 3D gamut plot comparisons may be used.

Lightfastness and Permanence of Digital Images

Color in images is generated by color forming chromophores on either dye or pigment molecules. Dyes are soluble chemicals that exist in an ink as individual colorant molecules. Pigments are insoluble chemicals that exist in groups of thousands of colorant molecules.

Fading of color is from chemical reactions that cause the chromophore element to break down. Dyes fade faster than pigments under the same conditions. When a photon hits a molecule, its energy is distributed across the molecule. If the chromophore element receives enough energy, it will break down. Photon energy hitting a pigment particle is distributed over many molecules. Less energy reaches any particular chromophore element.
Reactions occur at a lower percentage of the time. This difference can also be explained using the concept of activation energy. Distributing the energy, so that less gets to the reaction sites, is equivalent to increasing the activation energy barrier. More energy must hit the particle to get the same amount of reaction at the chromophore. For a given amount of incident radiant energy, less reaction occurs.\textsuperscript{52,53}

Dye images will last a long time under very controlled "standard" conditions. If those images are exposed to outdoor light or bright indoor light, the best of the dye inks will fail much earlier. In recent years techniques have been developed to decrease the rate of dye ink color fade. This just means that images made with these inks can now withstand low lighting display for a reasonably long time. Unfortunately, under bright light, they still fade relatively quickly.

There is a perception in the market that pigmented inks contain chunks of colorant that plug nozzles. This may happen with some inks; but not in quality pigmented inks. In order for any CMYK process ink set to give decent color, the ink must be transparent and must not scatter visible light. To do that, particles must be less than half the shortest wavelength of light, 400 nanometers. That means the pigment particles must be less than 200 nanometers.

There is also a perception that pigmented inks don't have much color gamut. The outdoor signs made with pigmented inks can have a dull and lifeless image, but the truth is this is caused by the mismatch of ink and media. That’s why correctly matched ink and media are critical to bringing
Optical Brightening Agents (OBA)

The first practical uses of OBA did not occur until 1943 when CIBA started the production of optical brighteners based on stilbene derivatives. Optical brightening agents (OBA), or fluorescent whitening agents (FWA), are a particular class of organic compounds that have very specific fluorescent properties. As mentioned before, their chemistry is based on the stilbene molecule and is modified to enhance solubility and uptake depending on the substrate in which they are used. One of the examples of fluorescent brighteners used in paper industry is a sulfonated derivative of stilbene (Figure 10.).

![Figure 10. Sulfonated Derivative of 4,4-bis(triazin-2-ylamino) Stilbene.](image)

Typically, molecules that display fluorescence are of two types - organic compounds with a high degree of conjugated unsaturation and an extended π-cloud structure, or inorganic compounds, where it is relatively easy to promote an electron to a higher vacant energy level (usually a d- or f-
level), and the molecule may also be excited to a higher vibrational and rotational energy state. Due to the conservation of energy, the emitted light is almost always at a higher wavelength. Molecules than have excitation maxima in the very near UV region (340-400 nm) and emit in the 430-460 nm wavelength ranges.\textsuperscript{57}

OBAs are widely used in paper coatings, textiles, and laundry detergents for hiding the yellowish tint of paper, textiles, coatings and plastics by giving them a bluish tint and to increase the superficial whiteness of the products.\textsuperscript{58} Many digital inkjet printmakers prefer a bright white surface to print on, to the true surface color of their naturally yellow substrate. But usually, the reflection of white light emanating from the OBAs will overwhelm the paper's natural color, creating a higher perceived whiteness, which may enhances the color gamut and color density of the prints.\textsuperscript{59}

On the other hand, OBAs can be a risk to the reliability and permanence of a fine art print by accelerating metamerism and causing color shifts, and yellowing over time. Also, problem with OBAs is that they have been known to decompose over time and can cause yellow stains to appear on the prints. Printmakers who use OBA free papers can reduce their entire element from their business.\textsuperscript{59}

Three Dimensional Printing Techniques

Three dimensional (3D) images can be produced by many ways. Old fashioned procedures employ special devices – e. g. embossers. These can
create raised image output when attached appropriately to computers. The speed of these generators ranges from 25 characters per second to 60 characters per second. There are several disadvantages related with the embossers. First of all, the cost of these embossers is somewhere around $20,000 or more and their embossing speed is very slow when compared to conventional or digital printers with digital printing inks. Additionally, paper that is used for embossing needs to be of a special grade.60

Another old style process is used to produce hectographic or spirit duplicating masters. Hectographic or spirit duplicating was a broadly used process, especially because of its low costs of a copy or equipment, and also because there was no special training required to operate or service the equipment. Usually, a spirit duplicating master includes a substrate, typically paper, carrying a hectographic ink mirror image of the material to be duplicated. The hectographic ink on the master contains a spirit or alcohol soluble dye which when pressed into momentary printing contact with a sheet of paper transfers dye from the master to the sheet.61

Raised xerographic printing with thermally intumesced electroscopic powders presents different way of creating 3D structures. Intumescent electroscopic powders with foamable microspheres are blended with the powdered ink or toner in the ink reservoir of a copying machine. The image is formed and transferred to a paper carrier in the Carlson process62. The heat used in thermoadhesively attaching the toner to the paper also causes great intumescence of the intumescent powder, resulting in a raised image. Immense benefit of this process lays in the price.63
In another approach, the recording material is first magnetized, and then it is induced by a magnetic field forming 3D dots. A magnetized thermoplastic recording material is heated to be liquefied in a small bath, and injected toward the printing paper surface through a nozzle. The hotmelt thermoplastic recording material is induced onto the paper surface by means of a leakage magnetic field from a gap in the magnet arranged on the back side of the paper surface, where it is deposited and solidifies. The characteristics for recording material include a certain viscosity at high temperatures, the formulation has to include material with properties that enable it to be subjected to the external magnetic force, and also the material should have good adherence to the substrate. The material consists of ethylene-vinyl acetate copolymer (EVA), paraffin wax and, of course, magnetic particles (diameter ~ 0.5 μm) used for magnetization.

Bruce Campbell’s group at Eastman Kodak Company worked on unique three dimensional imaging papers with randomly distributed fibers and uniformly dispersed unexpanded synthetic thermoplastic polymeric microspheres, which after exposition to heat are capable of producing a raised image by expansion of the caliper of the paper. This could be achieved by incorporating the unexpanded synthetic thermoplastic polymeric microspheres into dry cellulose fibers. A signal in the form of heat reaches the substrate; subsequently the caliper of the paper expands in areas heated above the expansion temperature of the microcapsules and thus provides a raised image.

A similar approach was offered by Torii, in which a heat transfer
printing sheet comprises a substrate sheet, and a thermally expandable ink layer. The ink layer contains thermally expandable microcapsules as expanding agents, and a binder resin. The process for producing raised images includes the steps of superposing, on an image receiving sheet, a heat transfer printing sheet, heating image wise the thermally expandable ink layer and bringing the heat transfer printing sheet into pressure contact with the image receiving sheet, releasing the heat transfer printing sheet from the image receiving sheet. By this the thermally expandable ink layer is separated from the heat transfer printing sheet and transferring it to the image receiving sheet. Applying light to the thermally expandable ink layer, which has been transferred image wise to the image receiving sheet, it is possible to obtain raised images.

Thermography is the process of spreading special thermal powders on the wet ink of a print application and heating it in order to melt the powder into a single solid mass, which is raised above the printed surface. The powdered resins are applied to a printed surface on which the printing ink is still wet. Sheets of suitable material such as paper bearing image areas overlaid with powder particles, which typically are made of thermoplastic resin, are transported through a heating chamber. Here, the powder particles are heated sufficiently to fuse them together into raised image portions fixed to the sheet. This also enables the powder to stick to the printed areas. Any powder on non-image areas and any excess powder on the image areas are suctioned off the substrate before the heating takes place. The heat is produced with electric heating elements that are placed inside an oven or
tunnel. The powdered substrate passes into the heat tunnel where the powder melts onto the heated substrate and is fused with the wet ink. The substrate must be raised to the temperature of the melting point of the powder in order for the process to work correctly. Generally, the temperature of the sheet itself must be raised to above 200 F, and the heating temperature used for economical production needs to be in the range of about 1000 F to 1200 F. The sheets then are passed through a cooling station in which, an air flow from above cools them to solidify the fused image portions.67

A method of screen printing raised 3D images involves the use of a stencil attached to the print side of the print screen. The stencil is made from a pre-fabricated, photosensitive thick film having a precision controlled thickness. The print screen is coated with a photosensitive emulsion, and the combination of the print screen and the attached photosensitive stencil blank are exposed to UV light in order to harden the non-exposed emulsion and stencil material. The screen and stencil are thereafter washed to remove the non-hardened emulsion and stencil material, thereby creating openings in the screen coating and stencil material to form a three dimensional image volume. Pigmented paste is screen printed through the one or more image openings in the coated screen and the associated one or more image volumes in the stencil to form a raised image on the substrate. Complex images can be built using a plurality of raised image layers. The raised image layers have a generally planar surface and sharp edges perpendicular to the planar surface.68

Another process used for building three-dimensional objects works by
building parts of ink in layers. Raised printing is the deposit of ink containing a raising agent on paper to cause the words or images being raised above the plane of the paper. This creates the effect of the words or images standing out from the page in order to emphasize their content. The method includes the steps of depositing a light curable photo-polymer material on the area selected for the printing effects and curing the area. The amount of material to be deposited corresponds to the area selected for the printing effects and the height of the raised area relative to the medium on which the photo-polymer material is deposited. Curing is carried out using ultra violet (UV) or infrared (IR) radiation.69

A very interesting approach has been recently introduced by 3D Systems, Inc. In their work they introduced ultra-violet light curable hot melt ink compositions that can be used either in a solid object printer to produce strong and desirable parts, or in the adhesive industry to produce adhesive and their film coatings. In particular, the UV curable phase change compositions is comprised of a urethane (meth)acrylate resin, a wax, low molecular weight diluents, a photoinitiator and a polymerization inhibitor. These mixtures of various waxes and polymers are solid at ambient temperatures, but convert to a liquid phase at elevated jetting temperatures in the print head. Such phase change materials have melting points of about 65°C and a viscosity of about 13 cP at jetting temperature (130°C to 140°C).70

Thermal Transfer Printing Technology

With thermal transfer printing and thermal wax transfer printing technology, phase-change inks (hot-melt inks or thermal waxes) are brought
into contact with the substrate and a thermal head. The hot melt ink printer is a variant of DOD ink jet printers, where the liquid for the printing is obtained by melting the hot melt inks. Thermal transfer and hot melt printers utilize wax-like hot melt ink, rather than the liquid or dry ink used in other processes. The simplicity of thermal transfer printers leads to low equipment cost, cleanliness and high reliability.\textsuperscript{18}

The thermal head is digitally addressed. The process is generally binary, although some higher-end models are capable of producing multi-level dots on special thermal paper. This print image is stored as a pattern of dots, at 300 dots per inch, and is reproduced by precisely timed and controlled exposure of the ink sheet to heating elements on a Thermal Print Head (TPH).\textsuperscript{71,72,73,74,75,76,77,78,79}

As mentioned before, for a hot melt printer, the ink is kept fluid in the reservoir by a heating component of the printer. The liquid ink is pumped through a nozzle, often using a piezoelectric crystal. Piezoelectricity is the ability of certain crystals to produce a voltage when subjected to mechanical stress or vice versa. The word is derived from the Greek "piezein", which means to squeeze or press. In a piezoelectric crystal, the positive and negative electrical charges are separated, but symmetrically distributed, so that the crystal is overall electrically neutral. When a voltage is applied, this symmetry is destroyed.\textsuperscript{80}

Phase-Change Inks

Inkjet printers use a few kinds of inks, either liquid inks with very low viscosity or solid inks with the phase-change ability occurring during the
printing process. The hot melt inkjet inks (Figure 11) have to stay solid at ambient temperatures, liquify at the moment of printing and promptly solidify when reaching the substrate. Upon hitting a recording surface, the molten ink drop solidifies immediately, thus preventing the ink from spreading or penetrating the printed media. The quick solidification ensures that the image quality is good on a wide variety of recording media. Because the inks are not substantially absorbed by the substrate, high color saturations and large gamuts are obtained on a wide variety of substrates.²²

Figure 11. Hot Melt Inkjet Ink Sticks.

Composition of Phase-Change Inks

Conventional hot-melt inks are composed of four main components: an ink binder comprising a wax with a melting point in the range of 50°C to 90°C, then a dispersant and a resin. Also, hot melt ink contains a pigment or a dye functioning as a coloring component.⁸¹

Waxes

Waxes are used alone or in the form of a mixture. If the wax component in the ink formulation is less than 5% by weight, the properties of
other additives may have a higher or unsettled melting point, which will negatively influence the ink composition (ink will not melt sharply below the ink-jetting temperature). If the wax component in the ink formulation is more than 95% by weight, the ink composition may have an insufficient melt viscosity, and adhesion to the substrate can be accompanied with various problems. Selection of waxes is wide, such as plant waxes, animal waxes, synthetic hydrocarbon waxes, higher fatty acid, higher alcohol, and their derivatives. The petroleum wax consists of paraffin wax and microcrystalline wax. The most essential synthetic hydrocarbon waxes are a polyethylene wax and a Fisher-Tropsch wax. Fisher-Tropsch (F-T) waxes, also known as polymethylenes, are chemically similar to polyethylene but are produced by the reaction of carbon monoxide and hydrogen.

The main representatives of plant waxes are candelilla wax and carnauba wax. Candelilla wax was found as an exudate on the leaves and stems of a plant (Euphorbia antisyphilitica) found in northern Mexico and the southwestern United States, and obtained by boiling the leaves and stems with water and sulfuric acid. It is yellowish-brown in color and is opaque to translucent. It is used in making varnish and as a substitute for carnuba wax to impart a high gloss to leathers that are not glazed. Carnauba wax is a yellowish-white or green, sticky exudation on the leaves, berries and stalks of the carnauba palm (Copernicia cerifera), found in South America, and especially Brazil. It is used to impart a high gloss to leathers that are not to be glazed, and by bookbinders to polish the edges of books after gilding and burnishing through paper. The wax imparts a high gloss to the edges and is
preferred to beeswax by some as it is less likely to streak. Carnauba wax has a softening range of 83 to 84°C, which makes it especially suitable for use in very hot climates.82

The most significant animal waxes are bees wax and lanolin. Composition of the higher fatty acids is based on stearic acid and lauric acid. Higher alcohols as stearyl alcohol and/or 12-hydroxystearic acids are found in different plant tissues.83

Resins

Thermoplastic resin is classified as to its macromolecular structure. An amorphous or unstructured plastic is irregular with highly branched molecular chains and is transparent. Semi-crystalline thermoplastics have molecules in orderly or linear chains and are cloudy or semi transparent.

Adhesion of the ink to printing substrate is assured by the resins. At the same time, resins control the viscosity of the ink at the melting point and inhibit the crystallization of the wax imparting the transparency of the ink. Generally, polymers that are used for hot melt inks have melting points in the range of about 40°C to 200°C. In a molten state, the polymer should be stable so that there is no formation of gaseous products or deposits on the printer device.

Examples of suitable polymers for ink compositions include, but are not limited to, one or more of the following: alkyd resins; amides; acrylic polymers; benzoate esters; citrate plasticizers; cumarone-indene resins; dimer fatty acids; epoxy resins; fatty acids; ketone resins; maleate plasticizers; long chain alcohols; olefin resins; petroleum resins; phenolic resins; phthalate
plasticizers; polyesters; polyvinyl alcohol resins; rosins; styrene resins; sulfones; sulfonamides; terpene resins; urethanes; vinyl resins; and derivatives thereof and combinations thereof. No limitation is placed on the type or the amount of the polymer that is present in the ink.

Additives

The polymer system of ink is intentionally influenced by the additives. Various minor chemical additives may be added to the ink composition. These include antiscratch additives, adhesion and surface additives, antioxidants, biocides, plasticizers, and corrosion inhibitors designed to improve the ink’s performance. They can advance compatibility and mixing or weaken the melt promoting separation and coalescing of polymers.

Antiscratch Additives. High molecular weight silicon rubber can improve scratch resistance of polymer mix. Generally, 1-4% is needed. High molecular weight polysiloxanes do not negatively impact adhesion and printability.

Adhesion and Surface Additives. Low molecular weight PTFE can enhance abrasion resistance, reduce the coefficient of friction and mechanical wear, reduce surface contamination, and modify appearance. For example, ultra high molecular weight polyethylene can be used for scratch resistant coatings.

Antioxidants. Phase change ink compositions are in a molten state during printing. To prevent thermally induced oxidation from occurring in this state, antioxidants may be added to the ink composition. An antioxidant is a substance that, when present in low concentrations relative to the
oxidizable substrate, significantly delays or reduces oxidation of the substrate. Suitable antioxidants, present preferably in the amount of about 0.1% to 1.0% by weight of the ink composition, include, for example, Irganox RTM. 1010 and Iragofos RTM. 168 (Ciba-Geigy Corp.).

Biocides. A biocide is a chemical substance, capable of killing different forms of living organisms. Biocides can also be added to other materials (typically liquids) to protect the material from biological infestation and growth. They may be added in the range of about 0.01% to 5%, based on the weight of the ink composition. Examples of suitable biocides include bis (trichloromethyl) sulfone, zinc pyridinethione, sorbic acid, and vinylenebis-thiocyanate.

Corrosion inhibitors. By definition, a corrosion inhibitor is a chemical substance that, when added in small concentration to an environment, effectively decreases the corrosion rate. The efficiency of that inhibitor is thus expressed by a measure of this improvement. One or more corrosion inhibitors may be added to inhibit the corrosion of the metal that comes in contact with the phase change (hot melt) ink. Suitable corrosion inhibitors, present in the range of about 0.1% to 5% (based on the weight of the ink composition), include ammonium dinonyl naphthalene sulphonate.

Plasticizers. Plasticizers are substances added to plastics or other materials to make or keep them soft or pliable and assure flexibility. Plasticizers react with the ink resin and reduce the crosslinking of the polymers. They improve gloss and adhesion, protect from becoming too brittle at low temperatures and prevent blocking. Their boiling points are
very high. That is why they do not evaporate easily and become an enduring part of ink film. It enables the inks to maintain a low viscosity at temperatures at which the ink is a liquid without impairing the phase change behavior of the ink. Some generally used plasticizers are phosphates, epoxy-compounds, polyesters, sulphonamides, polyglycol derivatives, phthalates, and citrates. Plasticizers are used to control the spherulite size for image hardness and flexibility.

Blowing Agents for Polymer Foams

The structure of cellular gas-filled polymers can be formed using two possible ways. Either by foaming a polymer system, by introducing gas-filled microspheres into a system, or by extracting material by a post-treatment which results in the cell or pore formation. The various compounds used for foaming polymers may be classified in several ways. The most general classification scheme is based on the mechanism by which gas is liberated by blowing agents (BAs).

Chemical blowing agents are individual compounds or mixtures of compounds that liberate gas as a result of chemical reactions, including thermal decomposition, or as a result of chemical reactions of CBAs or interactions of CBAs with other components of the formulations. Most CBAs are solids at room temperature.

Physical blowing agents are compounds that liberate gases as a result of physical processes such as evaporation or desorption, at elevated
temperatures or reduced pressures. PBAs do not undergo chemical transformation themselves, and most are liquids at a room temperature. PBAs include gases introduced directly into polymer compositions for the purpose of forming the cellular structure.8

Chemical Foaming (Blowing) Agents

When chemical foaming agents or blowing agents are put into the processed polymer, the agents are blended with the resin. Chemical blowing agents are individual compounds or mixtures of compounds that liberate gas as a result of chemical reactions, including thermal decomposition, or as a result of their chemical reactions or their interactions with other components of the formulations. Most of them are in solids.8

There is wide range of chemical blowing agents which are industrially used. They may be compounds that liberate gaseous product as a result of reversible equilibrium thermal decomposition. The ammonium salts of inorganic and organic acids, as well as bicarbonates and carbonates of alkaline and alkaline-earth metals, are the main representatives of this type. The formation of gaseous products (G) upon thermal decomposition of compounds of this group can be expressed by the scheme

\[
AB \leftrightarrow C + G \uparrow
\]

(7)

The reversible character of the reaction may result in a decrease of the gas content in the system, which can lead to a pressure drop in the cells of the foam and shrinkage of the material.
Another group represents compounds that liberate gaseous products as a result of irreversible thermal decomposition. Among these are various aromatic, aliphatic-aromatic, and aliphatic azo and diazo compounds, diazoamides, and other organic compounds that decompose at elevated temperatures according to the following scheme

$$\text{AB} \rightarrow \text{C} + \text{G} \uparrow \quad (8)$$

Gaseous products are primarily inorganic low molecular weight molecules as N$_2$, CO$_2$, and NH$_3$, but other gases are also possible. Thermal decomposition of gaseous material of this type is mainly an irreversible first-order reaction.

A third group of chemical blowing agents represent mixtures of compounds that liberate gaseous products as a result of chemical interaction of the components. Mixtures in which the liberation of gas occurs according to the scheme below falls into this category.

$$\text{A} + \text{BG} \rightarrow \text{AB} + \text{G} \uparrow \quad (9)$$

Examples include the interaction of sodium nitrite with ammonium chloride, and the reaction of acids, either organic such as stearic, and oleic or inorganic such as hydrochloric, sulfuric, orthophosphoric, with carbonates or with metals of the second or third group of the periodic table.

Endothermic foaming agents primarily generate CO$_2$, while exothermic ones mostly create N$_2$. The type of resin influences the solubility
or miscibility of the liquid. It is not considered as miscible or a homogenous solution by itself. CO₂ is a low vapor pressure gas with low-pressure solubility. It can become a super critical fluid at relatively low pressure. In the super critical state, CO₂ is a super solvent and can lower the T_g of most resins.⁹⁰,⁹¹,⁹²,⁹³

Blowing agents are often used to eliminate sink marks. The CO₂ will seek out areas of lowest resistance, which are the hottest areas. Cellular expansion fills the voids left from the cooling polymer. One key concept to remember is that the process parameters must be changed to take advantage of foam formation. In most cases, excess pack pressure will prevent foaming.

The basic particle size of the blowing agent will determine the size of the liquid/gas mixture in the melt. Large particles will tend to generate large liquid/gas mixtures and fine particles will tend to generate small liquid/gas mixtures. The size of these liquid droplets and the amount mingled in the polymer mixture has a lubricating effect. This not only reduces shear-heating forces, but also improves melt flow and consequently the polymer melt index. Fine particles that produce fine liquid droplets tend to produce fine emulsions.

The chemical reactions in the polymer melt are becoming more critical when trying to lower part weight and maintain or improve impact strength. All chemical blowing agents decompose thermally to produce gas and chemical by-products, which can be basic, neutral, or acidic and they can affect the pH balance of the complete polymer system. This has been the reason for a number of problems with other additives; especially flame
Types of Blowing Agents

Each blowing agent could offer a unique economic or performance advantage. The idea of using blowing agents is to find the agent that will match with the resin system. When this is achieved, there is an incredible processing advantage.94,95,96

There are a number of options available to a foam producer, when selecting a blowing agent. The first choice that needs to be made is that of the blowing agent's basic chemistry. There are eight key materials used as blowing agents around the world. These include: azodicarbonamide (ADC); 4,4-oxybis benzene sulfonyle hydrazide (OBSH); p-toluene sulfonyle hydrazide (TSH); 5-phenyltetrazole (5-PT); p-toluene sulfonyle semicarbazide (PTSS); di nitroso pentamethylene tetramine (DNPT); sodium bicarbonate (SBC); and zinc carbonate (ZnCO3).97

It is important that the decomposition reaction not be so fast as to damage the ink chamber and not be so slow that it is not complete before the ink hardens. The reaction cannot be so exothermic that it overheats the ink and burns the ink vehicle. Mixing should be easy at the processing temperature (~100°C), so that the blowing agent can be uniformly dispersed or dissolved. A sufficient gas yield with containment is essential. The required temperatures are in the range of the decomposition temperatures of many common blowing agents, such as 4,4-oxybis (benzenesulfonylhydrazide) (140-165°C), p-toluenesulfonylhydrazide (110-140°C), and sodium bicarbonate (120-150°C).
4,4'-oxybis (benzenesulfonylhydrazide) (OBSH) is principally used in low temperature processing and decomposes around 140°C, although the gas yield is comparatively low (Figure 12). Used in the rubber industry, its decomposition residues are non-polar oligomers that have found increasing importance in the foamed insulation of cables.

\[
\begin{align*}
\text{CH} &= \text{N} - \text{NH} - \text{S} \\
\text{O} &\quad \text{O} \\
\text{S} &\quad \text{NH} - \text{N} = \text{CH} \\
\text{CH} &= \text{N} - \text{NH} - \text{S} \\
\text{O} &\quad \text{O} \\
\text{S} &\quad \text{NH} - \text{N} = \text{CH}
\end{align*}
\]

Figure 12. Chemical Structure of 4,4'-Oxybis (Benzenesulfonylhydrazide).

P-toluenesulfonylhydrazide (TSH) is similar to OBSH and has a long been used for foaming rubber (Figure 13). While its use has declined over recent years in favor of OBSH and ADC, the material offers the benefit of a low decomposition temperature of approximately 120°C.
Sodium bicarbonate (SBC), an NaHCO₃, is an inorganic blowing agent that decomposes in an endothermic manner releasing carbon dioxide and water as the principle gases (Figure 14). Interest has grown in this material due to its endothermic nature in injection molding and as a combined blowing agent with azodicarbonamide for the extrusion of cellular unplasticised uPVC.
While it is a relatively low cost blowing agent, the cell structure is often more coarse than with other materials and it cannot be used for flexible foams, such as rubber or plasticized PVC, due to the high diffusion rate of carbon dioxide.  

Thermal Analysis of Polymers

Both the glass and melting transitions are strongly dependent on processing conditions and dispersion in structural and chemical properties of plastics. Characterization of polymers requires a detailed analysis of these characteristic thermal transitions, using either differential scanning calorimeter (DSC) or differential thermal analysis (DTA). Additionally, polymers are viscoelastic materials with strong time and temperature dependencies to their mechanical properties. A complete thermal analysis of a plastic sample yields inferential information concerning the chemical composition and structure of the material. Generally, thermal analysis is the easiest and most available of techniques to apply to a sample and, for this reason, thermal analysis is often the first technique used to analytically describe a plastic material.

Differential Scanning Calorimetry (DSC)

Calorimetry involves the measurement of relative changes in temperature and heat or energy, either under isothermal or adiabatic conditions. Chemical calorimetry, where the heats of reaction are measured, usually involve isothermal conditions. In materials characterization
calorimetry usually involves an adiabatic measurement. A calorimetric measurement in materials science is carried out on a closed system where determination of the heat, Q, associated with a change in temperature, ΔT, yields the heat capacity of the material, C:

\[ C = \frac{Q}{\Delta T} \quad (10) \]

At constant pressure:

\[ \frac{dQ}{dT} = \left( \frac{\partial H}{\partial T} \right)_{p,N} = C_p \quad (11) \]

The enthalpy is then calculated:

\[ H(T) = H(T_o) + \int_{T_o}^{T} C_p dT \quad (12) \]

The pan with the sample is placed in one of the compartments, and a blank pan is placed in the other compartment as a reference. The two compartments are heated at the same rate and then maintained at the same temperature. Both compartments are continuously purged. The independent variable here is the temperature, which is ramped at a controlled rate. Feedback loops control the feed of heat to the sample and reference so the temperature program is closely followed. The raw data from a DSC is heat flux to the sample compartment per time or power as a function of temperature at a fixed rate of change of temperature. The heat flux can be converted to \( C_p \) by dividing by the constant rate of temperature change.58

Major differences between the melting point (\( T_m \)), glass transition
temperature ($T_g$), weight loss, or decomposition temperature ($T_d$) between a test sample and the standard indicates thermal stability in the sample being tested for usability, or thermal stability, quality control problems of such properties as crystallinity, molecular weight, extent of polymerization etc.

For polymer samples, significant broadening of the melting peak is associated with the structural and kinetic features of polymer melting. Typically the peak value is reported for polymer melting points. The instrumental error in temperature for a DSC is typically ±0.5 to 1.0°C.99

Polymer Rheology

Rheology is the study of the deformation and flow of matter. Polymer latexes and suspensions are aqueous dispersions with viscosities dependent on solid content and additives. Polymer solutions may be more viscous, depending on the concentration, molecular weight and temperature.

The temperature dependence of the viscosity is most easily expressed according to the Arrhenius relationship:

$$\eta = Ae^{-B/T}$$

(13)

where T represents the absolute temperature and A and B are constants of the liquid. The Arrhenius equation may easily be shown to be an approximation of the WLF (Williams-Landel-Ferry)100 equation far above the glass transition temperature.

The rate of energy dissipation per unit volume of the sheared polymer
may be expressed as either the product of the shear stress and the shear rate or, equivalently, the product of the viscosity and the square of the shear rate. The rate of heat generated during viscous flow may be significant. Thus the heat generated may actually reduce the viscosity of the material.

All real liquids have both viscous and elastic components, although one or the other may predominate. For example, water behaves as a nearly perfect viscous medium, while a rubber band is a nearly perfect elastomer. A polymer solution may exhibit various ranges of viscoelasticity, depending on the concentration and temperature. According to Weissenberg\textsuperscript{101}, when an elastic liquid is subjected to simple shear flow, there are two forces to be considered:

1. The shear stress, characteristic of ordinary viscosity.
2. A normal force, observed as a pull along the lines of flow.

Polymer Melt Viscosity

Hooke’s law applies to small deformation of ideal solids and works reasonably well for many materials. Polymers, on the other hand, are much more complex in their mechanical response, and time dependent behavior often has to be considered when discussing viscous properties of the material.\textsuperscript{102}

Just as in the elastic properties of solids, there is a simple law describing flow of a liquid that is also an approximation, but provides an adequate description of the properties of many fluids. This is called Newton’s law and connects the shear stress and the shear rate:
\[ \tau = \eta \dot{\gamma} \]  

(14)

where the shear stress \( \tau \) is directly proportional to the rate of strain \( \dot{\gamma} \), and the constant of proportionality \( \eta \) is called the viscosity. The viscosity is a measure of the frictional forces between the molecules in a liquid and depends upon factors such as intermolecular forces and free volume. The free-volume theory, first developed by Eyring and others, says that the molecular motion in the bulk state depends on the presence of holes, or places where there are vacancies or voids.\textsuperscript{103,104} Just as with the treatment of Hooke's law, it is possible to formulate theories for simplified model systems. Suffice is to say that at low rates of strain a linear relationship is obtained, but at higher strain rates deviations are predicted to occur.

In real systems, two types of deviations from Newton's law are observed, characteristic of shear thinning and shear thickening fluids. Polymer melts and solutions are usually shear-thinning. Some polymers that crystallize under stress can be shear thickening. As the name suggests, this means that the viscosity decreases with increasing shear rate. This type of behavior is due to the variation of the rate of chain "disentanglement" with increasing strain rate. The melt viscosity is then a strong function of molecular weight and also temperature, as this affects molecular motion.

The Molecular-Weight Dependence of the Melt Viscosity

Viscoelasticity in polymers ultimately relates to a few basic molecular characteristics involving the rates of chain molecular motion and chain
As it was mentioned before, for non-Newtonian fluids the viscosity depends upon strain rate and we can therefore define an apparent viscosity, \( \eta_a \), according to following equation:

\[
\tau = \eta_a (\dot{\gamma}) \dot{\gamma}
\]  

(15)

The apparent viscosity at a particular point is given by the slope of the secant drawn from the origin to that point. With the known values of \( \eta_a \), the plot of \( \eta_a \) against \( \dot{\gamma} \) can be obtained. A linear proportionality between shear stress and strain rate is obtained at low values, which means the viscosity is constant. This leads to definition of the zero shear-rate viscosity, \( \eta_0 \). This property is used as a characteristic for describing the behavior of polymer melts.\(^{102} \)
DISCUSSION

Instead of answering Owen's question about the huge step that digital printing must make to become one of the traditional production tools, researchers and educators must continue in conducting explorations, studies and provoking new ideas and questions that will lead to new conclusions and products in ink jet printing, it's development and growth. Innovative techniques, novel materials and novel recommendations are presented here in order to enhance the progress in the area of ink jet technology in the near future.

In this work, a broader area that comprises ink jet inks, substrates and digital reproduction of prints is discussed. It presents an extensive view into the ink jet ink and substrate performance, the physical properties and optical properties of printed patterns, the interaction between ink and substrates, as well as an integration of gamut volumes into color output characterization.

Different inkjet printers and their corresponding ink sets were studied in terms of printability tests, including ink/printer/substrate interactions, particle size analyses, color gamut comparisons, the accuracy of a printer's color profile, and fading tests. Although the color capability of pigmented inks is still arguable, it can be clearly demonstrated that the new technology of the manufacturing the inks, with pigment particles encapsulated in specific resins, is able to approach the properties of the dye based inks, especially in terms of gamut size. The pigment based inks show much better lightfastness than the dye based inks, but for some substrates there is a drift towards the yellow region of the visible spectrum.
It is very important to be aware of the presence of OBAs in the paper, or its coating, and to know if their effect is diminished by extended light exposure, when assessing the effect of ink on image permanence. The presence of OBAs is signaled by a negative $b^*$ value, or by the peak in the blue portion of the spectrum of the unprinted or "white" patch of profiling targets.

It was discovered that even with the longer lasting pigmented inks, there was a change in color performance due to the presence of dye based OBAs in the substrate or coating and their ability to fade much faster and thus influence the ink layers. For this purpose the use of substrates that don't include brighteners versus those that include them is strongly recommended.

There is a continuous drive toward the development of new printing techniques suitable for smaller scale printing jobs, which can deposit certain amount of polymer based materials and hence create three dimensional structures on different types of substrates. With the intention of creation of three dimensional structures, the formulation of novel hot melt inks with the addition of special chemical substances, blowing agents, was then carried out.

With the new approach that employs the hot melt ink jet inks, it is possible to create raised images with the assistance of blowing agents, which decompose and deliver gas bubbles into the structures when printed. In order to print the three dimensional structures with a conventional phase change printer, the printer must be customized. The printing head doesn't have to consist of a large number of tiny nozzles. It is assumed the head would only operate a small number of larger nozzles, which will make the making of the head also less expensive. Also, the fusing part of process must be omitted.
The fuser must be demounted from the device to avoid collapsing the raised structures.

The final modified ink formula containing the selected blowing agent possesses the properties essential for this type of hot melt printing process, e.g. melting point of 100 to 130°C, sharp melting and freezing transitions, and viscosity of 10 - 20 cPs at 130°C. It was found that, while the linear alcohols reduce the melt viscosity of inks they might also interact with the added blowing agents and cause the shift in their decomposition temperatures to higher values. Thus, a very narrow range of industry available blowing agents could be utilized in the formula in order to achieve superior results.

A new way for evaluation of a substrate that will be used in a given printing process has been also presented in the work. Using the method, one is able to establish which substrate or ink set will perform better or worse by looking at the combination of substrates and inks in terms of color profile and color gamut volume. Also, it is easy to distinguish how the substrate properties do or don’t affect the overall final presentation of the outputs.

The results presented in this work showed that there is no correlation between the optical properties, e.g. brightness, whiteness and opacity, of the certain choice of substrates, and the specific range of colors that can be produced on such substrates. It was verified that the presence of optical brightening agents, which are responsible for a whiter look of the substrate, doesn’t necessary mean higher color output. From the closer look at the gamut projection, it is clearly seen that less bright and white substrates could reach more colors in mid and darker areas. Surprisingly, the samples also

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showed no evident correlation between the physical properties of the substrate and the size of the gamut volume. The results from this work make us start thinking if we are looking at the right things. What substrate properties are the most important ones?

As mentioned above, the effect of OBAs is vital when exploring the longevity and lightfastness of the prints. After submission to radiation, the gamut volumes of the printed samples decrease most of the time. Print stability was observed with time and lightfastness tests were performed in order to evaluate the stability of printed color patches on specific substrates. The color change can be presented two different ways, as a % of gamut volume loss before and after fading test, and as a ΔE, a color difference before and after fading. The smallest color difference, ΔE, and the least loss of color data was found for OBA-free substrates. It was also discovered that the longevity of the digital prints in most cases does not reach the levels claimed by manufactures and consumers should be aware of this fact.

Lastly, a special UV coating was applied to ink jet prints in order to study its protection level. The investigation of the UV post print coating did not show the expected results for its protective properties. Definitely, the gamut boundaries shift towards the darker areas of the spectrum and the lighter areas become affected as well. As a result of these observations the gamut volume size doesn't significantly change by applying the coat. Since the gamut volume loss and ΔE color difference did not show the expected favorable results when UV coating was applied, the alleged protecting role of this coating is questionable. It is supposed that the only role of the UV print
coat is to make the prints look glossier and darker giving the belief of denser appearance and better print longevity. The presence of UV light is necessary for OBAs to activate and emit light to higher wavelengths in order to create the whitening effect. The UV coating is suggested for use by manufacturers because of its great ability to inhibit ultraviolet light hitting the substrates in order to protect OBAs from fading. This controversy brings a question of real purpose of the coating. Is there a reason to apply the coating which will disable the OBAs then?
CONCLUSIONS

♦ New technology of pigment-based inks is able to approach the properties of the dye based inks in terms of color presentation and gamut size.

♦ Attributable to the presence of dye based OBAs in the substrate or coating and their ability to fade much faster, there will be still an apparent change in color performance of pigmented inks.

♦ A new approach for substrate evaluation, which incorporates color management techniques of creating ICC profile based on a large number of color patches and displaying two or three dimensional color gamut plots and gamut volume values, has been proposed.

♦ Using the method, one is able to establish overall final print performance of specific ink/substrate combination in terms of ICC color profile and color gamut volume.

♦ There was no direct correlation found between the optical properties within specific range of substrate and the size of the gamut volume.

♦ The aforementioned approach, where change can be expressed in gamut volume loss and 2D and 3D gamut plot comparisons, can be also used as an image permanence evaluation technique, in preference to the change in densities and L’a’b’ values of miniature charts.

♦ The presence of OBAs doesn’t necessary mean higher color output and the use of the OBA-free substrates is strongly recommended when high
fidelity color image permanence is required.

- The use of UV post print coating as a protection factor is irrational, when UV light is required for an accurate OBAs functioning.

- It is possible to create 3D images with a modified hot melt ink formulation from specially customized desktop printers.

- The novel formula incorporates special chemicals, blowing agents, which decompose and deliver gas bubbles into the ink and thus create raised structures when printed.
APPENDIX A
COLOR AND LIGHTFASTNESS PERFORMANCE OF DIFFERENT EPSON INK SETS

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Western Michigan University

Abstract

The development of high performance inkjet printers and inks is advancing rapidly. Presently, manufacturers seem to introduce their new technology inks to the market on an almost daily basis. Chemists in the ink laboratories are still fighting with the issue of combining the wide gamut of dye-based inks and the lightfast and weather resistance qualities of pigment-based inks into their new-age ink formulations. Simply, the evolution cannot be stopped!

Three different inkjet printers and inks were investigated in this work: the Epson Stylus® Pro 5000, using a dye-based ink set, the Epson Stylus® Pro 5500, employing Archival ink technology, and the Epson Stylus® Photo 2200, with 7-color UltraChrome™ inks. A number of different commercial and experimental substrates were sampled. Printability tests were carried out to test and evaluate ink/printer/substrate interactions. Particle size analyses of
the three ink types were investigated. Color gamuts and ICC profiles for each of the different printer/ink/substrate sets were compared. In addition, the accuracy of each printer's color profile was investigated. The results of the profile accuracy measurements were expressed in terms of CIE L'ab' coordinates and Root Mean Square (RMS) ΔE. Results of accelerated lightfastness tests for the different ink sets were interpreted in terms of change of profile and color gamut.

Introduction

Undoubtedly, we are now seeing wide development of novel technologies in manufacturing inks and substrates, and due to that, an expansion of inkjet printing technology into desktop, outdoor and industrial applications1^2.

Epson has recently introduced two types of pigment-based inks. They combine the advantages of both dye and pigment based inks in their formulations. Both their Archival and UltraChrome™ ink systems represent new ink solutions, where each pigment particle is encapsulated in a resin. This technology offers many advantages over conventional pigment and dye based inks. The primary advantages being those of uniform particle shape and particle size, greater color gamut, advanced optical density, exceptional gloss for photo prints, enhanced lightfastness and support for a wider range of media.

Pigment based inks tend to satisfy the requirements of most ink jet printing demands, but the suitable combination of ink and substrate is still crucial. Inkjet inks require a fine particle size, due to possible clogging of the printing head. For low viscosity inks there is a tendency of particle migration

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with time. Pigment based inks behave differently than dye-based inks. The spreading behavior of these inks is determined by the hydrodynamic properties such as the Weber or Reynolds's number. On the other hand, in pigment-based inks, after initial spreading, the pigment particles coagulate on the surface of the microporous layer, creating a filter cake that limits the penetration of the carrier liquid. This results in longer absorption times and recessed dots that stay on the top of the substrate layer, and affect all the other printability properties.

In addition, the precision of color reproduction depends on the image processing, e.g. color separation, rendering intent, and on the stability of the printing process, which usually is carried out with the help of an ICC profile and Color Management Modules. In order to understand the whole process, the influence of paper properties on color reproduction has to be taken into consideration. The grade or type of the substrate used will definitely affect the results of the profile calculations and therefore the printing gamut.

The ability of pigment- and dye-based inks to maintain accurate color strength over time due to light exposure and subsequent fading is as important as the printed color itself. Resistance to fading is significant in several situations. The archiving of sensitive documents is one affected by fading and light fastness. Another application is digital photography, where consumers are now producing ink jet prints of digital photographs. In both of these cases, inks and papers used for archival purposes should be reliable in their light-fastness because of the need for long-term storage. Photographic prints from digital files are also expected to maintain accurate color over a moderately lengthy period.
Procedures and Results

Preliminary results of these studies were presented elsewhere\textsuperscript{14}. All the printers (Epson Stylus Photo 2200, Epson Stylus PRO 5000, Epson Stylus PRO 5500) were profiled as CMYK devices, using the Best Designer RIP on the six selected substrates (Epson Archival Matte, Epson Premium Luster Photo, Epson Premium Glossy Photo, Kodak Glossy, Kodak Satin Paper and experimental substrates with a special inkjet coating applied\textsuperscript{10,11,15,16}), using a GretagMacbeth SpectroScan\textsuperscript{T} spectrophotometer (in reflection mode), Gretag-Macbeth ProfileMaker 4.1.5 and the ECI2002 Random Layout CMYK Target\textsuperscript{17}. Sample test prints were produced from Adobe InDesign. In “Color Settings” the CMYK working space was set to the appropriate ICC profile. The prints were made using the Best designer RIP, with color management set to source space as proof and the applicable CMYK profile for the print, with the intent set to Absolute Colorimetric for the sample output. (The “proof space” is the only management that allows the intent to be manually set.) Therefore, all output was set for an absolute colorimetric intent.

Particle Size Measurements

A NICOMP 370 Submicron Particle Sizer was used to measure the particle size of all the ink sets. As expected, no particles were detected in the dye-based ink set for the Stylus PRO 5000. The measured particle sizes of all pigmented inks are found in Table 1.

Table 1. Particle Size of All Ink sets in terms of Mean Intensity-Weighted Diameter.

<table>
<thead>
<tr>
<th>Particle Size</th>
<th>C (nm)</th>
<th>M (nm)</th>
<th>Y (nm)</th>
<th>K (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PRO 2200</td>
<td>119</td>
<td>172</td>
<td>74</td>
<td>99</td>
</tr>
<tr>
<td>PRO 5500</td>
<td>141</td>
<td>190</td>
<td>123</td>
<td>113</td>
</tr>
<tr>
<td>PRO 5000</td>
<td>Dye</td>
<td>Dye</td>
<td>Dye</td>
<td>Dye</td>
</tr>
</tbody>
</table>
ICC Profile Test

Profile accuracy tests were carried out using the following steps. The values of the ColorChecker® target in Photoshop with the profile applied for each paper sample were checked first. This was accomplished by selecting a large portion of each patch and then recording each of the $L'a'b'$ values from the “Histogram” palette. The Mean values obtained from the histogram were converted to actual $L'a'b'$ values. Using the GretagMacbeth SpectroScanT, $L'a'b'$ values were obtained under specific conditions; $D_65$, $2°$, no UV filter. The measurements were made for each of the sample patches of the ColorChecker® target for all of the substrates and for each of the sample printers. Employing the formula for color difference ($\Delta E$) equation 1, the actual $\Delta E$ values were calculated.

$$\Delta E = \sqrt{(L_1^* - L_2^*)^2 + (a_1^* - a_2^*)^2 + (b_1^* - b_2^*)^2}$$  \hspace{1cm} (1)

The original $L'a'b'$ values of the ColorChecker® target (Target values) were compared with the values from Photoshop with the profile applied (Profile values). These values were also compared with the actual values measured from the printed ColorChecker® portion of the verification samples produced from InDesign, and finally the original values were compared with the values measured from the printed ColorChecker® Target (Test values). The resultant values for $\Delta E$ are listed in Table 2.

IT8.7/2 Subset Test

A subset of the IT8.7/2 scanner chart was also included in the verification page layout. The $L'a'b'$ values of the patches were measured with the GretagMacbeth SpectroScanT and compared with the original data of IT8.7/2 chart in order to investigate the quality of the profiles made for each scanner/printer/paper set. The resulting RMS $\Delta E$'s are shown in Table 2. The
large values of ΔE for some of the papers represent out of gamut colors, in
addition to accuracy of, the printer and scanner (embedded in the IT8 subset
image, which is present for all papers) profiles.

Color Gamut Comparison

Using CHROMiX ColorThink 2.1.2, the profile gamuts for each of the
printers were graphically compared in this order: Epson Photo 2200, Epson
Stylus PRO 5000, Epson Stylus PRO 5500 (Figures 15-16).

Table 2. RMS ΔE Results.

<table>
<thead>
<tr>
<th></th>
<th>Target vs. Profile</th>
<th>Profile vs. Test</th>
<th>Target vs. Test</th>
<th>IT8.7 Test</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>EPSON Paper</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Photo 2200</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Archival Matte</td>
<td>2.42</td>
<td>2.11</td>
<td>2.54</td>
<td>7.55</td>
</tr>
<tr>
<td>Luster Photo</td>
<td>1.48</td>
<td>2.8</td>
<td>2.87</td>
<td>4.39</td>
</tr>
<tr>
<td>Glossy Photo</td>
<td>1.33</td>
<td>1.65</td>
<td>2.02</td>
<td>3.79</td>
</tr>
<tr>
<td><strong>PRO 5000</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Archival Matte</td>
<td>1.1</td>
<td>1.8</td>
<td>2.02</td>
<td>7.38</td>
</tr>
<tr>
<td>Luster Photo</td>
<td>0.91</td>
<td>2.09</td>
<td>2.3</td>
<td>3.27</td>
</tr>
<tr>
<td>Glossy Photo</td>
<td>2.04</td>
<td>2.55</td>
<td>3.59</td>
<td>4.86</td>
</tr>
<tr>
<td><strong>PRO 5500</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Archival Matte</td>
<td>4.5</td>
<td>1.37</td>
<td>4.55</td>
<td>12.86</td>
</tr>
<tr>
<td>Luster Photo</td>
<td>1.01</td>
<td>5.76</td>
<td>5.87</td>
<td>6.18</td>
</tr>
<tr>
<td>Glossy Photo</td>
<td>1.38</td>
<td>1.89</td>
<td>2.17</td>
<td>9.66</td>
</tr>
<tr>
<td><strong>KODAK Paper</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Photo 2200</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Satin</td>
<td>1.52</td>
<td>1.56</td>
<td>1.99</td>
<td>6.8</td>
</tr>
<tr>
<td>Glossy Photo</td>
<td>1.26</td>
<td>1.93</td>
<td>2.16</td>
<td>6.67</td>
</tr>
<tr>
<td><strong>PRO 5000</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Satin</td>
<td>1.24</td>
<td>5</td>
<td>5.17</td>
<td>5.43</td>
</tr>
<tr>
<td>Glossy Photo</td>
<td>1.18</td>
<td>5.76</td>
<td>5.87</td>
<td>6.18</td>
</tr>
<tr>
<td><strong>PRO 5500</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Satin</td>
<td>4.78</td>
<td>2.3</td>
<td>5.77</td>
<td>13.06</td>
</tr>
<tr>
<td>Glossy Photo</td>
<td>3.33</td>
<td>2.05</td>
<td>4.28</td>
<td>11.31</td>
</tr>
</tbody>
</table>
Figure 15. Gamut projection plots for Epson papers, Matte (red), Luster (green) and Glossy (blue) from different printers 2200 (left), PRO 5000 (middle), PRO 5500 (right).

Figure 16. Gamut plots for Kodak papers Satin (red) and Glossy (blue) from different printers 2200 (left), PRO 5000 (middle), PRO 5500 (right).

The axis represents the CIELab color space: from “-a” (green) to “+a” (red) and from “-b” (blue) to “+b” (yellow) colors.

Then we compared the similar substrates, glossy and matte/Satin, from each printer to each other. The results were combined and are shown on the 3D gamut plots (Figures 17-18).
Fig. 17. Gamut plots of glossy paper paper from all printers.

Fig. 18. Gamut plots of matte paper from all printers.

The gamuts are also compared with the Monaco GamutWorks 1.1.1 in the terms of “Gamut Volumes” (Table 3).

Table 3. Gamut Volume Results for All Substrates.

<table>
<thead>
<tr>
<th>EPSON Paper</th>
<th>Gamut Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Photo 2200</strong></td>
<td></td>
</tr>
<tr>
<td>Archival Matte</td>
<td>890,439</td>
</tr>
<tr>
<td>Luster Photo</td>
<td>1,196,587</td>
</tr>
<tr>
<td>Glossy Photo</td>
<td>1,225,282</td>
</tr>
<tr>
<td><strong>PRO 5000</strong></td>
<td></td>
</tr>
<tr>
<td>Archival Matte</td>
<td>933,011</td>
</tr>
<tr>
<td>Luster Photo</td>
<td>1,273,885</td>
</tr>
<tr>
<td>Glossy Photo</td>
<td>1,275,029</td>
</tr>
<tr>
<td><strong>PRO 5500</strong></td>
<td></td>
</tr>
<tr>
<td>Archival Matte</td>
<td>765,089</td>
</tr>
<tr>
<td>Luster Photo</td>
<td>1,079,069</td>
</tr>
<tr>
<td>Glossy Photo</td>
<td>1,045,882</td>
</tr>
</tbody>
</table>
Table 3 - Continued

<table>
<thead>
<tr>
<th>KODAK Paper</th>
<th>Gamut Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photo 2200</td>
<td></td>
</tr>
<tr>
<td>Satin</td>
<td>831,257</td>
</tr>
<tr>
<td>Glossy Photo</td>
<td>855,898</td>
</tr>
<tr>
<td>PRO 5000</td>
<td></td>
</tr>
<tr>
<td>Satin</td>
<td>1,347,120</td>
</tr>
<tr>
<td>Glossy Photo</td>
<td>1,384,975</td>
</tr>
<tr>
<td>PRO 5500</td>
<td></td>
</tr>
<tr>
<td>Satin</td>
<td>807,574</td>
</tr>
<tr>
<td>Glossy Photo</td>
<td>859,992</td>
</tr>
</tbody>
</table>

We also compare gamuts for experimental papers\textsuperscript{10,11,15,16}. These were formulated with a 50:50 ratio of alumina to boehmite nanopigments\textsuperscript{11}, at a pigment-to-binder ratio of 7:1 and final solids of 30 ±1%. The coatings were applied to a 75 g/m\textsuperscript{2} commercial base paper using a Cylindrical Laboratory blade coater at a speed of 2000 fpm. Coating weights between 6 and 12 g/m\textsuperscript{2} were obtained. Some of the 12 g/m\textsuperscript{2} samples were printed on the three printers with the il CMYK Target 1.1\textsuperscript{19}, before calendering. The remaining coated samples were calendered on one side, through 3 nips at 123 kN/m and 60 °C. Three 10 g/m\textsuperscript{2} calendered samples were printed with the il chart on the three printers. ICC profiles for the printers with the noncalendered and calendered papers were calculated using the printed il chart, with ProfileMaker.

The profile gamut plots for the experimental papers are given in Figures 19-21. Figure 19 and Table 4 show the effect of calendering on color gamuts.
Fig. 19. 3D Gamut plots for experimental papers using Epson Photo 2200 (left), Epson Stylus PRO 5000 (center), Epson Stylus PRO 5500 (Right).

While Figures 20 and 21 compare the calendered and noncalendered papers with the Epson glossy and matte, respectively on the three printers; Epson Photo 2200, Epson Stylus PRO 5000, Epson Stylus PRO 5500.

Figure 20. Gamut Comparison for Experimental Calendered Paper and Epson Glossy Paper for all Printers.

Figure 21. Gamut Comparison for Experimental non Calendered Paper and Epson Matte Paper for all Printers.
Table 4. Gamut Volume Results for Experimental papers before and after calendering.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Photo 2200</td>
<td>738,962</td>
<td>827,987</td>
<td>89,025</td>
</tr>
<tr>
<td>PRO 5000</td>
<td>701,520</td>
<td>740,994</td>
<td>39,474</td>
</tr>
<tr>
<td>PRO 5500</td>
<td>509,913</td>
<td>502,182</td>
<td>-7,731</td>
</tr>
</tbody>
</table>

Fading Tests

The patches of the ECI 2002 Random Layout CMYK Target were measured with the GretagMacbeth SpectroScanT before they were put into the Atlas fade meter. The Suntest CPS+ tabletop xenon exposure system was equipped with an 1100 watt air cooled xenon arc lamp light source. They were submitted to 129,600 kJ/m² of energy over 48 hours (@ 765 W/m²) with the uncoated quartz glass filter configuration and measured again. This represents about 4.5 months (June) of daylight exposure in Florida.²⁰

The L’a’b’ values of the printed patches for all the printers on Archival Matte substrate before and after the tests were taken from the data file and the ΔE calculation was performed to obtain the range of color difference between them. These are shown in Table 5.

Table 5. Average and RMS ΔE values before and after fading test for different printers and papers.

<table>
<thead>
<tr>
<th>Printer</th>
<th>Paper</th>
<th>Average ΔE</th>
<th>RMS ΔE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photo 2200</td>
<td>Archival Matte</td>
<td>2.20</td>
<td>2.74</td>
</tr>
<tr>
<td>PRO 5000</td>
<td>Archival Matte</td>
<td>10.62</td>
<td>11.34</td>
</tr>
<tr>
<td>PRO 5500</td>
<td>Archival Matte</td>
<td>2.19</td>
<td>2.76</td>
</tr>
</tbody>
</table>
Table 5 does show that the pigmented inks change colors much less than the dye inks, as expected. However, values ~ 3 for the pigmented inks are larger than expected for inks rated at more than 75 years, albeit for indoor conditions. Examination of the data shows that there is a systematic shift toward yellow and green. The Epson 2200 shows an average $\Delta b^*$ of 1.57, while the Epson 5500 shows an average $\Delta b^*$ of 1.89. Thus, for the pigmented inks, most of the average $\Delta E$ results from the systematic $\Delta b^*$ shift, reflecting the drop in the Optical Brightening Agent (OBA) contribution (see below). The Epson 5000 shows an average $\Delta b^*$ of only .77, but the average $\Delta L^*$ is 6.96. Therefore, that $\Delta E$ is mostly due to actual ink fading.

![Figure 22. Comparisons of projections of the color gamuts before (full color) and after (black) fading test for pigment-based Epson 2200 (left), dye-based Epson 5000 (middle) and pigment-based Epson 5500 (right).](image)

Again, the profile gamut plots for the papers are given in Figure 22. Figure 22 shows the gamut plots before and after the fading test. Gamut volume change representation is shown in Table 6.
Table 6. Gamut Volume Results Before and After Fading Tests.

<table>
<thead>
<tr>
<th>EPSON Printer</th>
<th>Gamut Volume</th>
<th>Gamut Volume Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before</td>
<td>After</td>
</tr>
<tr>
<td>Photo 2200</td>
<td>890,439</td>
<td>832,483</td>
</tr>
<tr>
<td>PRO 5000</td>
<td>933,011</td>
<td>723,520</td>
</tr>
<tr>
<td>PRO 5500</td>
<td>765,089</td>
<td>719,311</td>
</tr>
<tr>
<td>Photo 2200 (long term test)</td>
<td>890,439</td>
<td>814,679</td>
</tr>
</tbody>
</table>

Note that the Epson 5000 shows a significant decrease in color gamut. The printers with the pigmented inks, the Epson 2200 and 5000, show the aforementioned shift towards yellow, but little decrease in gamut.

The Epson Stylus Photo 2200 printer together with the Epson Archival Matte substrate was chosen for further investigation of the fading properties. This substrate with the printed chart from the 2200 was submitted to longer time light exposure equivalent to 13 months (June) of daylight exposure in Florida (104 hrs @ 765 W/m²). The gamut plot and gamut volumes of this test are shown in figure 23 and table 5, respectively. In this case, the color shift is even more significant in the yellow region of the spectrum.

Figure 23. Comparisons of color gamuts before and after fading test for Epson 2200 and Archival Matte substrate.
From this information we decided to look at the changes in properties of the plain substrates. L’a’b’ values of the substrates before and after the tests were taken. ΔE calculations for obtaining the range of color difference are shown in the Table 7.

Table 7. Average and RMS ΔE values for papers before and after fading test for different papers.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>ΔE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epson Archival Matte Before</td>
<td>96.1</td>
<td>0.8</td>
<td>-4.3</td>
<td>4.34</td>
</tr>
<tr>
<td>After</td>
<td>95.8</td>
<td>-0.4</td>
<td>-0.1</td>
<td></td>
</tr>
<tr>
<td>Kodak Satin Before</td>
<td>93.3</td>
<td>0.7</td>
<td>-6.3</td>
<td>2.49</td>
</tr>
<tr>
<td>After</td>
<td>93.4</td>
<td>-0.1</td>
<td>-3.9</td>
<td></td>
</tr>
<tr>
<td>Epson Premium Glossy Before</td>
<td>94.6</td>
<td>-0.4</td>
<td>-3.9</td>
<td>0.50</td>
</tr>
<tr>
<td>After</td>
<td>94.4</td>
<td>-0.6</td>
<td>-3.5</td>
<td></td>
</tr>
<tr>
<td>Kodak Glossy Before</td>
<td>92.8</td>
<td>0.3</td>
<td>-6.7</td>
<td>2.66</td>
</tr>
<tr>
<td>After</td>
<td>93.7</td>
<td>0.1</td>
<td>-4.2</td>
<td></td>
</tr>
<tr>
<td>Epson Archival Matte</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(long term test) Before</td>
<td>95.9</td>
<td>0.8</td>
<td>-4.0</td>
<td>4.91</td>
</tr>
<tr>
<td>After</td>
<td>95.8</td>
<td>-0.6</td>
<td>0.7</td>
<td></td>
</tr>
</tbody>
</table>

The GretagMacbeth MeasureTool 5.0.0 software was used to compare the spectra of the substrates before and after the fading test.

Figure 24. Reflection spectra of Epson Archival Matte paper before (left) and after fading (right).
Figure 25. Reflection spectra of Kodak Satin paper before (left) and after fading (right).

Figure 26. Reflection spectra of Epson Premium Glossy paper before (left) and after fading (right).

Figure 27. Reflection spectra of Kodak Glossy paper before (left) and after fading (right).

The spectra for the Epson Archival Matte substrate, claiming the best archival properties, Epson Glossy substrate, Kodak Glossy substrate and for Kodak Satin substrate are shown in Figures 24 to 27. The spectra and the
L’\(a'b'\) values suggest that the contribution of optical brighteners, added to improve the perceived whiteness of the paper, has been neutralized for the Archival Matte paper and greatly diminished for the Kodak Satin papers. OBAs are fluorescent materials that absorb in the ultraviolet and emit in the blue\(^{23,24}\). This is the source for the blue peak in the spectra and the negative values of \(b'\) before the fading test. These peaks and negative \(b'\) values are seen with the Illuminant A light source, which has little UV component, present in the GretagMacbeth Spectralino/SpectroScanT. A true daylight source or idealizations such as \(D_65\) will show more pronounced effects of OBAs\(^{23,24}\). This means that, regardless of the permanence of the printed dye or pigmented ink, there will always be some shift in the perceive color of printed images in virtually any light source, including indoors under glass\(^{12,13}\). Note from Tables 6 and 7 that the majority of the OBA neutralization has occurred in the first simulated 4.5 month period, with little (barely significant) additional change in the remaining simulated 8.5 months. Additional image permanence data are presented elsewhere\(^{25}\).

Other Properties of Printer/Substrate Combinations

Other properties of the Printer and substrate combinations are given in a companion paper\(^{26}\). In particular, the paper roughness by Parker Print Surf\(^{27}\), profilometer\(^{28}\) and Atomic Force Microscopy\(^{29}\) have been examined. In addition, ink and paper gloss were measured for both 60 and 75\(^{\circ}\).

Discussion

The comparison of the difference in \(\Delta E\) values for the original L’\(a'b'\) ColorChecker\(^{\circ}\) target to those of the values calculated in Photoshop indicate
small dissimilarities in almost all cases. The ΔE values for most of the patches on all substrates and from all printers were found to be generally less than two. Exceptions include the dark patches when printed on the matte papers and when printed from the Photo 2200 and PRO 5500 using pigment based inks. In the case of the pigment based ink printers (Epson 2200 and Epson 5500) the average and RMS ΔE were always higher for the matte substrates than for the luster, satin and glossy substrates. This is most likely due to out of gamut colors for the matte substrates.

The ΔE values for the comparison of the patches calculated in Photoshop to those measured with the SpectroScanT show similar values to the differences between the original values and the values from Photoshop in the case of the Epson papers. The only exception is the Epson Stylus PRO 5000 in combination with Kodak substrates.

Comparisons of the measured samples in most cases very closely approximate the values of the original ColorChecker® reference values, with the largest variances indicated on the glossy papers printed from the PRO 5000 and the matte from the PRO 5500. Matte paper printed from the PRO 5500 produced the largest variances of all the samples.

In comparing the profile gamuts it was noted in all cases that the matte paper profile represented the smallest gamut whereas the luster and glossy papers were generally similar and contained the complete matte gamut. Comparing the printers to each other on the same substrate the Photo 2200 generally included a similar size gamut to that of the PRO 5000 printer and dye based inks but the PRO 5500 represented the smallest color gamut. It could be seen from the gamut comparisons (Figure 17 and Table 3) that the
Photo 2200 with its pigment-based inks is able to provide a color range that very closely matches that of the dye based prints from the PRO 5000.

The smaller gamuts produced by the PRO 5500 printer, compared to the Photo 2200 (Table 3), result from the different technology, larger particle size of pigment, used in the ink manufacturing process. The archival properties of the ink set used by that printer are still better than dye-based ones. It can be stated that bigger particles offer better stability but are less chromatic. The fact that the pigment based inks used in the Photo 2200 printer closely match those of the dye based inks of the PRO 5000 is noteworthy, but it can be expected that the archival properties as advertised for this ink set may not be as good as those of the PRO 5500. It should also be noted that the increased archival properties of the matte paper in combination with archival pigment based inks produce the smallest color gamut of the samples analyzed.

For the Kodak paper, there is no significant difference in gamut size between glossy and satin substrate (Table 3). In addition, Epson vs. Kodak paper gamuts did not show any significant discrepancies in the terms of color gamut size. It is seen from Figures 3 and 4 that the widest gamut was obtained when printed from the Epson Stylus PRO 5000 dye based inkjet printer followed by Epson Photo 2200 and Epson Stylus PRO 5500, both pigment based inkjet printers.

After the printed samples were submitted to the fading test it could be seen that the gamuts decreased. The Epson 5000 showed a significant decrease (209,491 in terms of gamut volume difference), while the 2200 (57,967) and 5500(45,778) showed smaller changes. In the case of the Epson
Archival Matte and the Kodak substrates, it was found that, even without any change in ink composition, the color performance will change because of the loss of brightener effect (Figure 24-27). This led to a systematic shift toward the yellow, especially when exposed to longer time tests, as shown in Figure 9. This deviation was not seen when inspecting the Epson glossy substrate.

Thus, it is important to be aware of the presence of OBAs in the paper or its coating, and to know if their effect is diminished by extended light exposure, when assessing the effect of ink on image permanence. The presence of OBAs is signaled by a negative b' value or by the peak in the blue portion of the spectrum 23,24 of the unprinted or “white” patch of profiling targets. All of the papers studied here had OBAs present, but only the Archival Matte and the Kodak papers showed significant reduction in brightener activity.

The particle size of the pigment based inks were found to be <190 nm, most of them below 150 nm, showing smaller particle sizes for the PRO 2200 ink set than for the Photo 5500 ink set. The Particle Sizer’s light detector was not able to distinguish any intensity in the case of the PRO 5000-ink set, which is consistent with the dye based ink system of the printer. The color gamut decreases with increasing particle size, with the smallest particle size, the Epson 5000 dye, having the largest gamut, while the largest particle size, the Epson 5500, gives the smallest gamut. However, the dye based ink in the 5000 showed significant fading from only a simulated 4.5 month exposure.
Conclusions

Different inkjet printers and their corresponding ink sets were studied in terms of printability tests, including ink/printer/substrate interactions, particle size analyses, color gamut comparisons, the accuracy of printer’s color profile, and fading tests. It can be definitely said that the new technology of the manufacturing the inks with pigment particles encapsulated in specific resins is able to approach the properties of the dye based inks, especially in the term of gamut width. In addition, it has to be mentioned that the increased archival properties of the matte paper in combination with archival pigment based inks reflect in the smaller color gamut than the gamut of glossy paper. The pigment based inks show much better lightfastness than the dye-based inks, but for some substrates there is a drift towards the yellow as optical brighteners lose their effect.

For future work we suggest to investigate the substrates which do not include optical brighteners in their composition, e.g. art paper. In addition, there are newer dye based ink sets becoming available, with enhanced archival properties. HP\textsuperscript{31} and Epson\textsuperscript{32} have created a new generations of inks to achieve over 100 year predicted indoor lightfastness performance, while simultaneously improving the color gamut over previous products.

Acknowledgement: We thank Electronics for Imaging, CHROMiX, GretagMacbeth, and X-Rite for donation of color measurement/management hardware and software.
References


19. Distributed with GretagMacbeth ProfileMaker software.


APPENDIX B

NOVEL PHASE CHANGE INKS FOR PRINTING 3D STRUCTURES

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Abstract

Based on recent progress, non-impact print techniques can deliver the next generation of materials for an extensive set of novel applications. A hot melt ink composition useful for 3D structure printing comprising different waxes, tackifier and plasticizer resins, rheology modifiers, and/or gas releasing agent was designed and compared to commercial hot melt inks without gas releasing agents. Differential scanning calorimetry was used to evaluate thermal properties of the ink components and the extensive study of the thermal behavior of the proposed gas releasing agents has been carried out. The rheology behavior of inks was measured, and printability analysis, such as image detail, definition of dots (height, sharpness of the edges), dot formation, and spreading were investigated. Rub resistance tests were also
used together with tape adhesion tests for ink adhesion monitoring. The linear alcohols in hot melt ink formulations reduce the melt viscosity of inks and most likely interact with the added blowing agents causing the shift in their decomposition temperatures. Future work will address this issue.

Introduction

The ability to form a raised three-dimensional image makes possible the use of modified processes, inks and substrates in fine art work, such as children's books, business cards, postcards, and special type printing processes. If the raised image attains required height and firmness, it can be used in printing of Braille characters. Production of three-dimensional (3D) images on a substrate can be accomplished by old fashioned embossing techniques, hectographic or spirit duplicating masters raised Xerographic printing with thermally intumesced electroscopic powders, three-dimensional imaging paper, thermographic processes, a special printing process that works by building parts of light curable photo-polymer in layers, or heat transfer printing with a thermally-expandable ink layer.

3D Ink Writing Systems

Three dimensional digital imaging techniques can be divided into two categories:

- Droplet based inks
- Continuous inks

The main idea of ink writing techniques lays in the deposition of colloidal, nanoparticle, or organic based inks to create raised structures. Because of the containing self-supporting characteristics, 3D periodic
structures pose a great challenge for designing of those inks. Inks are typically formulated from colloids, polymeric materials, or polyelectrolytes suspended or dissolved in a liquid or heated to create a stable, homogeneous ink with the desired and reproducible rheological (or flow) behavior.9

3D printing, direct ink-jet printing, and related approaches such as hot melt printing10, involve patterning materials using a typical ink-jet print head, similar to one used in desktop printers. This approach requires wax-based inks that are heated during droplet formation and then solidify upon impact cooling. Cima11 and Sachs12 from Massachusetts Institute of Technology (MIT) pioneered the concept of using ink-jet printing to assemble broad array of materials by means of this printing technique. In their approach, a low viscosity binder is printed onto a powder coating to fuse materials together in a pattern.

Hot Melt (Phase-Change) Printing Technology

With thermal transfer printing and thermal wax transfer printing technology, phase-change inks (hot-melt inks or thermal waxes) are brought into contact with the substrate and a thermal head. Thermal transfer and hot melt printers employ wax-like hot melt ink, rather than the liquid or dry ink used in other processes. Thus, hot melt ink printer is a variant of Drop on Demand DOD ink jet printers, where the liquid for the printing is obtained by melting the hot melt inks.13-21 The simplicity of thermal transfer printers leads to low equipment cost, cleanliness of the image and high reliability.22

The thermal head is digitally addressed.23 The process is generally binary, although some higher-end models are capable of producing multi-
additives, adhesion and surface additives, antioxidants, biocides, plasticizers, and corrosion inhibitors designed to improve the ink's performance. Generally, hot melt ink contains a pigment or a dye functioning as a coloring component.\textsuperscript{18,26}

**Properties of Conventional Hot Melt Inks**

The most important properties of the hot melt inks are the following ones: melting point of 100 to 130 °C, sharp melting transitions as characterized by Differential Scanning Calorimetry (DSC), a viscosity of 10 - 20 cPs at 130 °C, non toxicity, transparency in the solid phase, good lightfastness, and wide color gamut size. Inks also have to be capable of dissolving printing colorant such as dyes or implement the pigments, and remain intact during long term heating in air and in contact with the print head. Additionally, no offset transfer or blocking of finished prints at 70°C or below should occur. Good adhesion to overhead transparency materials and flexibility towards bending when printed on different flexible substrates.\textsuperscript{13,27,28}

**Blowing Agents**

The structure of cellular gas-filled polymers can be formed using two possible methods. Either by foaming a polymer system, by introducing gas-filled microspheres into a system, or by extracting material by a post-treatment, which results in the cell or pore formation. The most general classification, which divides blowing agents into chemical and physical blowing agents (BAs), is based on the mechanism by which a gas is liberated to the system.\textsuperscript{29,30}
Chemical blowing agents (CBAs)

Chemical blowing agents are individual compounds or mixtures of compounds that liberate gas as a result of chemical reactions, including thermal decomposition, or as a result of chemical reactions of CBAs, or interactions of CBAs with other components of the ink formulation.\textsuperscript{30,31}

There are many options available when selecting a blowing agent. There are eight key materials used as blowing agents around the world. These include: azodicarbonamide (ADC); p-toluene sulfonylhydrazide (TSH); p, p'-Oxybis(benzenesulfonylhydrazide) (OBSH); 5-phenyltetrazole (5-PT); p-toluene sulfonylsemicarbazide (PTSS); dinitrosopentamethylene tetramine (DNPT); sodium bicarbonate (SBC); and zinc carbonate (ZnCO\textsubscript{3}).\textsuperscript{32} The aim of this work is to formulate hot melt ink with the blowing agent, capable of creating raised image.

Experimental

Materials

Various thermoplastic resins, waxes and alcohols, solid at ambient temperature, were used for formulation of inks for 3D structures.

Mixing

All of the inks were prepared the same way. The ingredients were mixed in a Lightnin\textsuperscript{®} High Speed Mixer equipped with a mixing blade. The components were placed into a kettle, heated to about 85°C and the stirring was commenced. The kettle was heated to 120°C and stirring continued until a homogenized state of the mixture was achieved. The formulations were
then cooled to ambient temperature at which they transitioned from the flowable to the non-flowable state.

**Calorimetry**

A Perkin Elmer Pyris 1 Differential Scanning Calorimeter (DSC) was employed for ink calorimetric analysis.

**Viscometry**

A Brookfield digital viscometer DVLV II with spindle #1 was used to measure hot melt inks flow viscosity. Ink temperatures were maintained between 100 - 160°C during the measurement.

**Printability**

The FTA32 Video 2.0 software from First Ten Ångstroms, Inc. was used to capture images of solid ink droplets and provided the printability analysis in terms of droplet height, contact angle, base area, etc.

**Results and Discussion**

A very important property is the sharp melting point of the phase change ink. The differential scanning calorimeter was used to obtain the range of melting temperatures for commercially produced hot melt inks used in thermal transfer desktop printers. Figure 28 represents melting and freezing profile of a commercial hot melt ink.
Figure 28. DSC plot of melting and freezing profiles of commercial hot melt ink.

We formulated an experimental hot melt ink, which possesses very similar properties to a commercial one. The composition of the ink includes commercially available resins, waxes, and high molecular weight alcohols. The approximate formula of experimental ink can be seen in the Table 8.

Table 8: Composition of experimental hot melt ink.

<table>
<thead>
<tr>
<th>Component</th>
<th>Function</th>
<th>Melting Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carnauba/PE wax alloy</td>
<td>Ink vehicle</td>
<td>111</td>
</tr>
<tr>
<td>Polyamide resin</td>
<td>Imparts adhesion</td>
<td>103</td>
</tr>
<tr>
<td>High molecular weight alcohol</td>
<td>Lower viscosity</td>
<td>109</td>
</tr>
<tr>
<td>Hydrogenated rosin ester</td>
<td>Tackifier</td>
<td>69</td>
</tr>
</tbody>
</table>

The differential scanning calorimetry was performed in order to check the melting and freezing profiles of the experimental ink (Figure 2).
Figure 29. DSC plot of melting and freezing profiles of experimental hot melt ink.

Viscosities of both types of the ink were compared (Figure 30).

Figure 30. Viscosity measurements of commercial and experimental hot melt ink.

The main melting ($T_m$) and solidifying ($T_s$) temperatures for both hot melt inks are shown in the Table 9. The commercial ink shows two peaks in the melting area and also two peaks in the solidifying area. Generally, melting points of these inks vary in the range of 90-110°C. The experimental
ink showed satisfactory hardness and adhesion to the substrate. The viscosity of the ink at 130°C was in the acceptable range as well (10-15 cPs).

Table 9. Melting and solidifying temperatures of commercial and experimental hot melt ink.

<table>
<thead>
<tr>
<th>Ink</th>
<th>$T_m$ (°C)</th>
<th>$T_s$ (°C)</th>
<th>Viscosity at 130°C (cPs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial hot melt</td>
<td>89.5</td>
<td>109.7</td>
<td>74.1</td>
</tr>
<tr>
<td>Experimental hot melt</td>
<td>108.8</td>
<td>102.6</td>
<td></td>
</tr>
</tbody>
</table>

In the second stage of the project, the screening of suitable chemical blowing agents was done. The decomposition of the selected blowing agents must be higher than the ink melting temperature and also should not chemically react with other components of ink formulation. The blowing agent and thermoplastic polymers were selected according to the temperature in the hot melt printer print head (~ 135°C) and the chemical compatibility with all of the ink ingredients.

Figure 31. Chemical structure of sodium bicarbonate (SBC), p-toluenesulfonylhydrazide (TSH), azodicarbonamide (ADC) and p,p'-oxybis (benzenesulfonylhydrazide) (OBSH), respectively.
Various blowing agents based on different chemistry were analyzed (Figure 31). Corresponding decomposition temperatures are shown in the Table 10.

Table 10. Decomposition temperatures of different blowing agents. (exo- exothermic mechanism; endo- endothermic mechanism).

<table>
<thead>
<tr>
<th>Name</th>
<th>Composition</th>
<th>Decomp. T (°C)</th>
<th>Decomp. Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrocerol BIH</td>
<td>SBC</td>
<td>145</td>
<td>endo</td>
</tr>
<tr>
<td>Celogen® OT</td>
<td>OBSH</td>
<td>179</td>
<td>exo</td>
</tr>
<tr>
<td>Ficel HFVP</td>
<td>OBSH/ADC</td>
<td>183</td>
<td>exo</td>
</tr>
<tr>
<td>Celogen® AZ</td>
<td>ADC</td>
<td>238</td>
<td>exo</td>
</tr>
</tbody>
</table>

The two most fitting chemical blowing agents were selected according to the thermal analysis: Hydrocerol BIH (SBC encapsulated in polyethylene) and Celogen OT (OBSH). Also, they represent two different types of decomposition, exothermic and endothermic, as shown in the graphs in Figure 32.

![Figure 32. Thermal analysis of p, p'-oxybis (benzenesulfonylhydrazide) and sodium bicarbonate blowing agents, respectively.](image-url)
In the next steps we combined previously mixed experimental with the selected blowing agents. The melting points of the ink components and the decomposition point of the blowing agent are shown in the following figures. Figures 33 and 34 show thermal trace of the ink composition with two different blowing agents incorporated in them. For better proof of the presence of the blowing agents they were added in two amounts; 2% and 4% of the ink composition.

**Figure 33.** Thermal analysis of the experimental ink with 2% and 4% of BIH, respectively.

**Figure 34.** Thermal analysis of the experimental ink with 2% and 4% of OBSH, respectively.
The hot melt ink formula has a melting temperature well segregated from the decomposition points of the blowing agents. In addition, an appearance of the peak at 76°C was observed in the graphs (Figures 33 and 34). We presume this peak corresponds to one of the chemicals used in the formula. The hot melt ink formula including the BIH blowing agent shows a shift in the decomposition temperature of the blowing agent. The point shifts from 145°C to 191°C. This phenomenon was observed with almost all tested blowing agents. The gap created by the shifting seems to be too large for the intended function. This was not observed with the other blowing agent studied. The OBSH possesses the same decomposition point over the whole experiment. In previous work it was found that the low molecular weight alcohols present in the ink formula most likely interact with one of the components in the ink formula in the previous works. It is expected that the shifts in the blowing agent decomposition could be caused by similar interactions.

FTA32 Video 2.0 software was used to capture images of the final ink droplets (Figure 35).

Figure 35. FTA 32 Video 2.0 projection for experimental ink without and with OBSH.
The simulated droplets were created by deposition of molten inks on the regular paper substrates using the micropipettes. The images of droplets were taken after solidification of the ink. Fta32 Video 2.0 also provided the printability analysis in terms of droplet height, contact angle, and base area (Table 11).

Table 11: Printability analysis of droplet on paper substrate.

<table>
<thead>
<tr>
<th></th>
<th>Ink</th>
<th>Ink + OBSH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact Angle (deg)</td>
<td>69.42</td>
<td>83.34</td>
</tr>
<tr>
<td>Base (mm)</td>
<td>2.21</td>
<td>2.07</td>
</tr>
<tr>
<td>Base Area (mm²)</td>
<td>3.41</td>
<td>3.08</td>
</tr>
<tr>
<td>Height (mm)</td>
<td>0.72</td>
<td>0.94</td>
</tr>
<tr>
<td>Sessile Volume (ml)</td>
<td>~1</td>
<td>~1</td>
</tr>
</tbody>
</table>

The Figures 35 and Table 11 clearly show the increase in height of droplet and consequently possess higher contact angle. It is predictable that the high temperature of the heating system after printing will release the gas within the deposited structure. In order to entrap the gas bubbles the addition of nanostructured materials to the ink formula will be investigated.

Conclusions

The formulation of hot melt inks with the addition of blowing agent was carried out. Differential scanning calorimetry was used in evaluating the thermal behavior of novel phase change inks. The modified ink formula containing the selected blowing agent possesses the properties essential for this type of hot melt printing process, e.g. melting point of 100 to 130 °C, sharp melting and freezing transitions, and viscosity of 10 - 20 cPs at 130 °C. In addition to important ink properties, based on the type of the substrate the
surface tension of the ink needs to be modified to achieve proper ink/substrate interaction. It was found that while the linear alcohols reduce the melt viscosity of inks they might also interact with the added blowing agents and cause the shift in their decomposition temperatures to higher values.

In order to print the three dimensional structures with a conventional phase change printer, the printer must be further customized. The printing head doesn’t have to consist of big amount of tiny nozzles. It is assumed the head would only operate small amount of larger nozzles, which will make the making of the head also less expensive. Also, the fusing part of process must be omitted. The fuser must be demounted from the device to avoid collapsing the raised structures.

There is a continuous drive toward the development of new printing techniques suitable for a smaller scale printing jobs, which can deposit certain amount of various polymer based materials that would create three dimensional structures on different types of substrates.

Acknowledgement

Authors would like to thank following corporations for providing the instrumentation and samples, used in this project: Arakawa Chemical, Inc., Arizona Chemical, Inc., Michelman, Inc., Pfizer, Shamrock Technologies, Inc., UniRoyal Chemical, Inc., etc. We thank the Western Michigan University Office of the Vice President for partial financial support for this work.
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APPENDIX C

COLOR GAMUT – NEW TOOL IN PRESSROOM?

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Abstract

The world is demanding the best it can get and this applies not only for print. Costumers want the best ink set on the brightest, whitest and best looking substrate that can be used on the fastest press or printer. However, sometimes using the most excellent choices won’t give the greatest overall results. Not to mention that usually the better the more expensive materials become.

We can establish which substrate or ink set would be better or worse, but how can we look at both factors as a whole? We have tried to look at the combination of substrates and inks. We considered different substrates, high end fine art ink jet papers and gravure magazine grade media, to show how the substrate properties do or don’t affect the overall final presentation of the prints.

The results presented in this work show that there is no correlation
between the optical properties of the substrate, e.g. brightness, whiteness and opacity, and the specific range of colors that can be produced on such substrates. In case of ink jet substrates, the smoother and less permeable substrate can reach the highest values of colors printed. Gravure samples showed no evident correlation between any of the properties, optical or physical, and the gamut volume.

Introduction

What do we need to know about substrate? Before we print we usually pick what we think is the best substrate for our purpose. And we have a lot of choices to pick from. Here are few examples what can be used in our decision process:

*Paper grade:*
- Free coated sheet, LWC, SCA, SCB, Board, e.g.
- Uncoated, Coated, 100% cotton, pH, Buffered, Lignin free, OBA or OBA free, e.g.

*Surface properties:*
- Roughness, Porosity, Permeability, e.g.

*Optical properties:*
- Brightness, Whiteness, Opacity, Gloss, e.g.

The market in these days is driven by customer’s requests. In the case of substrates, the brighter or whiter paper will be more expensive, but will give the customers’ expected appearance. For this purpose the papermakers stack specific chemical substances into a paper base and coating. These substances are called optical brightening agents (OBAs) or fluorescent...
whitening agents (FWAs). The major uses of these products are for hiding the yellowish tint of paper, textiles, coatings and plastics by giving them a bluish tint.\textsuperscript{12}

The real question is what do we really want? The smoother substrate, the brighter one or very opaque paper for our jobs? And what do we need to know about substrate? It has been proposed that the right combination of different properties, e.g. brightness and opacity, can offer the highest print quality.\textsuperscript{3} The OBA manufacturers try to sell their product using the best arguments they can use. With the whiter paper you’ll get better or more color coming from your paper. But, do we really need that special, more expensive, white background? Is it really going to give us the best results? In the end, how much of the substrate do we see? Aren’t we trying to cover it with a layer of special colored chemicals?

![Image](image_url)

Figure 36. Examples of Different Final Prints; Inkjet Fine Art and Gravure Printed Magazine, respectively.
Experimental

We investigated several different samples of substrates closely. The first set of substrates represent high end fine art ink jet coated papers and are recommended to be used for ink jet pigmented ink sets, such as Epson’s Ultrachrome pigment based inks. The printer employs 7 different color channels, cyan, light cyan, magenta, light magenta, yellow, black and light black. Half of the samples contain certain amount of the optical brightening agents in the coating and also in the paper base. The other half of papers doesn’t use optical brightening agents at all. The second set represents magazine grade, free coated sheets, samples printed by gravure printing process on the Cerutti Gravure Press at University the Western Michigan University Printing Pilot Plant, with 4 process inks, cyan, magenta, yellow and black.

The samples names were assigned as follows:

Inkjet substrates with OBA: A1, A2, A3
Inkjet substrates with no OBA: B1, B2, B3
Gravure substrates: C1, C2, C3

Porosity, Roughness and Permeability

The surface porosity and roughness/smoothness of the sheets were measured using a Parker Print Surf (PPS) tester (TAPPI T555 PM-94) at different clamping pressures. The permeability was calculated using the following equation derived from Darcy’s Law.\(^4\)
Permeability, $K$ (μm²) = 0.048838*Porosity, $Q$ (ml/min)* Caliper, $L$ (m)  \hspace{1cm} (1)

The PPS porosity was measured at 1000 kPa clamping pressure and the standard parameters for the Parker Print Surf tester were set as follows:

- Air viscosity = 1.801E-5 Pa.s at 23 °C
- Standard pressure drop = 6.17 kPa
- Cross-section area = 10 cm²

### Brightness, Whiteness and Opacity

TAPPI Brightness and Opacity were measured for all the substrates. TAPPI brightness is used as a measure of the reflectance of papers at specific wavelength. The spectral and geometric conditions for TAPPI Brightness are specified in TAPPI Method of Test T452, “Brightness of pulp, paper and paperboard (directional reflectance at 457 nm).” Opacity is a measure of media ability to avoid penetration of light from one side to the other. Opacity is expressed as a ratio of the single sheet reading to the reference one. The standard procedures are described in TAPPI test method T 425 om 01 Opacity of paper (15/d geometry, illuminant A/2°, 89% reflectance backing and paper baking). The CIE Whiteness was calculated from measured XYZ data using the following equation:

$$W_{\text{CIE}} = Y + 800(x_n - x) + 1700(y_n - y), \hspace{1cm} (2)$$

where: $x = X/(X+Y+Z)$,

$y = Y/(X+Y+Z)$,

$x_n = 0.3138$, and $y_n = 0.3310$
Color Gamut

All the colors can be represented as a point in a three dimensional coordinate system, e.g. the CIELab Color Model. Knowledge of the color gamut surface is also useful for color science related tasks, such as visualization, gamut volume calculation and deciding how many colors outside the color gamut can or can't be reproduced. There are two different methods that are used to reconstruct the gamut surface. First, the colorant space method is based on an assumption that the maximum or minimum color coordinate points lies on the surface of the gamut. The second, the geometric method is based only on a set of point coordinates in a device-independent color space. In both cases, a large number of color space points is needed in order to precisely describe the color gamut surface and volume. Different approaches to obtain color gamut boundary characteristics have been published.6-12

A color gamut is a delimited region in color space, containing colors that are physically achievable by a given device or that are present in a given image. The set of all colors which can be produced by a printing system is that system's color gamut. If all of the colors in a color gamut were plotted in a three dimensional coordinate system they would form a color solid. The volume of the solid would be proportional to the effective number of colors in the gamut. Color gamut mapping is an integral part of color management and has become a very important research tool. It is used for the quantitative comparison of the effects of colorants, media, and other variables that affect
printer's behavior. Often the color gamut is displayed as a full 3 dimensional volume because critical data are generally lost in the 2D representation, which may lead to incorrect interpretations of the results. Many software packages are commercially available that use the gamut's full profile data to display 2D and 3D chromaticity plots together with all the statistics. The gamuts are always generated from measuring a large set of printed color patches that were created to define the gamuts profile.

In order to obtain the large amount of data, the ECI 2002 Visual CMYK Chart and ECI 2002 Random CMYK Chart, respectively, were used (Figure 37 a and b).

![Figure 37. a. ECI 2002V CMYK Target, b. ECI 2002R CMYK Target](image)

The ECI 2002 CMYK chart is a superset of the current ISO 12642 target. All 928 patches of the current ISO 12642 (also known as ANSI IT8.7/3) chart are contained in the 1485 patches of the new ECI 2002 CMYK chart. In case of gravure samples, the ECI 2002 Random CMYK Chart was included in the layout of the cylinders as shown in the picture below.
Figure 38. ECI 2002R CMYK target on gravure cylinder layout.

**Printing Process**

*Ink jet substrates:*

All ink jet substrates were printed on an Epson Stylus Pro 4000 ink jet printer that employs 7 color pigmented inks, CcMmYKk. The ECI 2002R Chart was displayed in Adobe Photoshop and sent with no color management settings applied through the PowerRIPX RIP (Raster Image Processor) to the printer (Figure 39). No linearization of the printer was conducted since it has been found that the process does not improve the final print quality and may even decrease the amount of ink deposited on the media and thus alter the total color gamut that could be obtain.\textsuperscript{15}
Figure 39. Printer Setup.

Since all the substrates were coated microporous art papers the ink level was set to 400 and 1440 dpi resolution for Premium Glossy Photo paper to ensure the high ink load. The conditions were kept the same for whole time of the experiment. The printed samples were analyzed in terms of L'a'b' values. All the 1485 patches were read by an automated spectrophotometer, and the data were collected in order to calculate the ICC profile. All the profiles were generated with D50/2° setup by GretagMacbeth ProfileMaker 5.0.4 software.

**Gravure substrates:**

The gravure substrates were printed on the Cerutti press under the same conditions. The densities were set to fall in the range: C = 1.35, M = 1.35, Y = 0.95 and K = 1.5. Samples were collected and the ECI 2002R CMYK chart was measured, followed by profile generation and gamut calculation. The color gamut was calculated with CHROMIX ColorThink Pro 3.0. This software was also used as a tool for 3D color gamut comparison at different L* values.
Results and Discussion

OBA Presence Test

All the samples were submitted to the test by which the presence of OBA can be easily proven. The spectral data of the substrates were measured with a spectrophotometer under D50/2° geometry with no UV filter applied. That means all the UV energy was included in the illumination and thus could be transmitted by OBAs to the higher wavelengths, which will show up as a higher peak in the blue region of visible spectrum. The spectra of all ink jet and gravure samples are shown in following figures.

Figure 40. Visible reflective spectra of ink jet samples with OBAs, A1, A2 and A3, respectively.

Figure 41. Visible reflective spectra of ink jet samples no OBAs, B1, B2 and B3, respectively.
Figure 42. Visible reflective spectra of gravure samples with no OBAs, C1, C2 and C3, respectively.

Apparently, the first set of ink jet substrates confirms the existence of OBAs in the receiving coating layer. None of the gravure samples shows an apparent peak in blue region of visible light. There is no presence of any type of OBA in these substrates.

Porosity, Roughness and Permeability Results

The data obtained from these measurements can be seen in the appendix. The graphical representation of the results is shown in graphs below. The star is always assigned to the highest values from all the samples.

Figure 43. Parker Print Surf porosity at 500 kPa and 1000 kPa for ink jet substrates and gravure substrates, respectively.
Figure 44. Parker Print Surf roughness at 1000 kPa for ink jet substrates and gravure substrates, respectively.

Figure 45. Permeability calculated from Parker Print Surf porosity measured at 1000 kPa for ink jet substrates and gravure substrates, respectively.

It is evidently shown in the graphs above, the Sample A2 has the highest permeability coefficient and PPS “porosity”, which is sensitive to permeability but gives no measure of available pore space. The lowest values were found for Sample B3 with almost no flow capability. The value of the permeability coefficient indicates a flow controlling pore size of order of 5 nm! The least rough or the smoothest ink jet substrate was found to be B2 Sample followed by B3 Sample. In this case the star indicates the smoothest substrate from all.

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In the case of gravure substrates the highest PPS "porosity" media was found to be the sample C1. The sample C1 also had highest permeability coefficient Sample C2 was the smoothest substrates from the whole set.

**Brightness, Whiteness and Opacity Results**

The results obtain from all the tests are graphically presented in the following figures. All the relevant data can be found in the appendix.

![Figure 46: TAPPI Brightness for ink jet substrates and gravure substrates, respectively.](image)

![Figure 47: CIE Whiteness for ink jet substrates and gravure substrates, respectively.](image)
As well shown the substrates showed different maxima for different tested substrates, the brightest being A3, the whitest paper being A1 and the most opaque substrate being Sample A2. Expectably, the set of substrates that contain optical brightening agents shows higher values for brightness and even more visible differences within whiteness values. Sample C2 from the gravure substrate set possesses the highest brightness and whiteness value as well as the highest opacity. All the inkjet samples are in fact brighter papers with higher opacity levels compared to the gravure samples.

How do we decide on the best substrate for our purpose now? It looks quite difficult to make the decision based on the information we gathered from the optical and physical tests done on all the substrates. What if we had one more tool, which would tell us right away which of all the substrates will provide us with the most exceptional properties? That tool would be the color gamut volume number.
The color gamut volume of all the ink jet substrates printed with the same pigment based ink set under the same conditions are graphically presented in Figure 49.

The highest number of colors, discernible with a tolerance below $\Delta E=\sqrt{\beta}$, that could be produced by specific ink jet printer and pigmented ink set was achieved using substrate B3 closely followed by Sample B2. Surprisingly, there is no correlation between the optical performance of the substrate and the ability to reach the highest possible ink level in order to obtain more vivid and colorful prints. On the other hand, color gamut does correlate with permeability, i.e. the less permeable the substrate the higher the higher the color gamut volume that can be achieved. Also, the smoothness of the substrate can play an important role in the way ink jet pigment based ink is placed on top of the receiving layer.

![Color Gamut Volume](image)

Figure 49. Color gamut volume for ink jet OBA (blue) and OBA-free (yellow) substrates, respectively.
In addition, the comparison of two different substrates, A1 and B3, was performed. These samples reached the highest gamut volume values $A1 = 417,193$ and $B3 = 439,721$, respectively, in their groups (OBA and OBA free substrates). The 3D plot is shown to provide the geometrical representation of the gamut boundaries differences (Figure 50).

The 3D plot and 2D projection definitely supports the fact that the B3 sample reaches the higher gamut volume. In the 3D plot the black boundary of A1 sample is all included within the true color wireframe boundary of the B3 sample.

![Figure 50. 3D and 2D gamut comparison for samples A1 (black solid) and B3 (true color wireframe).](image)

In order to analyze the color gamuts closer, one has to look very precisely at the plots at different lightness values. Different levels of $L^*$, lightness value, prove the presence of OBA and different performance of the ink jet ink on different substrates as shown in the Figure 51.
As mentioned above, a very useful tool when comparing color performance on various substrates is a projection plot of gamut boundaries at different lightness values. The lightest areas (Figure 51), \( L^* = 93 \), clearly show the shift of the gamut towards the yellow region for the OBA free and the shift towards the blue region for OBA papers. At midtones the gamut projection doesn't show any significant discrepancies or shifts. As predicted, the darker colors, \( L^* = 28 \) can be reached with the OBA free substrates (Figure 51), since the whiter paper moves the gamut toward the lighter colors. This may be the reason why OBA free papers are able to display a larger number of colors.

The gamut volume values for three gravure magazine grade substrates printed by gravure are shown in the graph below.
Figure 52. Color gamut volume for gravure substrates.

It was found that the highest color gamut volume was obtained for substrate C3 printed on the gravure press. Evidently, there is no correlation between the optical properties of the substrate and the size of gamut volume, since the results from all the tests showed that the sample C3 didn’t reach highest or lowest values within the measured characteristics.

The gamut surface for all the gravure samples are graphically displayed in figure 53.

Figure 53. 3D plots of the gravure substrates gamut boundaries.
Conclusions

In this work we have presented a new way for evaluation of a substrate that will be used in a given printing process. We are able to establish which substrate or ink set will perform better or worse by looking at the combination of substrates and inks in terms of color profile and color gamut volume. We decided to pick different substrates, high end fine art ink jet papers and gravure magazine grade media, to show how the substrate properties do or don’t affect the overall final presentation of the prints.

The results presented in this work showed that there is no correlation between the optical properties of the substrate, e.g. brightness, whiteness and opacity, and the specific range of colors that can be produced on such substrates. It was verified that the presence of optical brightening agents, which are responsible for a whiter look of the substrate, doesn’t necessary mean higher color output. In case of ink jet substrates, the smoother and less permeable substrate can reach the highest values of colors printed. This could be explained by wider ink layer deposited on the top of a coated sheet due to less permeable substrate characteristic. From the closer look at the gamut projection, it is clearly seen that less bright and white substrates could reach more colors in darker areas as well. Surprisingly, the gravure samples showed no evident correlation between any of the properties, optical or physical, and the size of the gamut volume.

The results from this work make us start thinking if we are looking at the right things. Here is the question once again: What substrate properties are the important ones? How far we have to go to obtain the best results?
Acknowledgements

Authors would like to thank Ralph Roessler who supported this project from the beginning and closely cooperated and helped in the process. Also, we would like to express our gratitude to the Printing Pilot Plant and Coating Pilot Plant at Western Michigan University for their great assistance.

We thank the following companies for providing the software and hardware that allowed this work to be done: Epson, X-Rite, GretagMacbeth iProof Systems, CHROMIX.
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## APPENDIX

### Table 12. Porosity, Roughness and Permeability results.

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<thead>
<tr>
<th>Paper:</th>
<th>Porosity (ml/min)</th>
<th>Roughness (microns)</th>
<th>Caliper (mm)</th>
<th>Permeability µm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>207.1</td>
<td>191.8</td>
<td>8.45</td>
<td>17.25</td>
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<tr>
<td>A2</td>
<td>998</td>
<td>936.3</td>
<td>8.56</td>
<td>23.31</td>
</tr>
<tr>
<td>A3</td>
<td>786.6</td>
<td>757.8</td>
<td>8.75</td>
<td>14.64</td>
</tr>
<tr>
<td>B1</td>
<td>111.3</td>
<td>102.7</td>
<td>8.24</td>
<td>10.66</td>
</tr>
<tr>
<td>B2</td>
<td>119.3</td>
<td>113.3</td>
<td>6.03</td>
<td>9.87</td>
</tr>
<tr>
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</tr>
<tr>
<td>C1</td>
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<td>1.2</td>
<td>2.5</td>
</tr>
<tr>
<td>C2</td>
<td>2.43</td>
<td>2.04</td>
<td>1.13</td>
<td>2.6</td>
</tr>
<tr>
<td>C3</td>
<td>3.75</td>
<td>2.94</td>
<td>1.19</td>
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</table>

### Table 13. Brightness, Whiteness and Opacity results.

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<th>Paper:</th>
<th>TAPPI Brightness</th>
<th>CIE Whiteness</th>
<th>TAPPI Opacity</th>
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<tr>
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<td>98</td>
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<td>C1</td>
<td>93.78</td>
<td>94.4</td>
<td>99.6</td>
</tr>
<tr>
<td>C2</td>
<td>90.94</td>
<td>92.51</td>
<td>99.1</td>
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<tr>
<td>C3</td>
<td>84.65</td>
<td>82.95</td>
<td>92.1</td>
</tr>
</tbody>
</table>

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APPENDIX D

EFFECT OF OPTICAL BRIGHTENING AGENTS AND UV PROTECTIVE COATING ON PRINT STABILITY OF FINE ART SUBSTRATES FOR INK JET

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Abstract

Non-impact printing is gaining wider acceptance in the printing world with one of the rapid growing applications being fine art color printing technology. With the right amount of artist's imagination and combination of the right substrate and ink, it is possible to create piece of art work that will last for a long time.

This study includes a comprehensive look into ink/substrate combinations. The output should be evaluated in terms of overall printer capability, not only in terms of a substrate quality (price, grade, optical and physical properties), the type of ink set, and the basic level of color reproduction (density, Lab values). All these should be taken into consideration together with other very important factors, such as the length of time required for colors to stabilize, the image permanence of the printout, and the ink levels in terms of color gamut surface and volume with which a
wide range of media can be characterized.

The choice of proper substrate and coating, ink jet inks, together with some form of protection for ink jet printouts, is discussed here. Substrates with special ink jet receptive layers, with and without optical brightening agents (OBAs), were chosen for this work. The correlation between substrate’s characteristics and final print performance was established. Ink stability of prints with time was observed and lightfastness tests were performed in order to evaluate the stability of printed color patches on specific substrates. A special UV coating was applied to study its protection level. Results of accelerated lightfastness tests for the different substrates are interpreted in terms of change of color gamut volumes and delta E.

Introduction

The ability of pigment based inks to maintain accurate color strength over time due to light exposure and subsequent fading is as important as the printed color itself, especially, when the industry is so fixatedly bound to color precision and long term print permanence. Resistance to fading is significant in several situations. First, archiving of sensitive documents is affected by fading and light fastness. Another one is digital photography, where consumers are able to produce their own ink jet prints of digital photographs at home now, and they expect these prints to maintain accurate color over a moderately lengthy period. In either situation, the need for longer storage times drives the industry towards inks and papers that should be reliable in their lightfastness performance.

The first type of digital printer used to produce fine art prints on
traditional fine art papers was the IRIS ink jet printer around 1991. The only drawback was the dye based ink's longevity. The prints faded significantly with couple months of indoor display. Within a couple of years, new dye based inks were developed that had resistance to fading caused by light caused by the UV wavelengths. In late 1990s two large ink jet printer manufacturers, Epson and Roland, came out with new technology that offered very accurate and precise ink droplet placement. They used this new technology in their new wide format piezo head ink-delivery ink jet printers. These printers were still problematic in terms of media compatibility, especially, textured and more porous fine art substrates. In 1998 and 2000, Roland and Epson, respectively, introduced new pigment based ink sets that could be used in the new age piezo ink jet printers and provide the user with long term stability of his prints. However, these pigmented inks were still difficult to use with textured or uncoated papers. For this reason the popularity and demand for coated fine art papers has significantly increased the last decade.5

Almost all the types of ink jet ink can comprise dyes or pigments as colorants and an ink carrier, e.g., water or solvents. The type of ink to be used is also substantially determined by the properties of the substrate, the surrounding conditions of the print substrate, e.g. light, wear, weather resistance, and the drying process required during printing with different printing systems. If liquid inks are used, the drying process occurs through evaporation and absorption. The evaporation process can be accelerated by the application of heat or UV drying unit.6

Color in images is generated by color forming chromophores, hydroxy
or amino substituents, on either dye or pigment molecules, which have
delocalized $\pi$-electrons conjugated to a $2p_z$ orbital. These electrons can
interact to form a charge transfer band in the visible portion of the
electromagnetic spectrum and thus create a color. In other words, a
chromophore is a region in a molecule where the energy difference between
two different molecular orbitals, highest occupied molecular orbital (HOMO)
and lowest unoccupied molecular orbital (LUMO), falls within the range of
the visible spectrum. Visible light that hits the chromophore can thus be
absorbed by exciting an electron from its ground state into an excited state.

A dye is a colorant which is dissolved or dispersed in the carrier
medium. A pigment is a colorant that is insoluble in the carrier medium, but
is dispersed or suspended in the form of small particles, often stabilized
against flocculation and settling by the use of dispersing agents. Because
pigments exist as discrete particles in ink, pigments have a strong light
scattering effect. As a result, pigmented inks usually have lower chroma
values as compared to dye based inks. The carrier medium can be a liquid or
a solid at room temperature in both cases. Commonly used carrier media
include water, mixtures of water and organic co-solvents and high boiling
organic solvents, such as hydrocarbons, esters, ketones, etc.

Fading of color is from chemical reactions that cause the chromophore
element to break down. Dyes fade faster than pigments under the same
conditions. When a photon hits a molecule, its energy is distributed
across the molecule. If the chromophore element receives enough energy, it
will break down. Photon energy hitting a pigment particle is distributed over
many molecules. Less energy reaches any particular chromophore element.
Reactions occur at a lower percentage of the time. This difference can also be explained using the concept of activation energy. Distributing the energy, so that less gets to the reaction sites, is equivalent to increasing the activation energy barrier. More energy must hit the particle to get the same amount of reaction at the chromophore. For a given amount of incident radiant energy, you get less reaction. In the past there was a perception that pigmented inks contain may contain lumps of colorant particles that could plug printer head nozzles. Therefore, it was determined that particles must be less than half the shortest wavelength of light, 400 nanometers, that means they should be less than 200 nanometers in diameter.

The market in these days is driven by customer’s requests. In the case of substrate, the brighter or whiter paper will be more expensive, but will give the customer expected appearance. For this purpose the papermakers stack specific chemical substances into a paper base and coating. These substances are called optical brightening agents (OBAs) or fluorescent whitening agents (FWAs). The major uses of these products are for hiding the yellowish tint of paper, textiles, coatings and plastics by giving them a bluish tint.

Typically their chemistry is based on the stilbene molecule and is modified to enhance solubility and uptake depending on the substrate in which they are used. When these compounds absorb light, an electron is excited to a higher vibrational energy state. The molecule then loses its excess of vibrational energy by collisions or by emitting a photon in the infrared or microwave bands and falls to the lowest vibrational level of the energy state. From this level, the molecule can return to any of the vibrational levels of the...
ground state, emitting its energy in the form of fluorescence.\textsuperscript{14}

Surprisingly, a recent study on papers for digital printing conducted by team at the School of Print Media at Rochester Institute of Technology and Institute of Paper Science and Technology at Georgia Institute of Technology showed that the main factors that influence users' decision to pick up the right substrates was their runnablility and printability.\textsuperscript{15} A performance related factor was found to be more important than substrate appearance factor, the leading characteristics being toner/ink adhesion, uniformity and surface finish among all.\textsuperscript{15} Another study supports the fact that paper's appearance related characteristics, such as brightness and whiteness, do not necessary reach the best prints performance results overall.\textsuperscript{16,17}

Experimental

At the beginning of the work we chose different examples of high end fine art ink jet coated papers used by new digital age artists. All of these are recommended for use with ink jet pigmented ink sets, such as Epson's UltraChrome pigment based inks. The Epson printer employs 7 different color channels, cyan, light cyan, magenta, light magenta, yellow, black and light black (CcMmYKk). Half of the samples contain a certain amount of the optical brightening agents in the coating and also in the paper base. The other half of the papers claims no use of the optical brightening agents in their composition. At the end we looked at two different canvases, OBA and OBA free, in order to attain a broader area for our investigation. All of the ink jet papers are bright white or natural white, depending on the OBA presence, acid and lignin free, water-resistant fine art paper made from 100% cotton fiber. The sample names used in for the testing follow:
Ink jet 100% cotton papers with OBA:

- Hahnemühle Photo rag
- Sterling smooth Fine Art Paper (Sterling I)
- Elegance Velvet Fine Art Paper
- Somerset Velvet smooth
- Somerset Velvet textured

Ink jet 100% cotton papers with no OBA:

- Sterling Rag (Sterling II)
- Sterling Rag Platinum (Sterling III)
- Arches Infinity smooth
- Illuminata Photo Rag smooth
- Arches Infinity textured

Inkjet canvases:

- Brilliance Chromata White with OBA
- Brilliance Natural OBA-Free

The testing procedures were the same for all the substrates to be able to achieve comparable results. CMYK testing chart, ECI 2002\textsuperscript{th} Random Layout CMYK Target, was generated. This chart’s layout includes 1485 randomly positioned color patches that can characterize color gamuts most truthfully.

An Epson Stylus PRO 4000 printer with PowerRIP X software was used to produce the CMYK outputs for further testing. The PowerRIP X software has been shown to provide the full color gamut of the printer.\textsuperscript{19} In order to create new ICC profile for the printer/substrate combination the output options were set to "Not Color Managed". For higher ink load the
1440 dpi resolution and Premium glossy photo paper for media were chosen.

For testing the substrates, Lab values of printed charts were measured with a spectrophotometer. First, the stability of pigment on the substrates was investigated. The ECI 2002R chart was printed on two different substrates and the Lab values were gathered in the following sequences: 0 hr, 1 hr, 2 hr, 3 hr, 6 hr, 18 hr, 24 hr, and 48 hr (Figure 54). Measured values were used to generate ICC profiles for each substrate. Gamut volumes were calculated from the corresponding ICC profiles.

![Gamut Volumes Graph](image)

**Figure 54.** Gamut volume change with the time.

The ink/substrate combinations reach constant values 6 hours after outputting the prints (Figure 54). Taking into consideration fact that the stable image is obtained 6 hours after printing, the testing of the color stability should starts at least 6-12 hours after printing. No linearization of the printer was conducted since there was found that the process does not improve the
final print quality and may even decrease the amount of ink deposited on the media and thus alter the total color value that could be achieved.\textsuperscript{19}

Substrates can be submitted to the test by which presence of OBA can be easily deduced. The spectral data of the substrate are measured with a spectrophotometer under D\textsubscript{50}/2\textdegree geometry with no UV filter applied. That means all the UV energy was included in the illumination and thus could be transmitted by OBAs to the higher wavelengths. This phenomenon can be then seen in the visible light spectral graphs of the substrates as a higher peak in the blue region.\textsuperscript{20}

It was found that samples claiming no OBA existence in their composition did not exhibit peaks in the blue region of the visible light and thus no presence of brightener. Unexpectedly, the one of the substrates, Hahnemühle Photo Rag, that does not claim no OBA presence, and thus suggested to be an OBA paper, did not show presence of brighteners based on the spectral data (see appendix).

The surface porosity and roughness/smoothness of the sheets were measured using a Parker Print Surf (PPS) tester (TAPPI T555 PM-94) at different clamping pressures (Table 14). The permeability coefficient was calculated using the following equation derived from Darcy's Law.\textsuperscript{21}

\begin{equation}
\text{Permeability Coef., } K (\mu m^2) = 0.048838 \times \text{Porosity, } Q (ml/min) \times \text{Caliper, } L (m)
\end{equation}

The PPS porosity was measured at 1000 kPa clamping pressure and the standard parameters for the Parker Print Surf tester were set to: air viscosity = 1.801E-5 Pa.s at 23 °C, Standard pressure drop = 6.17 kPa and cross-section area = 10 cm\textsuperscript{2}.\textsuperscript{21}
Table 14. Porosity, Roughness and Permeability results for the ink jet substrates.

<table>
<thead>
<tr>
<th>Paper:</th>
<th>PPS Porosity (ml/min)</th>
<th>PPS Roughness (microns)</th>
<th>Permeability Coefficient (µm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hahnemühle Photo Rag</td>
<td>910.8</td>
<td>897.9</td>
<td>7.0</td>
</tr>
<tr>
<td>Sterling I</td>
<td>207.1</td>
<td>191.8</td>
<td>8.5</td>
</tr>
<tr>
<td>Elegance smooth</td>
<td>998.0</td>
<td>936.3</td>
<td>8.6</td>
</tr>
<tr>
<td>Somerset Velvet smooth</td>
<td>786.6</td>
<td>757.8</td>
<td>8.8</td>
</tr>
<tr>
<td>Somerset Velvet textured</td>
<td>1634.0</td>
<td>1524.0</td>
<td>11.9</td>
</tr>
<tr>
<td>No OBA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sterling II</td>
<td>111.3</td>
<td>102.7</td>
<td>8.2</td>
</tr>
<tr>
<td>Sterling III</td>
<td>119.3</td>
<td>113.3</td>
<td>6.0</td>
</tr>
<tr>
<td>Arches Infinity smooth</td>
<td>4.1</td>
<td>1.1</td>
<td>7.1</td>
</tr>
<tr>
<td>Illuminata smooth</td>
<td>239.2</td>
<td>220.7</td>
<td>6.9</td>
</tr>
<tr>
<td>Arches Infinity textured</td>
<td>12.1</td>
<td>1.8</td>
<td>10.7</td>
</tr>
<tr>
<td>Canvases</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brilliance Chromata White</td>
<td>7.5</td>
<td>1.7</td>
<td>8.7</td>
</tr>
<tr>
<td>Brilliance Natural</td>
<td>36.0</td>
<td>5.5</td>
<td>12.5</td>
</tr>
</tbody>
</table>

TAPPI brightness is used as a measure of the reflectance of papers at specific wavelength and is specified in TAPPI Method of Test T452, “Brightness of pulp, paper and paperboard (directional reflectance at 457 nm).” Opacity is a measure of media ability to avoid penetration of light from one side to the other, expressed as a ratio of the single sheet reading to the reference one. The standard procedures are described in TAPPI test method T425 om 01 Opacity of paper with 15/d geometry, illuminant A/2°, 89% reflectance backing and paper baking (Table 15).
Table 15. Brightness, Whiteness and Opacity results for the inkjet substrates.

<table>
<thead>
<tr>
<th>Paper:</th>
<th>TAPPI Brightness</th>
<th>CIE Whiteness</th>
<th>TAPPI Opacity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hahnemühle Photo Rag</td>
<td>91.01</td>
<td>88.21</td>
<td>98.4</td>
</tr>
<tr>
<td>Sterling I</td>
<td>93.55</td>
<td>93.11</td>
<td>98.3</td>
</tr>
<tr>
<td>Elegance smooth</td>
<td>93.55</td>
<td>88.88</td>
<td>98.9</td>
</tr>
<tr>
<td>Somerset Velvet smooth</td>
<td>94.17</td>
<td>92.26</td>
<td>97.5</td>
</tr>
<tr>
<td>Somerset Velvet textured</td>
<td>92.86</td>
<td>92.99</td>
<td>97.8</td>
</tr>
<tr>
<td>No OBA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sterling II</td>
<td>90.63</td>
<td>80.93</td>
<td>95.8</td>
</tr>
<tr>
<td>Sterling III</td>
<td>90.09</td>
<td>79.63</td>
<td>96.3</td>
</tr>
<tr>
<td>Arches Infinity smooth</td>
<td>90.91</td>
<td>82.23</td>
<td>98</td>
</tr>
<tr>
<td>Illuminata smooth</td>
<td>89.65</td>
<td>78.16</td>
<td>99.1</td>
</tr>
<tr>
<td>Arches Infinity textured</td>
<td>90.17</td>
<td>80.23</td>
<td>96.4</td>
</tr>
<tr>
<td>Canvases</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brilliance Chromata White</td>
<td>93.78</td>
<td>94.4</td>
<td>99.6</td>
</tr>
<tr>
<td>Brilliance Natural</td>
<td>90.94</td>
<td>92.51</td>
<td>99.1</td>
</tr>
</tbody>
</table>

The CIE Whiteness was calculated form obtained X, Y and Z data as follows:

\[ W_{CIE} = Y + 800(x_n - x) + 1700(y_n - y), \]

where: \( x = X/(X+Y+Z), \)
\( y = Y/(X+Y+Z), \)
\( x_n = 0.3138, \) and \( y_n = 0.3310 \) for D65/10 Illuminant/Observer combination.

A single ink dot printed on the substrate creates color that can be represented as a point in a three dimensional coordinate system, e.g. CIELab.

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Color Model. The set of all colors which can be produced by a printing system is that system’s color gamut. If all of the colors in a color gamut were plotted in a three dimensional coordinate system, they would form a color solid. The volume of the solid would be proportional to the effective number of colors in the gamut. Color gamut mapping is an integral part of color management and has become a very important research tool. Knowledge of the color gamut surface is useful for color science related tasks, such as visualization, gamut volume calculation and deciding how many colors outside the color gamut can or can’t be reproduced. It is used for the quantitative comparison of the effects of colorants, media, and other variables that affect printer’s behavior. Different approaches to obtain color gamut boundary characteristics have been published.23-29

Often the color gamut is displayed as a full 3 dimensional volume because critical data are generally lost in the 2D representation, which may lead to incorrect interpretations of the results.30 Many software packages are commercially available that use the gamut’s full profile data to display 2D and 3D chromaticity plots together with all the statistics. The gamuts are always generated from measuring a large set of printed color patches that were created to define the profile’s gamut.

In order to obtain the large amount of data the ECI 2002 Random CMYK Chart was printed on all the substrates with the Epson Stylus printer. First, the Lab values of the tested printouts are measured and color gamuts were calculated before fading procedures. Then, the printed charts were submitted to the 48 hours exposure in the fademeter. The Suntest CPS+ tabletop xenon exposure system was equipped with an 1100 watt air cooled
xenon arc lamp light source. The samples were submitted to 129,600 kJ/m² of energy over 48 hours (@ 765 W/m²) with the uncoated quartz glass filter configuration and measured again. The temperature in the chamber was 70°C. This represents about 4.5 months (June) of daylight exposure in Florida. In all cases the color gamut volume changed from the initial testing time to the short submission to the radiation (Figures 55, 56).

![GAMUT VOLUME]

**Figure 55.** Gamut volume of ink jet papers that claim to contain OBAs.

The change in volume and percentage of loss can be calculated as a difference between the gamut volume value before and after the fading. For representation of color change caused by fading, \( \Delta E \) values, the color difference before and after the short term fading tests, can also be calculated (Table 16).
Figure 56. Gamut volume of ink jet OBA-free papers.

Table 16. Gamut volumes before and after fading, delta volume, % of loss, and delta E, color difference for all of the ink jet substrates.

<table>
<thead>
<tr>
<th>Paper:</th>
<th>Gamut Volume</th>
<th>Delta E</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before</td>
<td>After</td>
</tr>
<tr>
<td>Hahnemühle Photo Rag</td>
<td>460,752</td>
<td>452,280</td>
</tr>
<tr>
<td>Sterling I</td>
<td>417,193</td>
<td>359,814</td>
</tr>
<tr>
<td>Elegance smooth</td>
<td>405,129</td>
<td>349,550</td>
</tr>
<tr>
<td>Somerset Velvet smooth</td>
<td>378,696</td>
<td>353,296</td>
</tr>
<tr>
<td>Somerset Velvet textured</td>
<td>386,200</td>
<td>345,204</td>
</tr>
<tr>
<td>OBA-Free</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sterling II</td>
<td>398,273</td>
<td>368,323</td>
</tr>
<tr>
<td>Sterling III</td>
<td>433,931</td>
<td>406,867</td>
</tr>
<tr>
<td>Arches Infinity smooth</td>
<td>439,721</td>
<td>402,889</td>
</tr>
<tr>
<td>Illuminata smooth</td>
<td>417,145</td>
<td>374,362</td>
</tr>
<tr>
<td>Arches Infinity textured</td>
<td>432,696</td>
<td>402,636</td>
</tr>
<tr>
<td>Canvases</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brilliance Chromata White</td>
<td>416,453</td>
<td>285,052</td>
</tr>
<tr>
<td>Brilliance Natural</td>
<td>412,196</td>
<td>379,744</td>
</tr>
</tbody>
</table>
Post print coatings should be able to protect, conserve and enhance the color presentation of fine art and photographic prints printed by digital inkjet printers. They can enhance the look of the prints by adding a shinier finish and by increasing densities, protect and preserve prints by inhibiting harmful UV light from destroying the optical brightener additives and fluorescent whitening additives included in the canvas and paper receptive coating layers. They can also protect prints against moisture and abrasion.

To be able to obtain an evenly spread post print coating layer on a print, a foam roller applicator or spraying system must be used. In order to verify the manufacturers statements, one of the OBA substrates (Sterling I) with the larger color gamut (417,193) and the highest loss of color performance (14%) with time was submitted to the test.

Table 17. Gamut volumes before and after fading, Δvolume, % of loss, and ΔE, color difference for Sterling smooth Fine Art paper with and without UV protective post print coating.

<table>
<thead>
<tr>
<th>Paper</th>
<th>Gamut Volume</th>
<th>Δ</th>
<th>(% Loss)</th>
<th>ΔE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before</td>
<td>After</td>
<td>Δ</td>
<td>Loss</td>
</tr>
<tr>
<td>Sterling I</td>
<td>417,193</td>
<td>359,814</td>
<td>57,379</td>
<td>14</td>
</tr>
<tr>
<td>Sterling I w/UV coating</td>
<td>415,864</td>
<td>347,671</td>
<td>68,193</td>
<td>16</td>
</tr>
</tbody>
</table>

As claimed, the applied UV protective coating should cause an increase in the gamut volume, even before the fading test because of the higher densities to be reached. The protective effect of the coating should also appear as a decrease of the gamut volume loss after the submission to the fading test (Table 17). On the contrary, the gamut volume is virtually
unchanged from the uncoated print before the fading test and the loss in gamut volume is greater for the coated one than the uncoated. Furthermore, the coated sample shifts the gamut boundary towards lower L values (Figure 57).

Figure 57. 3D and 2D gamut comparison for Sterling smooth Fine Art paper with (black) and without UV (true color) protective post print coating.

Discussion

Different ink jet substrates can provide the consumer with a wide range of properties, even though they all claim to be suitable for a given printer. The different media provide consumers with special receptive coating layers and thus attain wide range of PPS porosity and permeability values. The smoothness of the investigated substrates falls into a very narrow gap (6-
12 microns at PPS roughness). Usually, the textured materials exhibit rougher surface and thus give higher roughness readings (Table 14). Since permeability is strongly dependent on PPS porosity readings of the substrate, the permeability coefficients also vary significantly within the sample sets. On the average, the OBA-free substrates were found to be having lower PPS porosity and smoother surface finish when comparing to the substrates containing OBAs (Table 14).

As expected the OBA substrates can provide one with a brighter and whiter look of the substrate (Table 15). The Hahnemühle Photo Rag, which was considered as an OBA substrate, was found to be an exception. This substrate did not show a significant peak in the blue region of the visible light spectrum, and thus presence of brighteners (see appendix). Also, the brightness and whiteness values were found to be the lowest from all the OBA samples, being closer to the OBA-free ones. As expected, the OBA-free samples possess lower brightness and whiteness due to the lack of OBAs (Table 15). In case of opacity, the OBA-free samples were able to reach high readings for Arches Infinity smooth and Illuminata smooth fine art papers (98.0 % and 99.1 %, respectively).

Another way to look at the substrate’s performance is to gather L*a*b* values from patches included in the test chart, create a profile, which will characterize the ink/substrate combination for a specific printer, and calculate gamut volume for specific substrate/ink combination. When using the same setup and the same ink set, the color performance is only dependent on substrate properties, most of the time the physical ones. As seen from figures 55 and 56, the highest gamut volume number was achieved using
Hahnemühle Photo Rag (OBA), followed by Arches Infinity smooth (OBA-free) and Sterling Rag Platinum (OBA-free) substrate, respectively (Table 16). Surprisingly, two of three substrates that were able to achieve the highest gamut volumes were OBA-free paper. Even more interesting is that the Hahnemühle Photo Rag substrate achieved the highest gamut volume from all the samples with brightness and whiteness values very close to the OBA-free ones, which makes us think there is insignificant presence of OBAs, if any, in this substrate. As stated before, there is was no correlation found between the optical properties of the substrate, e.g. brightness, whiteness and opacity, and the specific range of colors that can be produced on such substrates. Based on these facts and results, it is assumed that the presence of optical brightening agents, which are responsible for a whiter look of the substrate, doesn't necessary mean higher color output.

The effect of OBAs is vital when exploring the longevity and lightfastness of the prints. After submission to radiation, the gamut volumes decreased for all the samples as seen from the figures 55 and 56 and table 16. The color performance change can be presented two different ways, as a % of gamut volume loss before and after fading test, and as a $\Delta E$, a color difference before and after fading. The most negligible loss of the gamut volume after fading was calculated for the Hahnemühle Photo Rag (OBA/OBA-free), followed by Sterling Rag Platinum (OBA-free) substrate, Somerset Velvet smooth (OBA), and Arches Infinity textured (OBA-free), respectively. On the other hand, the smallest color difference, $\Delta E$, was found for Sterling Rag Platinum (OBA-free), Arches Infinity smooth (OBA-free), and Hahnemühle Photo Rag (OBA/OBA-free) substrate, respectively (Table 16).
The investigation of the UV post print coating did not show the claimed protective properties. Definitely, the gamut boundaries shift towards the darker areas of the spectrum and thus the lighter areas become affected as well (Figure 57). As a result of these observations the gamut volume size doesn’t significantly change by applying the coat. The protective level of this coating is questionable, since the gamut volume loss and ΔE color difference do not verify the claimed results (Table 17).

Contrary, the presence of UV light is necessary for OBAs to activate and emit light to higher wavelengths in order to create the whitening effect. The UV coating is suggested for use by manufacturers because of its great ability to inhibit ultraviolet light hitting the substrates in order to protect OBAs from fading. This controversy brings a question of real purpose of the coating. Is there a reason to apply the coating which will disable the OBAs then?

Conclusions

The optical properties, physical properties and color performance of different substrates with special ink jet receptive coating layer with and without optical brightening agents (OBAs) were investigated in this work. There was no correlation found between the optical performance of the substrate, brightness and whiteness, and the ability to display all possible colors in terms of gamut volumes. It was found that the OBA-free substrates were capable of demonstrating the larger gamut volumes when compared to the OBA substrates. Print stability was observed with time and lightfastness tests were performed in order to evaluate the stability of printed color patches.
on specific substrates. The smallest color difference, ΔE, was found for two OBA-free substrates and arguable Hahnemühle Photo Rag (OBA/OBA-free). In terms of the least loss of color data, again the OBA-free substrates showed the best results. Lastly, a special UV coating was applied to study its protection level. Since the gamut volume loss and ΔE color difference did not show the expected favorable results when UV coating was applied, the alleged protecting role of this coating is questionable.
References:


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APPENDIX

Figure 58 Reflective spectra of OBA papers: Hahnemühle Photo rag, Sterling smooth Fine Art Paper (Sterling I), Elegance Velvet Fine Art Paper, Somerset Velvet smooth, Somerset Velvet textured, respectively.

Figure 59 Reflective spectra of OBA-free papers: Sterling Rag (Sterling II), Sterling Rag Platinum (Sterling III), Arches Infinity smooth, Illuminata Photo Rag smooth, Arches Infinity textured, respectively.

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Figure 6. ANSI IT8.7/3 Target Chart.

ECI 2002 CMYK Chart

The new ECI 2002 CMYK target has been developed by European Color Initiative (ECI) working group led by Dr. Günter Bestmann from Heidelberger in cooperation with GretagMacbeth. The ECI 2002 CMYK chart is a superset of the current ISO 12642 target. All 928 patches of the current ISO 12642 chart are contained in the 1485 patches of the new ECI 2002 CMYK chart.

The ECI 2002 CMYK package contains the new target in two variations: one with a structured layout of the patches (Figure 7.a) and the second one with randomized positions of all the patches (Figure 7.b). When using the ECI 2002 CMYK target for characterizing a press, it is recommended to use the random layout version. Most vendors of measurement devices and
level dots on special thermal paper. This print image is stored as a pattern of dots and is reproduced by precisely timed and controlled exposure of the ink sheet to heating elements on a thermal print head (TPH). Spectra, Inc., one of the leaders in ink jet head manufacturing has elaborated a model for the interaction of a hot melt ink drop with a substrate in early stage of hot melt ink developments. According to this model, if a drop is ejected at 125°C and travels about 1 mm, the drop temperature decreases by less than 1°C. At 1 cm of travel distance, one expects only about 5°C cooling. Even at 10 m/sec drop velocity, hot melt ink droplets do not produce impacts with much spreading; the droplet hits the substrate with a splat not a splash.24

Hot Melt Inks

Inkjet printers use a several kinds of inks, either liquid inks with very low viscosity or solid inks with the phase-change ability occurring during the printing process. The hot melt inkjet inks have to stay solid at ambient temperature, liquefy at the moment of printing and promptly solidify when reaching the substrate. When reaching a surface, the molten ink drop solidifies immediately, and prevents the ink from spreading or penetrating into the printed substrate. The quick solidification ensures that the image quality is good on a wide variety of recording media.17,18,25

Composition of Hot Melt Inks

Conventional hot-melt inks are formulated using four main components: an ink binder comprising a wax with a melting point in the range of 50°C to 90°C, which works as a ink vehicle, a resin, representative of tackifiers and adhesion promoters and different additives, such as antiscratch