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The degree of UV-curing using NIR

Fluorescent brightening agents for inkjet-based white point simulation

Skills Gap in the creative industries at the national level

Influencing an inkjet printer layer through optimized solvent mixtures

Image quality on frosting sheets with edible ink

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Dear Reader,

I am proud to present to you the 10th edition of the IC Circular. The on-line version of this journal can be found at

This Circular features six articles that focus mainly on science and technology side of the journal.

The first article talks about international cooperation and how we can all benefit from it. More and more international cooperation is talking place these days, while the partners don't lose the eye on their local market.

The second article talks about the determination of the degree of curing UV printed material has, once it has been exposed to UV light. This will have later on application in measuring the rate of curing of UV inks through an in-line measurement device.

The third article talks about the challenges of colour calibrating an inkjet printer that is used for printing images on frosting sheets used for cake decoration.

The last article in the science & technology section talks about the interesting concept of applying a defined amount of optical brightening agents onto a proofing media to simulate the amount of optical brightening agent on a press sheet.

The Education section features an article that is the continuation of an article by the same group of authors that wrote about the skills gap in cross-media design and production in the creative industries at the EU level in the 9th edtion of the Circular.

From this short editorial you can see that the articles in this edition are quite diverse and there should be at least one interesting article for each reader.

If you have an article yourself that you would like to get published please send them to me. I can be reached via email at mhabekos@ryerson.ca. You can write to me in German or English, but your articles need to be in English.

Interesting developments are in store for the Circular. The President of the IC will share these developments with you in one of the upcoming newsletters.

Best regards,

Martin Habekost

## reviews

## science & technology

## education

# An ocean refuses no river.
# Expanding the borders of international cooperation

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**Keywords:**

This article builds on the opening speech of Luk Bouters at the 49th Conference of the ICEIGATM and the 8th China Academic Conference on Printing and Packaging, held in Beijing May 14-16, 2017. We provide four sets of arguments to continue investing in an international network of professional contacts as a good return on investment for a Higher Education Institution (HEI): the benefits for educational quality, the benefits for the necessary specialization and collaboration, the benefits for research, and finally our moral obligation as educational institutions.

The International Circle of Educational Institutes of Graphic Arts, Technology and Management, better known under its abbreviation the International Circle, was established in 1957 in Lausanne. Initially founded by representatives of higher education in Europe, it gradually expanded its network from higher education institutes to partners from relevant industries and research institutes. The network currently spans the five continents and counts over 150 institutional members. As the IC does not require the payment of membership fees, it operates thanks to the continuous effort and dedication of volunteers active in the organization.

At the time when the IC was established, its founding fathers felt the need to interconnect and exchange views and experiences across national borders. As universities specialized in the very specific niche of printing, they realized that they had to go abroad to meet colleagues and peers, and that an international learning environment provides a favorable context for a conducive learning environment for the students. Today, this vision is as accurate as ever. There is a huge and daily need for a platform like the IC to exchange project ideas and expertise in our sector and to promote joint research and education. It is a starting point for meeting educational institutions, printing and publishing businesses, suppliers and organizations, and a necessary platform to turn these meetings into sustainable collaborations.

The necessity for international connection, exchange and collaboration obviously holds for all economic sectors and higher education institutions. But it is particularly relevant for the domain of information and communication technology. This should be no surprise given the technological innovations in those areas and their effect on changing consumer preferences. Driven by these changes, completely new industries have arisen (such as computer gaming, 3D printing, web design and mobile app development), and traditional consumer industries have been forced to redesign and repackage their offerings to suit consumers' desires while combatting disruptors (see, e.g., [1] and [2] , or specifically for our industry [3, pp. 9–10]).

Higher Education Institutions (HEIs) have a pivotal role to play in international exchange and collaboration. The Erasmus Impact Study from 2014 [5] underscores the fact that higher education, with its links to research and innovation, strongly influences not only economic growth but also the personal development and the mindset of people, both students and staff. They need to be aware of the new skills portfolios in order to shape educational programmes accordingly to ensure that their graduates competence profile is 'future proof'. Integraf notes especially "[h]igher VET [has gotten] an increasingly important role" in the industry. [4, p. 9] Today, our knowledge is outlived quickly and developing abilities to cope with these challenges is imperative and vital to remain relevant.

In what follows, we focus on four arguments supporting the need for continuous investment in international collaboration from the perspective of HEIs specialized in (print) media production. It should be noted however, that the impact of mobility on the institutional development of higher education transcends the perspective of structural and institutional change and the quality of the professional education; it touches on and affects the whole person and the individual personality.

## Educational quality

First of all, the internationalization of the industry and the globalization of our society have an effect both on our work and the (future) work of our students. Business has more than ever gone international and this trend will only intensify. Many of the companies that will employ our students will recognise one or more of the following:

- they serve customers in different national markets;
- they are subsidiary to an international corporation or network;
- they feel new competition from international players on their market;
- they innovate together with partners from other countries;
- they use technologies or products from international vendors.

To underline this: Intergraf reports that the EU imported €3.1 billion worth of printed products from outside Europe in 2016, while exporting €5.6 billion in the same year, with China, the United States and Switzerland being the biggest trading partners. [6, pp. 32–33]

This implies that the higher education students, who are these businesses' future employees, need to have an international perspective on business. They need to be able, e.g., to recognise international business opportunities, to spot international innovations, to be alert for international competition, and to analyse international trends and predict the impact on their local markets. As a consequence, "[t]he share of employers who considered experience abroad to be important for employability also nearly doubled between 2006 and 2013 from 37% to 64%" [5, p. 16]. This clearly requires a specific curriculum at least partly inspired by the international developments themselves.

Secondly, employers increasingly emphasise the importance of soft skills of graduates. As Intergraf notes: "training needs will not just be in technical areas […] but also in "soft skills" such as sales, marketing and customer service." [4, p. 35] This list can be extended with soft skills that play on an international dimension. Students need to have sufficient language skills and intercultural understanding to be competitive in the job market and to be valuable employees, excelling in cross-cultural competency. [7, p. 7] They must be open to other cultures and other ways of doing business, while at the same time realising that their own culture is not universal. Intercultural learning opportunities occur mostly after being exposed to others' experiences [8], which suggests facilitating intercultural dialog should be an important task within higher education. Studies on the impact of the Erasmus-programmes demonstrate that "[o]n average, Erasmus students have better employability skills after a stay abroad than 70% of all students. Based on their personality traits, they have a better predisposition for employability even before going abroad. By the time they return they have increased their advantage by 42% on average." [5, p. 14]

There are also arguments that relate to the intrinsic quality of education in the digital age. The developments in the communication and information technology require 'digital competence' [9] from all involved and are affecting the way we learn and teach. Online learning (whether it be blended or fully digital), simulations (including the use of virtual reality and augmented reality), new methods of storytelling, and leveraging the opportunities of the internet for learning are important developments in this respect. Presently, teachers and students are often thinking about learning in different ways. As the digital gap will most probably expand in the near future, how will we cope with this? How will we organize our education and professionalize our staff? How will we make not only our students but also our colleagues future proof? Also in this respect, international collaborations might hold some of the answers.

## Specialisation and collaboration

Universities for a long time have lived in splendid isolation. They had a critical distance to the industry, which allowed them to observe objectively and act neutrally. In the last decades, the role of these institutes has changed: more than impartial observers, they have become partners of the industry. This means that trends and changes in the industry, have a direct impact on the universities and their educational programmes. More and more, higher education and the industry have come to realise that the most highly valued educational programs are characterized by a generic basis, complemented with an increasing emphasis on soft skills [10, p. 10], and completed with additional specialisations of excellence. Students as well have come to expect and appreciate a customised curriculum, where they can deepen their knowledge on the specialised topics they are the most passionate about. HEIs can provide the broad basis, and a handful of topics of specialisation, but few can be holistic in this and cover all the various specialisations. This calls for international exchange for students and professors in expert networks, where each of the educational partners involved has a few specialised topics of expertise that the others cannot offer in depth.

Many specialisations require large infrastructure investments. Whether it ranges from domes for immersive media, labs for usability studies, exclusive software, fast 3D printers or the newest flexo press, only exceptionally few single universities can keep up with all this hardware and infrastructure. A good cooperation network with clear specialisations between the participating institutions allows for targeted investments, while the whole network can benefit by exchanging students (and professors) with a desired area of specialisation.

Technology and market trends are developing in a rapid way. Teachers are usually good at keeping up with this, but converting them into the curriculum and blended learning materials requires investments in analysis, co-ordination, time and money. International cooperation between universities in the same field can provide great benefits in this respect, e.g., by developing learning materials together, or by sharing each other's specialised learning materials. Our educational field features some excellent examples of the qualitative output these cooperative frameworks can generate.

## Research

There are also good arguments for galvanizing the international dimension of our research in a networked society. On a global scope developments in research, both fundamental and applied, are increasingly characterized by multi-disciplinary and interdisciplinary approaches, (international) collaboration between research institutes and business partners, and an openness towards sharing findings, data and methods. In this regard, universities, research centres and their partners not only need each other and each other's expertise to study a specialised topic but also need to involve more actively the end users of products in development This is made explicit, for example, in the EC research agenda, with a focus on open innovation and citizen science, acknowledging that "a specific innovation can no longer be seen as the result of predefined and isolated innovation activities but rather as the outcome of a complex co-creation process involving knowledge flows across the entire economic and social environment." [11, p. 11]. So here too, as a general and international trend, cooperation between knowledge institutions and exchange of expertise is now the default modus operandi.

This does not however, imply a disregard for the local context. Of course, local markets have their own characteristics, while some trends have a global impact. International research networks can spot and analyse these global trends and at the same time create a structured approach to facilitate the analysis of the opportunities and impacts for each local market by local institutes. There is no universal way for industries to respond to certain trends but using international analyses, benchmarks and cases studies, universities can provide valuable lessons and recommendations for their national and local industries.

Additionally, funding opportunities increasingly demand international cooperation in project consortia, not only between HEIs but in many cases also between knowledge institutions and partners from industry. International funding agencies require project partners to demonstrate that by joining their complementary expertise they will have a critical and lasting impact beyond the institutional and regional borders and that they are part of international networks to ensure effective cross-national dissemination of the project results. Strong international cooperation constitutes the basis for successful research projects with a lasting impact.

## Moral obligation

Finally, besides all the didactic, organisational and financial arguments, we must adhere to our moral obligation. Students are enthusiastic and interested in travelling abroad for their studies or to work in multicultural settings. Top motivations to study or train abroad remain the same in recent years. "Students choosing a study abroad like the opportunity to live abroad and to meet new people, improve their foreign language proficiency, develop transversal skills. Just after comes the wish to enhance employability abroad for more than 85% of students." [5, p. 14] Due to their different situations, they may not all have the possibilities to do so for a longer period of time, but their curiosity is authentic and their motivation is sincere. As educational institutions, it is our responsibility and mandate to come to grips with their petition for the internationalisation of the curriculum with regards to the various programmes we offer.

These four sets of arguments underscore the need for more international collaboration and co-operation. Not taking advantage of this, would be a missed opportunity.

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# Determination of the UV-curing degree of thin films by crosslinking byproducts of reacted photo initiators in the UV-A & VIS-region of the spectra with actual polymerization degrees obtained from NIR-readings

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**Keywords:**
UV-curing degree, polymerization, yellowing, photo initiator, inline UV-curing check, UV varnish

**Abstract**

**The importance of an inline determination of the UV-curing degree during production increases. Practical offline techniques like i.e. the acetone rub test are in use to ensure a sufficient production process. The scientific crosslink between these test results and the actual polymerization degree is hardly given. This study shows a validated crosslink between established laboratory NIR analysis and UV-VIS readings. In conclusion it is shown that for practical application all necessary data can be acquired with industrial inline VIS spectral photometers.**

## Introduction

The usage of UV-curing inks and coatings increased significantly, in the recent past. PIRA released in 2014 a market survey that indicates growth rates of up to 60% within the next five years (PIRA, 2014).

In the context of these growth rates the industry asks for reliable technologies to check the UV-curing degree inline and during production. Unfortunately, there is no control technology available that fulfills the industry's requirements for inline polymerization degree inspection. On a practical scale, only offline tests help the operator to check the polymerization degree (Stropp, 2009).

Reliable laboratory methods are known to determine the actual polymerization degree. These methods base on FFT (Fast Fourier Transformation) analysis of IR (infrared) spectral data or on measurements in the NIR (near infrared) region of the electromagnetic spectra (Rauh et al., 2015).

First in this study, a detailed analysis of two typical photo initiators (PIs) is carried out for multiple radiation doses. On the basis of high resolution UV-VIS (ultraviolet & visible) spectral measurements, the resulting absorption and reflection spectra are analyzed regarding emerging reaction products.

Second, selected coating variants containing different PIs and monomer / oligomer ratios are applied to a substrate and irradiated with several radiation doses. These samples are again measured using a UV-VIS spectral photometer. Next, these samples are measured and analyzed on the basis of NIR measurements to gain information about the actual polymerization degree.

Finally, the crosslink between secondary reaction products of typical PIs and the actual polymerization degree is presented and discussed. These byproducts show a certain absorption in the close UV and visible spectra and are therefore linked to the well-known "yellowing" of UV cure able inks and coatings (Schär et al., 2015) (Segurola et al. 1999, p. 39).

## State of the scientific knowledge

### The principle of photo polymerization

The basic principles of radical based photo polymerization, as well as the chemical properties of associated substances in UV-curing inks and varnishes, are well known and documented (Slugovc, 2011) (Schwalm, 2006).

In principle, at the beginning of a radical induced polymerization, PIs decay under the influence of UV radiation in start radicals "R·", shown in figure 1. During the start phase of the photo polymerization these radicals break C=C double bonds of binders (such as tri(propylene glycol) diacrylate (TPGDA)) to reactive diluents and initiate a chain reaction. During the growth phase split up C=C double bonds are continuously attached to the polymer chain without losing their radical character. This chain reaction continues until the "activated" chain reacts with another radical and the process is terminated this way.

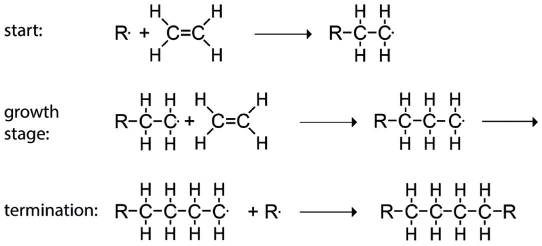

Figure 1: Stages of the radical polymerization process
Experimental study for determination of the actual curing degree of coatings with UV radiation

The absorption of a photon with a suitable energy (hv) by a PI molecule results not directly in the creation of a free radical. First in this process, the PI molecule shifts by absorption to an excited singlet state ($S_1$), shown in figure 2. The PI molecule stays in this state only for 1ns up to 0.1ms. During this time, the excited PI molecule relaxes back to the ground state ($S_0$) by emitting heat or photons (fluorescent effect). Similarly, it is possible that the singlet state can be transformed to the favorable energetic triplet state ($T_1$). This triplet state has a lifetime of up to several ms, which is significantly longer compared to the singlet states life time. Coming from the triplet state ($T_1$), the PI relaxes either again to the ground state ($S_0$) or it disintegrates into free radicals. The number of free radicals that are created depends on the type of PI.

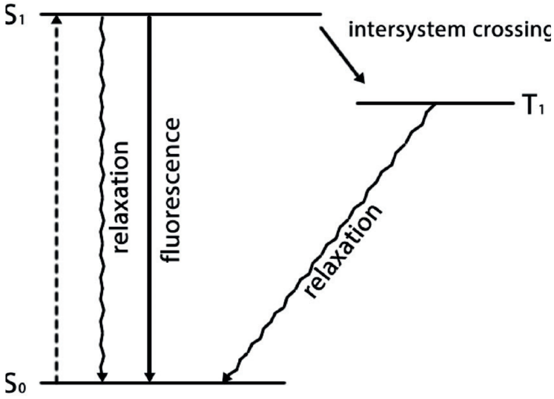

Figure 2: Excitation- and relaxation-processes of PIs

The rate of free radical creation can be calculated by using equation 1 (cf. Eq1), if the absorption behavior of a PI is well known.

$$r_i = \Phi_i I_a \qquad \text{(Eq 1)}$$

with:

$r_i$ as the rate of free radical creation

$\Phi_I$ as the quantum yield of the reaction

$I_a$ as the absorbed radiation dose

The radiation dose (I), which is available for polymerization at a depth x of a coating, can be calculated with the Lambert-Beers law (cf. Eq2).

$$I = I_0 e^{-\alpha x c} \qquad \text{(Eq 2)}$$

with

$I_0$ as the incoming radiation power

I as the available radiation power

$\alpha$ as the natural molar extinction coefficient

c as the molar concentration of the absorbing substance

x as the path length of the radiation

It is not only relevant how many free radicals are created but also the deletion process of these radicals: In case the mentioned ratio becomes negative, the polymerization stops, because more radicals are terminated than created. If at this point in time, all C=C double bonds are broken and chained to a polymer and all involved PI are exhausted, the curing degree would be 100% (Pieke, 2009).
Actually, this case of a 100% completed polymerization is in practice not achievable: the PI concentration in the recipe is for process safety higher than required, or free radicals are trapped in the more and more cured mass and cannot participate in the ongoing polymerization process.
Summarized, the creation of new free radicals depends on several parameter that can be influenced by, for example:

- PI concentration
- radiation dose
- reactivity of the PI
- quantum yield of the reaction of the PI

A simplified visualization of the polymerization process is given by Figure 3.

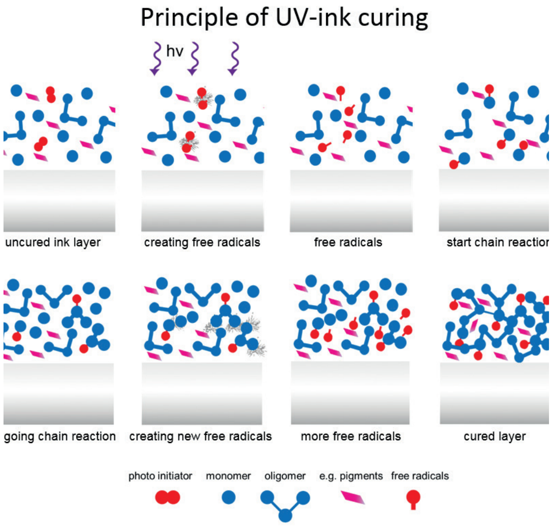

Figure 3: Principle of photo initiator induced polymerization

Figure 4 gives an overview about the structure of typical used photo initiators and related main applications (cf. figure 4). We focus in this study on the first two types.

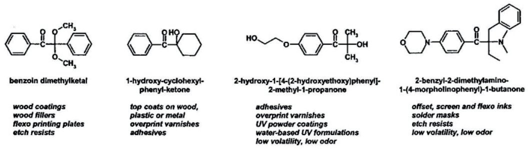

Figure 4: Structure of typical photo initiators and their main application areas (Dietliker et al. 2004, S. 78)

## Approaches to determine the photo polymerization degree

It is important to distinguish between the actual polymerization degree and the resulting adhesion of the applied ink or varnish. While the adhesion is important for the quality of the final print product and the production process, the actual polymerization degree is crucial for migration critical applications, such as food packaging. Established test methods to check the polymerization degree can be split into spectral based methods and manual methods. Therefore, this chapter is split into two parts.

**IR and NIR analysis of acrylic polymerization degrees:**
On a laboratory scale IR spectroscopy based analysis can be used to determine the actual polymerization degree.
For example, by utilizing FTIR spectroscopy in ATR (attenuated total reflection) mode the polymerization degree can be determined at 810 $cm^{-1}$ if calibrated against 1720 $cm^{-1}$ (Rauh et al., 2015). However, ATR-measurements of solid state samples cannot be done inline. Furthermore, this contact technique requires repeated cleaning of the ATR-crystal to avoid sample cross contamination and is therefore not well suited for measurements of semi polymerized samples.
*Scherzer* showed on a pilot scale that the acrylate polymerization can be monitored inline with NIR spectroscopy at 1620nm for clear layers (Scherzer et al. 2004, S. 151), but the signal to noise ratio has shown to be critical in many cases.
The TPGDA photo polymerization process includes the free radical induced breaking of the vinyl group (R–CH=CH2) double bonds resulting in a cross-linking polymerization of TPGDA monomers and thus increases with decreasing double bond concentration. Thus, the degree of acrylate coating polymerization can be described quantitatively as a function of the C=C double bond concentration, which can be determined spectroscopically. With a TPGDA molecular weight of 300.35g/mol and a density of 1.036 $g/cm^3$ (BASF, 1996) the specific double bond concentration of a 6µm thick TPGDA layer is $2.5 \cdot 10^{18} cm^{-2}$ and decreases to about zero in the fully polymerized coating.
IR and NIR absorption measurements with quantitative analysis are widely used for concentration measurements of chemical compounds and of specific functional groups of compounds and mixtures. These analytical methods are based on quantum theoretical principles, relating specific quantum energies of absorbed photons to specific molecule excitation energies. The excitation energies are quantum energies in form of vibrational modes of oscillating molecules or sub-structures of molecules, e.g. functional groups. For coating and solid state applications the fundamental vibrational modes can be described in a simplified manner by symmetric or asymmetric stretching vibrations due to bond length variations and several bending vibrations due to bond angle variations.
Beside these fundamental vibrations, also combinations of vibrational modes and configurations of neighboring atoms influence the absorption spectra. However, the absorption spectra of chemical compounds allow a qualitative relation of absorption lines to functional groups and quantitative measurements. Typical fundamental vibrational modes correspond to IR wavelengths above 2.5µm (< 4000$cm^{-1}$) to more than 25µm (< 400$cm^{-1}$).
Excitations with higher quantum energies, due to overtone oscillations modes, result in relatively weak NIR absorptions

at wavelengths above 0.8µm. This is related to approximately double or multiple quantum energies of the fundamental modes (Günzler, 1975, pp. 20-31).

The concentration of C=C double bonds can be related directly to the vibrational modes at 1410cm$^{-1}$ and at 810cm$^{-1}$ (Pieke, 2009). Since the concentration of the carbonyl group (…C=O) does not change during polymerization the normalization of acrylate IR spectra can be carried out. Therewith, using the strong absorption band of the carbonyl group C=O double bond which is in the range of 1715 -1740cm$^{-1}$ for the C=C configuration of glycol acrylates (Günzler, 1975, p. 203) and at 1730cm$^{-1}$ for TPGDA according to figure 5.
Transmission measurements of IR spectral absorbance have been carried out with a Mattson Galaxy FTIR spectrometer with coated polymer samples. However, the polymer substrate material of the samples was not suited for the concentration determination due to its significant absorptions at 1410cm$^{-1}$ and 810cm$^{-1}$ due to C=C double bonds, which inhibit a precise concentration determination.
Alternatively, the degree of acrylate coating polymerization can be determined in the NIR range. The breaking of the vinyl-group double bonds during polymerization can be described as the disappearance of =CH2 groups with hydrogen unsaturated carbon (unsaturated CH2 groups) which are converted to -CH2 groups with hydrogen saturated carbon (saturated CH2 groups). This conversion can be used for the NIR measurement of this chemical reaction.
Unsaturated CH2 groups have stretch modes in the wave number range above 3000cm$^{-1}$ and specifically, the vinyl group asymmetric stretch mode is generally in the range of 3075 - 3090cm$^{-1}$. Whereas, the saturated CH2 groups have stretch modes in the wave number range below 3000cm$^{-1}$ according to the spectral interpretation of Smith (Smith, 1998, pp. 44-46). The unsaturated CH2 groups of TPGDA in figure 5 are represented by relatively weak absorption peaks of stretch modes at about 3055cm$^{-1}$, 3087cm$^{-1}$, 3114cm$^{-1}$, and 3126cm$^{-1}$. According to Smith, the absorption peak at about 3087cm$^{-1}$ is related to the asymmetric stretch mode. This asymmetric stretch mode relates to a first order overtone mode at about 6172cm$^{-1}$ which causes a relatively weak NIR absorption at about 1620nm. Due to the polymerization related conversion of unsaturated CH2 groups to saturated CH2 groups this absorption and the three other mentioned absorptions shift to below 3000cm$^{-1}$ and may alter their magnitude. The shift relates to a NIR absorption shift from about 1620nm to below 1667nm. Measurements of the NIR absorption at about 1620nm before polymerization and its decrease with increasing polymerization due to the conversion related overtone shift, have been carried out. This has been done with an IndiSpectro NIR sensor system concerning coated paper samples to determine the degree of polymerization (cf. figure 6).

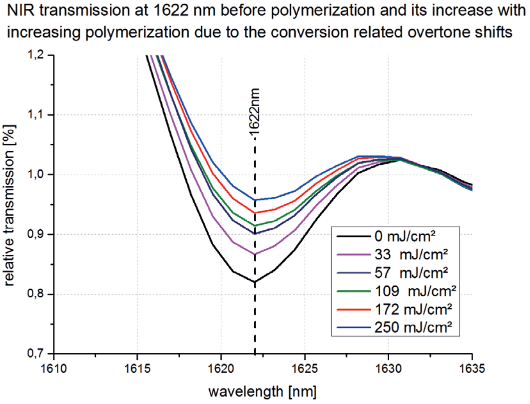

*Figure 6*: Relative NIR transmission spectra with the overtone absorption peak of unsaturated CH2 groups before polymerization and at various ultraviolet radiation doses.

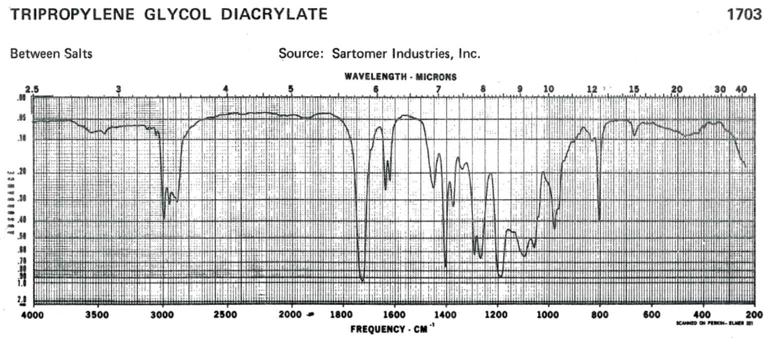

Figure 5: Spectral absorbance of TPGDA over wave number (lower abscissa) and wave length (upper abscissa) from transmission measurements (Sadtler, 1980)

**Manual UV-curing degree check methods:**
A brief overview about manual & semi-manual polymerization degree test methods, like acetone rub test, methyl ethyl ketone rub (MEK) test and talcum test, is given by *Stropp* (cf. Stropp, 2009).
A very popular method is the acetone rub test. Hereby, 0.2ml of acetone is applied on a cured layer. After 10 seconds of reaction time a cotton fabric is used to remove the acetone with "only a little pressure". A visual inspection has to be correlated to a scale that ranges from "no visible alteration" to "destruction of the test area" (cf. Stropp 2009). This test can only be done offline. Furthermore, it is highly depending on the executing person (e.g. pressure, speed, …) and the used type of cotton fabric.
The MEK rub test is very similar to the acetone test application and also the talcum test bases on a visual inspection concerning how much talcum stays on the surface after removing the powder with a cotton fabric.
An additional, on visual inspection based method is the "grid cutting test": A grid is carved into a cured surface and the damage that occurs to the surface due to placing and removing an adhesive tape has to be classified.

### UV-curing induced yellowing effects

Next to the actual desired free radicals, which are products of PIs that were broken open by UV radiation to start the polymerization process, several other "unwanted" byproducts are created. Thereby, the type of byproduct depends on the type of PI (cf. Segurola et al. 1999, S. 40) and the actual chemical reaction.
These byproducts do not support the actual polymerization process, but show a temporary increase of the absorption in the close UV-VIS range of the spectra.
This effect is subject of intense research of *Segurola* (Segurola et al. 1999, S. 44) and *Studer* (Studer und Königer 2001, S. 32), because the resulting "yellowing effect", that is visible to the bare eye, is unwanted. The CIE-Lab* system is used to describe the yellowing of varnish coatings and *Segurola* used $\Delta E$ values to describe the degree of yellowing, while *Studer* described differences on the basis of Db* values. Moreover, *Segurola* and *Studer* do not describe if their measurements have been done directly after the curing or after a timeframe, after which the temporary yellowing effect has come down to a stable condition.

## Methods

### Used materials

**Substrates:** Two substrates are considered in this study:

1. The fiber based substrate "ProNatur" is chosen for the spectral analysis because of its low absorption, even in the UV region of the spectra.
2. A typical HDPE (high density poly ethylene) foil with a typical absorption in the UV range.

The spectra of both substrates are shown in figure 7 (cf. figure *7*).

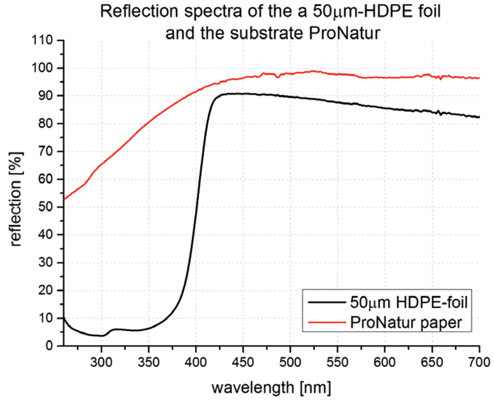

Figure 7: Reflection spectra of a 50mm-HDPE foil and the fiber-based substrate „ProNatur" in the wavelength range 250-700nm

**Varnish components and application:** The following two PIs and the two agents for diluting and binding were mixed for laboratory UV varnishes. For the reproducible application of layer thicknesses of 6mm and 12mm to the substrate, wire rods were used.

- "Irgacure 184" of the a-hydroxy-alkylphenones group
- "Irgacure 369" of the a-aminoalkylphenones group
- TPGDA (CAS: 42978-66-5) a diluting agent
- DPGDA (CAS: 57472-68-1) a diluting agent
- "LEO10801" (polyester acrylates) a binding agent

Table *1* gives a brief overview over created and analyzed mixtures and layer thickness combinations. In total, 120 coatings form a data base. In the results we focus on two very conclusive combinations.

Table 1: Used substances and concentration ranges

| Photoinitiator [name] | Concentration [%] | binding agent [name] | binding agent [%] | diluting agent [name] | diluting agent [%] | Layers [µm] |
|---|---|---|---|---|---|---|
| Irgacure 184 | 1, 2, 4, 8, 16 | LEO 10801 | 9 - 29 | TPGDA, DPGDA | 70 - 90 | 6, 12 |
| Irgacure 369 | 0.5, 1, 2 | LEO 10801 | 9 - 29 | TPGDA, DPGDA | 70 - 90 | 6, 12 |
| Esacure One | 1, 2, 4 | Only solved in acetone | | | | |

Devices

**Laboratory UV-curing station:** For the actual curing a laboratory UV-curing station "AKTIPRINT Mini" from the company *Technigraf* is being used. This device allows to control the radiation intensity and the time of exposure.
Furthermore, radiation doses resulting from combinations of radiation intensity and time of exposer have been determined by utilizing TESA UV strips (Tafelmeier, 2008).
Figure *8* shows that the absorption spectra of the TESA strip correlates very well with the relative spectral power distribution of the curing lamp.

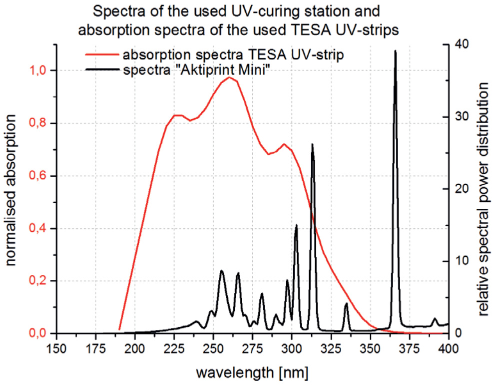

Figure 8: Absorption spectrum of the TESA UV strips in comparison to the relative spectral power distribution of the used UV-curing station "Aktiprint Mini"

**UV-VIS Spectrometer:** A UV-VIS laboratory reflectance spectrophotometer "MultispecPro" of Tec5 GmbH is used to obtain detailed spectral readings of 1nm bandwidth between 250nm and 780nm with a 45°/0° degree geometry. The illumination is realized by a 200W high pressure xenon lamp.

**NIR Spectrometer:** The spectral transmission measurements with coated paper substrates were carried out with the IndiSpectro® sensor of BST ProControl. The used wavelength range is 0.95µm up to 1.70µm with a resolution of 5nm. The radiation direction is perpendicular to the substrate with a 0°/0° degree geometry.

## Results & Discussion

*To communicate our results, this chapter is organized as follows: First we focus on the scientific background of the reaction of (pure) PIs due to radiation using UV-VIS analysis. This identified yellowing occurs comparable with laboratory varnishes (PIs with mentioned additives) and prepares the next step to show the correlation of UV-VIS based results and NIR based results for the determination of the actual polymerization degree. Finally, the crosslink of actual NIR determined polymerization degrees with effects observed in the visible spectra is shown.*

Reaction of PIs due to irradiation

*For an analysis of PIs, without being in contact with oligomers and monomers, the PIs "Irgacure 184" and "Irgacure 369" have been solved in acetone and were applied using an Eppendorf pipette with a constant volume (20 microliters) to the substrate "ProNatur" (cf. chapter Methods).*
*For reasons of simplified interpretation both, absorption as well as reflection spectra are plotted next to each other, where needed. Please notice that mainly data obtained regarding the PI "Irgacure 184" are discussed in detail since the PI "Irgacure 369" shows in many aspects a comparable behavior, which is presented for concept validation.*
Figure 9 (top-left) shows the absorption spectra and figure 9 (top-right) the reflection spectra of the PI "Irgacure 184" for several concentrations (1%, 2%, 4%, 8%, 16%) in a wavelength range of 225nm to 600nm without being irradiated with an UV curing lamp (0mJ/cm$^2$). The PI shows thereby a strong absorption behavior for all concentrations, especially at 260nm (up to 0.6 for the 16% concentration). Another, medium-strong absorption band can be found at 340nm (up to 0.32 for the 16% concentration). Thereby, this specific PI shows only a low absorption of 0.008 (reflection: 96.84) for the 1% concentration or rather 0.023 (reflection: 94.993) for the 16% concentration in the visible part of the spectra at 420nm and above.

In contrast, figure 9 (bottom-left) shows the absorption spectra and figure 9 (bottom-right) the reflection spectra of the PI "Irgacure184" for the same concentrations as discussed above for a radiation dose of 250mJ/cm². Comparable spectra to the un-irradiated samples are obtained. But at a closer look, especially an increased absorption in the wavelength range of 310nm to 450nm for all concentrations is found. This effect becomes even more obvious in the related reflection spectra (cf. figure 9 (bottom-right)). While the obtained maximum reflection difference of the un-irradiated sample at 420nm is -1.85%, a reflection difference of -4.89% can be found for the irradiated sample. This can be interpreted as a shift of bands, indicating the creation of reaction products (cf. chapter "UV-VIS-based analysis of UV-curing ink-systems") by an irradiation induced decomposition of the PI. In conclusion, the pure PI "Irgacure 184" shows upon irradiation a certain yellowing (absorption at 420nm) that can be used to identify weather the PI has been reacted or not with common spectrometers.

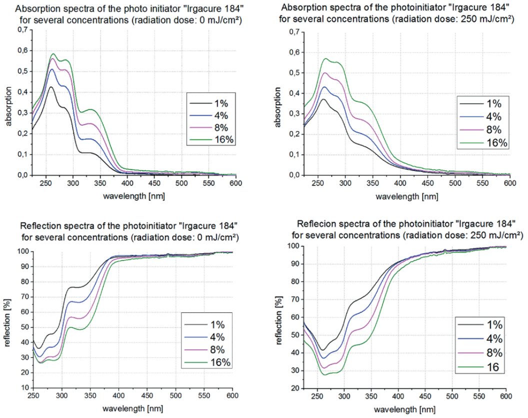

Figure 9: Absorption and reflection spectra in the wavelength range 225nm – 600nm for concentrations of 1%, 4%, 8% & 16% of the PI "Irgacure 184". Absorption spectra with a radiation dose of 0mJ/cm² (top-left). Absorption spectra with a radiation dose of 250mJ/cm² (top-right). Reflection spectra with a radiation dose of 0mJ/cm² (bottom-left). Reflection spectra with a radiation dose of 250mJ/cm² (bottom-right)

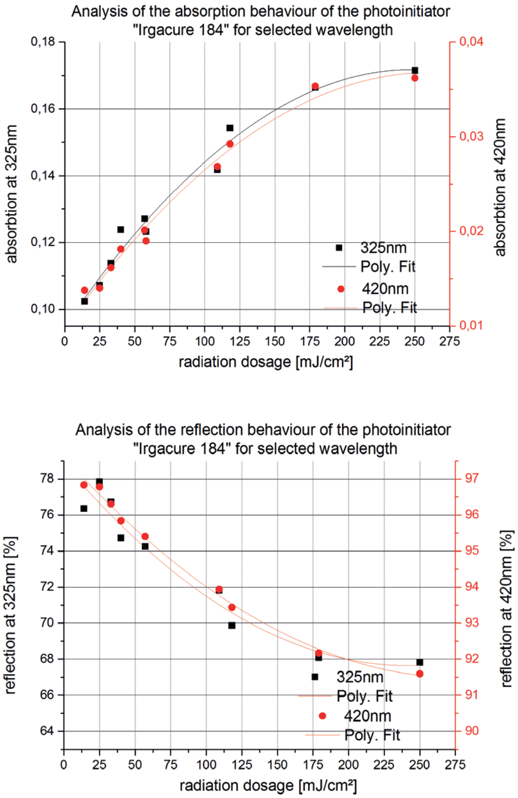

Figure 10: Comparison of obtained absorptions of the photo initiator "Irgacure 184" at 325nm and 420 for several radiation doses (top). Comparison of obtained reflections of same photo initiator and same wavelengths (bottom).

Next, figure 10 (top) shows the dependency of the actual radiation dose and the obtained change of absorption spectra for two wavelengths: 325nm (main absorption in the UV-range) and 420nm (significant absorption in the visible range of the spectra). In contrast, figure 10 (bottom) shows the corresponding data on the basis of reflection values. For both wavelengths significant and correlating changings in the signal can be obtained. Furthermore, readings at 325nm correlate very well with readings at 420nm. Only in term of intensity, readings at 420nm are weaker but still very significant. Anyhow, it can be seen, that with an increasing radiation dose a saturation can be found in both considered wavelengths. This indicates that no more reaction products of the PI are created due to decomposition.

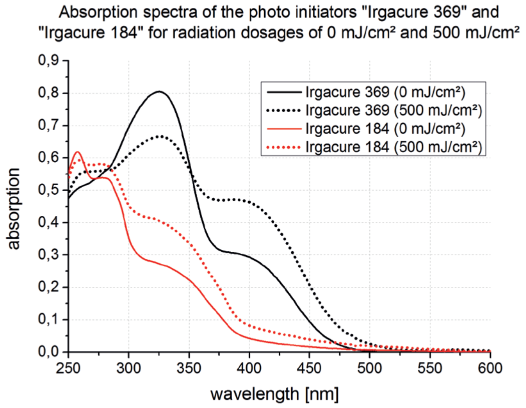

Figure 11: Absorption spectra of "Irgacure 369" and "Irgacure 184" for radiation doses of *0mJ/cm$^2$ and 500mJ/cm$^2$*

For reasons of completeness, figure 11 shows the absorption spectra of the PIs "Irgacure 184" and "Irgacure 369" in the uncured state and a maximum radiation dose of 500mJ/cm$^2$ in comparison.

*Finally, these findings are considered for an in depth analysis on the basis of actual varnishes, including mentioned PIs mixed with monomers and oligomers, in the next chapter.*

## Correlation of UV-VIS & NIR for deriving the actual polymerization degree out of UV-VIS data

*As already pointed out, it is the goal of this study to find for thin UV varnish layers a correlation between PI byproducts appearing in the visible spectra and the actual polymerization degree that can be measured in the NIR range. Therefore, in the next chapter two laboratory UV varnish formulations (based on the PIs "Irgacure 184" and "Irgacure 369", respectively) are analyzed in depth on a UV-VIS basis, in a first step (cf. chapter "UV-VIS based analysis of UV-curing varnishes"). Following, NIR-spectra of the same samples are used to analyze the actual polymerization degree (cf. chapter "Crosslinking of actual NIR analysis determined polymerization degrees with effects observed in the visible spectra").*
*Finally, both examination results are linked together to obtain a crosslink between the PI induced yellowing effect and the actual polymerization degree.*

## *UV-VIS based analysis of UV-curing varnishes*

**Photo Initiator "Irgacure 369":** Figure 12 shows the absorption spectra (250-600nm) of a laboratory varnish applied to the substrate "ProNatur" for several radiation doses. The varnish formulation contains 1% of the PI "Irgacure 369", 80% of the diluting agent "TPGDA" and 19% of a binding agent "LEO10801" for a 6mm thick layer. This particular varnish shows already for a radiation dose of 14mJ/cm$^2$ an intense peak absorption at 325nm. Another peak, with a moderate intense absorption is found at 400nm, which is located in the visible region of the spectra. This particular absorption band is very broad and reaches up to 500nm, even in the uncured state.
By increasing the radiation dose, an increase of absorption occurs for wavelengths at 300-550nm. Therewith, the absorption of the 400nm band is even further broadened, leading to a red-shift. This red-shift provides a very significant yellowing due to an intensive absorption in the visible region of the spectra.
By performing a multi-peak analysis of the minimal irradiated (14mJ/cm$^2$) and the maximum irradiated sample (500mJ/cm$^2$) the spectra can be deconvoluted (cf. figure 13). This analytical technic provides data about individual absorbing components of samples. By comparing figure *13* (left) and figure *13* (right) it is found that certain chemical structures related to the absorption band at 330nm are reduced due to irradiation, while other structures related to the absorption bands at 260nm and 410nm are intensified. Basically, increasing bands intend newly formed products due to photon initiated decomposition of PIs.

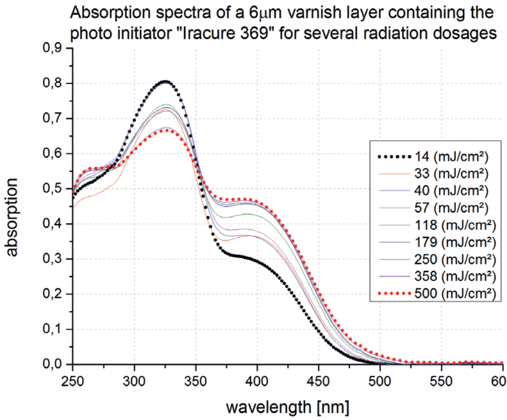

Figure 12: Absorption spectra of a 6mm varnish layer containing 1% of the photo initiator „Irgacure 369" solved in 80% "TPGDA" and 19% "LEO10801" for several radiation doses

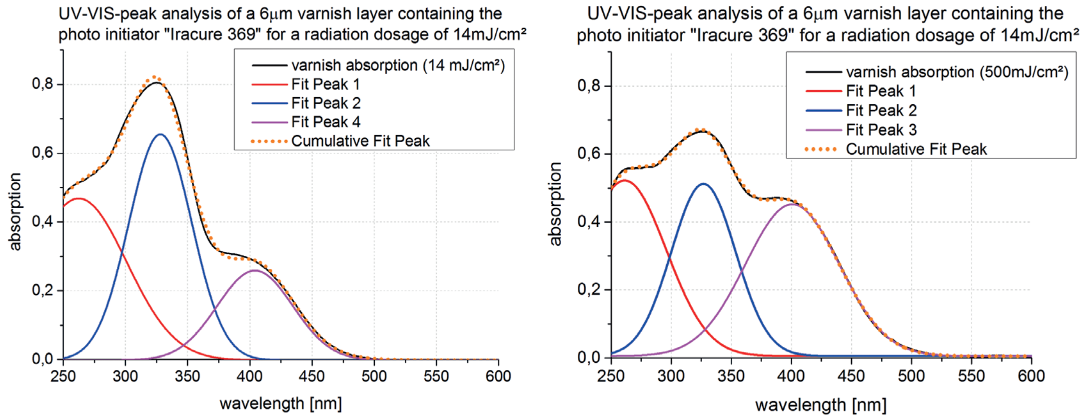

Figure 13: UV-VIS analysis of the absorption spectra of a 6mm varnish layer containing 1% of the photo initiator „Irgacure 369" solved in 80% "TPGDA" and 19% "LEO10801" for radiation doses of 14mj/cm$^2$ (left) and 500mJ/cm$^2$ (right)

**Photo Initiator "Irgacure 184":** Figure 14 shows the absorption spectra (250-600nm) of a laboratory varnish for several radiation doses, consisting of 4% of the PI "Irgacure 184", 77% of "TPGDA" and 19% of "LEO10801" for a 6mm thick layer again applied to the substrate "ProNatur". This particular varnish shows already for a radiation dose of 14mJ/cm$^2$ an intense double-peak absorption at 250-280nm. Another peak, with a moderate intense absorption is found for 325nm that is *not* located in the visible region of the spectra. This particular absorption band shows just like the PI "Irgacure 369" a broad absorption that also reaches up to 500nm even in the uncured state but in this case with a low absorption of 0.04 at 420nm and decreasing above.

For increasing radiation doses an increase of absorption at the wavelengths range 300-550nm is found. Therewith, the absorption of the 325nm band is even further broadened, leading to a red shift. This red-shift leads to a low yellowing due to a low absorption in the visible region of the spectra. By performing a multi-peak analysis of the minimal irradiated (14mJ/cm$^2$) and the maximum irradiated sample (500mJ/cm$^2$) the spectra is again deconvoluted (cf. figure 15). By comparing figure 15 (left) and figure 15 (right) it is found that certain chemical structures related to the absorption band at 250nm are reduced due to irradiation, while others are intensified (related absorption bands at 275 & 340nm). Again, increasing bands indicate newly formed products due to photon initiated decomposition of the PIs.

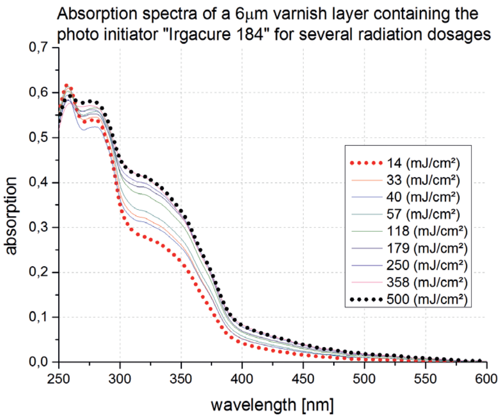

Figure 14: Absorption spectra of a 6mm varnish layer containing 4% of the photo initiator „Irgacure 184"solved in 77% "TPGDA" and 19% "LEO10801" for several radiation doses

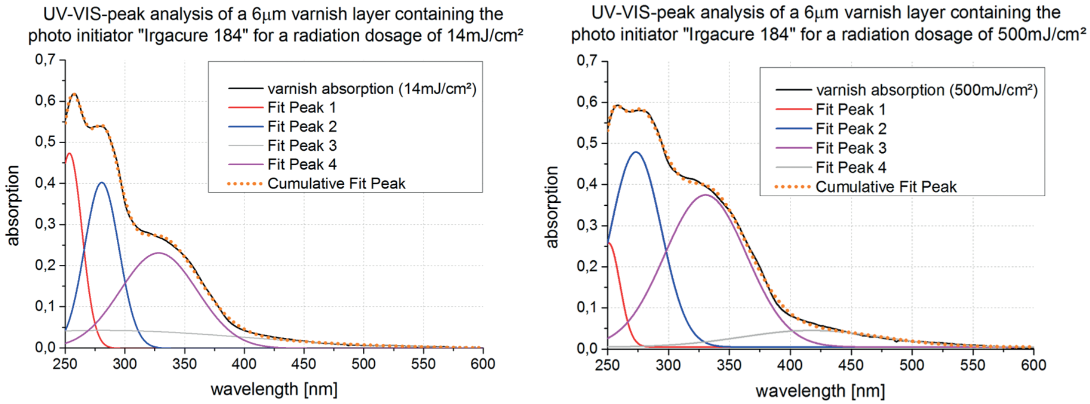

Figure 15: UV-VIS peak analysis of the absorption spectra of a 6mm varnish layer containing 4% of the photo initiator „Irgacure 184" solved in 77% "TPGDA" and 19% "LEO10801" for radiation doses of 14mj/cm$^2$ (left) and 500mJ/cm$^2$ (right)

*Crosslinking of actual NIR analysis determined polymerization degrees with effects observed in the visible spectra*

The black data points in figure 16 show the absorption of the PI "Irgacure 369" based varnish at 420nm for several radiation doses. It is found that the absorption increases from 0.25 to 0.4 in the range of 0 – 179mJ/cm$^2$. This effect is, as already described in chapter "Reaction of PIs due to irradiation", related to the decomposition of the PIs. For higher radiation doses no additional absorption is observed, which indicates that all PIs are decomposed.

In contrast, the red data points in figure 16 show the actual normalized absorption change obtained from NIR-readings at 1622nm. This wavelength is known to show an overtone shift which is directly correlated to the actual polymerization (cf. chapter "IR- and NIR-analysis of acrylic polymerization degrees"). It is found, that a significant absorption change occurs for low radiation doses (0 – 118mJ/cm$^2$), indicating that acrylates are being polymerized. For higher radiation doses no more change in absorption is observed, indicating that the polymerization was already completed. Both datasets combined show a significant correlation. It can be concluded that the actual polymerization is completed if no more absorption change is observed in UV-VIS readings at 420nm.

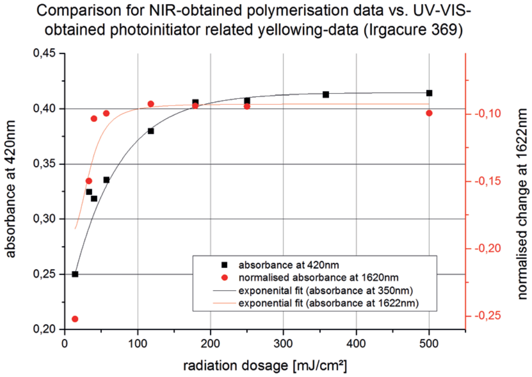

Figure 16: Comparison of NIR-overtone shifts at 1622nm and obtained absorptions at 420nm for several radiation doses of a varnish containing the PI "Irgacure 369"

The black data points in figure 17 show the absorption of the "Irgacure 184" based varnish at 420nm for several radiation doses in combination with NIR-obtained readings for 1630nm. A comparable behavior, just like for the PI "Irgacure 369" is obtained.

Again, both datasets combined show a significant correlation. Also for this example, it can be concluded that the actual polymerization is completed if no more absorption change is observed in UV-VIS readings at 420nm.

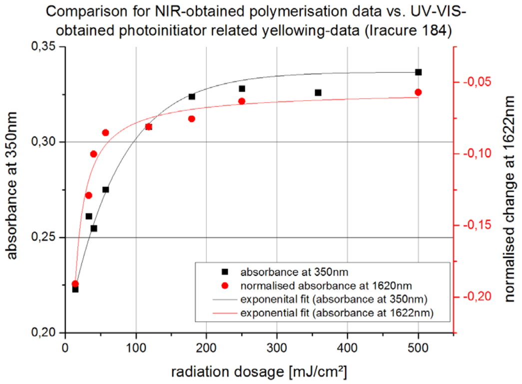

Figure 17: Comparison of NIR-overtone shifts at 1622nm and obtained absorptions at 420nm for several radiation doses of a varnish containing the PI "Irgacure 184"

## Practical significance

Several industries ask for a reliable technology to check the UV-curing degree of thin layers during production and inline. Since there is currently no established inline technology available to check the actual polymerization degree, the presented indirect approach offers a practical solution for the first time: The yellowing effect can be identified with commercial inline spectral photometers and the crosslink between this identification of the (unwanted) photo initiator byproduct and the actual polymerization degree of a complete varnish has been shown (cf. chapter: "Crosslinking of actual IR-spectrally determined polymerization degrees with effects observed in the visible spectra", figure 17 & figure 18).

Identifying the yellowing effect requires a sufficient signal-to-noise ratio at relevant wavelengths. 350nm and 420nm were identified to be most relevant with several varnishes and the laboratory substrate "ProNature" (cf. Figure 7) but especially typical foils and many paper substrates show a strong absorption below 380nm. Fortunately, most of the white and transparent substrates have minor absorptions in the visible wavelength range above 380nm, where also commercial photometers are sensitive. Therefore, the identified effect at 420nm is most important for the practical realization.
Particularly, the temporary characteristic of the yellowing effect is of practical significance, because an UV color system has to avoid a permanent color shift due to curing. Figure 19 (left) shows this temporary characteristic: Spectra of a commercial varnish before curing (black), immediately after curing (red) and 1440 minutes later (blue). The related reflection values at 420nm for 0, 30, 60, 120, 180, 240, 1200, 1750, 2400 minutes after curing (cf. Figure 18 (right)) verify this declining yellowing.

But since this effect is temporary and therefore without any negative impact on the desired production result, it helps to do a reliable inline polymerization check immediately after curing. These fundamental findings allow to think about a camera based 100% inspection of the UV-curing degree with a sufficient illumination in combination with a sufficient sensor sensitivity in the identified wavelength range.

## Outlook

The indirect check of the polymerization degree already works with several transparent varnish substrate combinations, even if the used PIs are known to show only a very

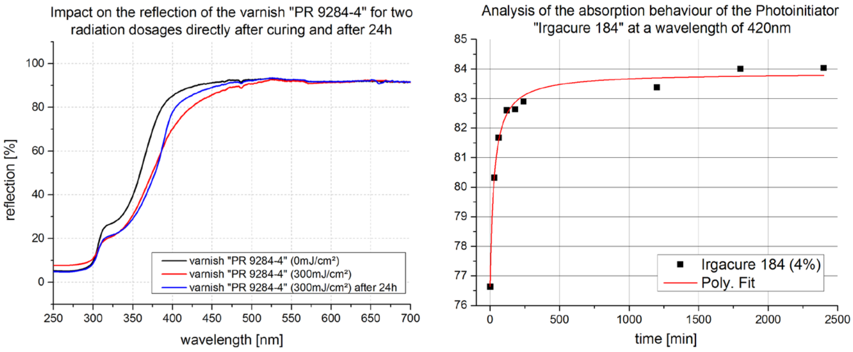

Figure 18: Reflection of the commercial varnish „PR 9284-4" (including the PI "Irgacure 184") of one identical varnish sample: Black for the sample being uncured, Red for cured state immediately measured after curing and Blue for the cured sample but measured 1440min after curing (left). Reflection of the PI "Irgacure 184" at 420nm for a radiation dose of 300mJ/cm$^2$ over a period of 2400min (right).

limited yellowing. This holds true, even if pigmented inks are involved that have a low absorption at 420nm. But the mentioned temporary effect with an explicit more intensive characteristic may help to specify special recipes for PIs in pigmented inks to achieve a sufficient signal-to-noise ratio. Up to now, the aim in ink formulation was to eliminate this yellowing effect in all states of production. But with this new fundamental knowledge, it will be possible to check the polymerization degree and handle the related temporary color shift. Even now, this optical effect should be considered and compensated. This is especially important in process control, because spectral data generated immediately after curing is found to be significantly different (1.55 ΔE) to the data that is obtained 24 hours after production. In future research additional PIs- and concentrations will be analyzed to refine the presented method. Furthermore, pigmented UV-curable color-systems will be analyzed as well.

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# Quality Evaluation of Images Printed on Frosting Sheets with Edible Inks

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**Keywords:** Edible Inks, Frosting Sheets, Inkjet, Quality

Abstract

Edible printing is the process of printing images with edible food colors onto various food products such as candies, cakes, cookies, pastries, and even dinner. The advancements of digital printing technologies along with consumers' demands have stimulated the growth of the edible printing market. One of the fastest growing business sectors is bakery, where photo cakes are getting more and more popular. Inkjet printers with edible ink cartridges are used to print images on a sheet of edible paper called frosting sheet, which is then applied to a cake. With the boom of the edible printing market, print quality becomes more and more important. Consumers would want legible small text and color-accurate photo images. In this study, two test charts were printed on frosting sheets with edible inks and image quality was evaluated.

An inkjet printer was used to print gray-scale and ColorChecker test charts on frosting sheets. The tints on the printed gray-scale test chart were used to measure dot gains. The color patches on the printed ColorChecker test chart were used to measure L*a*b* values, which were then used to calculate color difference delta E ($\Delta E_{ab}$) values. In order to note any changes in quality within a short, realistic time frame, the prints were measured on the day they were printed as well as seven days later after being placed in an airtight, tin foil folder and stored inside a refrigerator.

It is found that fonts of 5 points or smaller were illegible and lines below 1-point thickness became nonuniform. The dot gain curve peaked at 15% for the 40% tint. This could be easily improved by adjusting the calibration curve of the inkjet printer. As for color reproduction, cool colors showed lower $\Delta E_{ab}$ values around 5, while warm colors had higher $\Delta E_{ab}$ values with patch 15 (red) having the highest $\Delta E_{ab}$ value of 46. Creating a printer profile for this specific frosting sheet is needed for color management. However, even a basic IT8.7/3 test chart has 182 color patches, and since it is difficult to measure on a brittle frosting sheet using an automatic measuring table, it would be time-consuming to measure all the patches by hand. Meanwhile, each substrate requires its own printer profile, so color management for edible printing substrates is very challenging. It is also found that one-week storage under low temperature didn't affect the print quality of edible inks, which indicated that they had good resistance to chilling.

## Introduction

Edible printing is the process of printing images with edible food colors onto various food products such as candies, cakes, cookies, pastries, and even dinner (Knight, 2008). When thinking about edible printing, people might immediately relate to the letter m printed on m&m candies. An early patent (Bowling, 2001) described the method of applying a logo and/or trademark including ink jet printing or printing with a roller or plate and an edible coating. This was followed by dozens of other patents related to edible printing that described different processes, inks, substrates, apparatus, etc. The advancement of digital printing technologies, along with consumer demands, has stimulated the growth of the edible printing market (Ngo, 2015; Anonymous, Edible printing: a tasty market application, 2005). One of the fastest growing business sectors is bakery, where photo cakes are getting more and more popular (Stroh, 2000).

Designs can be either pre-printed or created with an edible printer, a specific machine which produces a food coloring-based ink image onto a provided sheet of edible paper. Specific printers may be available to convert, using edible ink cartridges, for recreational use, while professional-grade edible printers remain widely used for commercial use. The inks used within edible printing must be approved by the U.S. Food and Drug Administration (FDA), as well as the cartridges, as plastics used could react harmfully with the inks used (U.S. Food and Drug Administration, 2015). Switching from edible to non-edible inks is not viable, as residue can form from previous printing runs and cause issues concerning image and print quality as well as individual health and safety. The common ingredients in edible inks, essentially food coloring (Anonymous, Colorants: edible inks print on food surfaces, 1999), are propylene glycol, propylparaben, and water (Inkedibles, 2015). While substrates vary in nutritional information due to the variability in the flavors used, typical ingredients include water, cornstarch, corn syrup, cellulose, sorbitol, glycerine, sugar, vegetable oil, Arabic gum, polysorbate 80, vanilla, titanium dioxide, and citric acid (Inkedibles, 2015). Some edible inks and paper materials have been approved by the U.S. FDA and appropriately carry the generally recognized safety certification.

Industrially, online and local resources are available to produce edible prints. Due to the large market for recreational use of edible printing, there are printers, inks, and substrates available for purchase. Epson and Canon are the largest suppliers of edible printers and inks available on the current market, and allow for their printer models to be fitted with edible ink cartridges. Some custom edible printers can even directly print onto cakes, cupcakes, and edible sheets. Commercial edible printing availability is also valued online. Some of the major online vendors available include sites such as edibleprints.com, inkedibles.com, and sweetespressimages.com. Local bakeries such as Kroger and Meijer bakeries typically carry edible printers capable of commercial orders.

With the boom of the edible printing market, print quality becomes more and more important. Consumers would want legible small text and color-accurate photo images. However, there has been very few literature on quality evaluation of edible printing. It would be valuable to conduct a study on this topic. Therefore, in this study, test charts were printed on frosting sheets with edible inks and the image quality was evaluated as follows.

## Methods

The experiment was completed with the help of Taylor's Bakery in Fishers, Indiana. The bakery used an Epson Workforce 30 inkjet printer, which includes a 4-color CMYK inkjet system, outputting up to 5760 x 1440 dpi, with a maximum sheet size of 8.5" x 44" (Epson America, Inc., 2015).

Two test charts were printed on frosting sheets at the bakery, a gray-scale test chart (Figure 1) and a 24-patch ColorChecker test chart (Figure 2). The gray-scale test chart was created using Adobe InDesign CS4 in the CMYK working space – U.S. web coated (SWOP) v2, but only black was used. The color test chart was a TIFF file in the Lab color space, which was obtained from former Candela, Ltd. The printing process and color management were controlled by Epson Printer Driver v6.63, which was released on October 9th, 2009 (Epson America, Inc., 2015).

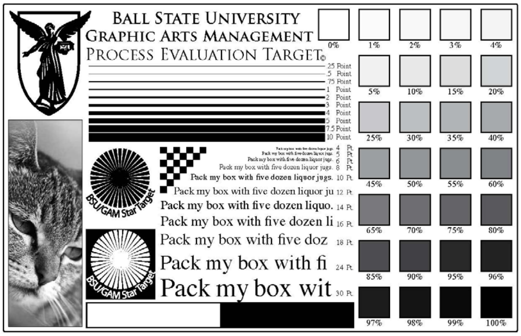

Figure 1. Gray-scale test chart

Figure 2. ColorChecker test chart

The print images were measured with an X-Rite SpectroDensitometer 528. The tints on the printed gray-scale test chart were used to measure dot gains, for which three measurements were taken and then averaged. The L*a*b* values of the 24 color patches on the printed ColorChecker test chart were also measured three times and then averaged. Color difference Delta E ($\Delta E_{ab}$) values were calculated using the following equation:

$$\Delta E_{ab} = \sqrt{\left(\Delta L^*\right)^2 + \left(\Delta a^*\right)^2 + \left(\Delta b^*\right)^2}$$

where ΔL*, Δa*, and Δb* are the differences between the reference and measured L*, a*, and b*, respectively. CIE L*a*b* values for the 24 color patches on the ColorChecker given by X-Rite, Inc. were used as the reference values (X-Rite, Inc., 2009).

In order to note any changes in quality within a short, realistic time frame, the prints were measured on the day they were printed as well as seven days later after being placed in an airtight, tin foil folder and stored inside a refrigerator.

## Results and Discussion

The output quality of the edible printed objects in the gray-scale test chart had difficulties in some areas as seen in Figure 3, when compared to its original in Figure 1. The fonts used remained legible down to the 5-point range, while font sizes 6 through 30 points were moderately to considerably legible. The negative and positive star targets were mostly reduced in resolution and showed very obvious detail loss. Lines and margins of the edible print were fine above the 1-point mark, whereas below 1-point their thicknesses varied at inconsistent levels. The raster image of the cat was clearly visible and appeared to retain the majority of its detail. These visual strengths and weaknesses of the edible print in Figure 3 remain consistent with the contemporary uses of edible printing – bitmap image reproduction and font legibility.

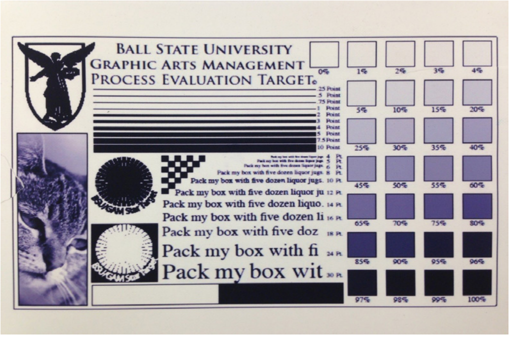

Figure 3. Printed gray-scale image

Although the gray-scale test chart only calls for black ink to reproduce the image, it is evident that the printer driver used a 4-color process, which resulted in a colored image. The blue casting indicates that higher amounts of cyan ink were used than magenta and yellow inks. The reason might be that frosting sheets usually have a yellow shade, so cooler grays were printed to counter that.

Figure 4 shows the dot gain curve of black in the printed gray-scale test chart. As expected, the curve is peaked at the midtones, measuring as high as 55% at the 40% tint for a 15% dot gain. The darker the tint, the more accurately the edible printing process was able to reproduce the original image, with dot gain steadily decreasing down to 4% at the 90% tint. Such high dot gains at midtones were probably caused by the substrate. Frosting sheets are made of fine particles and thus have very rough and porous surface, which makes ink holdout more difficult.

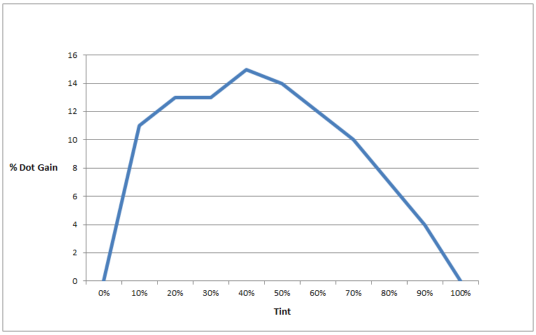

Figure 4. Dot gain curve of black

The printed ColorChecker image is shown in Figure 5. Visible strips on the printed image indicate the moving direction of the inkjet printhead. When visually compared with the original test chart in Figure 2, some color patches show significant variations, especially the red patch (third on the third row).

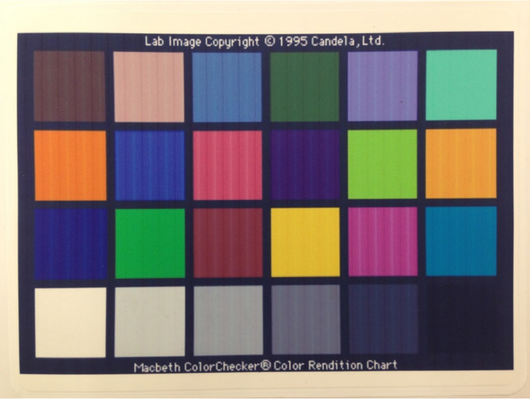

Figure 5. Printed ColorChecker image

To evaluate quantitatively, the calculated $\Delta E_{ab}$ values of all 24 color patches are illustrated in Figure 6, with the color ID numbers representing the corresponding color patches numbered from 1 to 24, as shown in Figure 7.

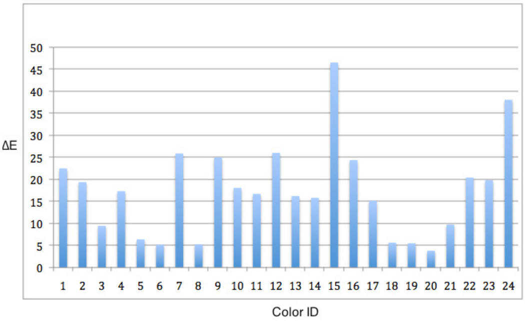

Figure 6. Delta E ($\Delta E_{ab}$) values

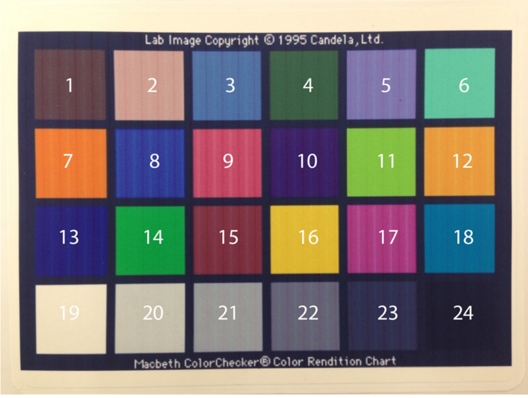

Figure 7. Printed ColorChecker image with color ID numbers

The colors that had the least significant color differences were the cool colors, with patches 6, 8, 18, and 5 having $\Delta E_{ab}$ values of around 5. The warm colors, however, showed intense variations from their original L*a*b* values, with patch 15 (red) having the highest $\Delta E_{ab}$ value of 46 while patches 12, 7, 9, and 16 having $\Delta E_{ab}$ values of around 25. It is well known that unlike cyan and yellow pigments/dyes, a close-to-ideal magenta pigment/dye has not yet be found to absorb all green light and reflect all red and blue lights (Eldred, 2001). That is why there are different magenta pigments/dyes used for printing inks, and magenta inks have higher hue errors than those of cyan and yellow inks. Warm colors in the ColorChecker image were printed with higher percentages of magenta ink, so it is no surprise that they had higher $\Delta E_{ab}$ values. The frosting sheet also had a yellow shade, which also contributed to higher $\Delta E_{ab}$ values for printed warm colors.

After closely observing and measuring the printed images on the day they were printed and then again on the seventh day of being stored in a refrigerator, it was found that any physical changes between the two sets of the gray-scale and ColorChecker images were restricted to the substrate itself and had little to no effect on the image quality. The only notable change that the prints showed upon being chilled for seven days was that they became slightly firmer and more brittle than their earlier counterparts. According to the nearly identical measurements taken from both prints on both days, the images were essentially unaffected, which indicated that the edible inks had very good resistance to low temperature within a week.

## Conclusions

This study evaluated the image quality of edible printing on frosting sheets. It is found that fonts of 5 points or smaller were illegible and lines below 1-point thickness became nonuniform. The dot gain curve peaked at 15% for the 40% tint. This could be easily improved by adjusting the calibration curve of the inkjet printer. As for color reproduction, cool colors showed lower $\Delta E_{ab}$ values, while red and warm colors had higher $\Delta E_{ab}$ values. Therefore, creating an ICC printer profile for this specific frosting sheet is needed for color management. However, even a basic IT8.7/3 test chart has 182 color patches (ANSI, 2010), and since it might be difficult to measure on a brittle frosting sheet using an automatic measuring table like iOi1, it would be time-consuming to measure all the patches by hand. An alternative way might be using a scanner or camera to digitize a printed IT8.7/3 test chart. Then, the scanner or camera profile could be used to assign the scanned IT8.7/3 test chart to transform the device RGB values to CIELAB values. Consequently, the obtained CIELAB values could be used to generate a custom ICC printer profile. However, each substrate requires its own printer profile, so color management for edible printing substrates is very challenging.

It is also found that one-week storage under low temperature didn't affect the print quality of edible inks, which indicated that they had good resistance to chilling. There are other factors that affect print quality, such as printer, substrate, ink, and cartridge variation. This study is limited to one printer, one substrate, and one type of ink and cartridge. More knowledge would be gained with these factors being individually controlled and studied.

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# Influencing the profile of an inkjet printed layer on glass by using optimized solvent mixtures

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**Keywords: drying, evaporation, ink chemistry, profile, glass**

## Abstract

**In this paper it is shown that variations of layer thickness of a dried inkjet printed layer on non-porous substrates can be affected strongly by simple variation of ink solvents. Inkjet printed layers on substrates like standard glass have often non- uniform layer thicknesses. One known reason for this is referred as the Coffee- Stain Effect. In such a case the layer thickness is up to four times higher at the edges than at the center. An extended evaporation rate at the edge is driver for that effect. In other cases, agglomeration of particles in the center of a printed layer can also be found. Marangoni Convection driven by thermal gradients are often referred as the main cause. Both deviations of layer thickness are common in functional printing applications if low viscous inks with a high amount of solvents are used. This variations of structures might lead to issues in subsequent processes, e.g. defects in top coatings or even short circuits in electric components. One of the key goals of this paper is to identify one parameter to control the uniformity of such printed structures. Therefore, a better understanding of the influence of solvents, evaporation and drying conditions is goal of this work. The drying mechanism is observed by printing model inks of a well-known and simple composition of ethylene glycol (EG) and 1-butanol and the colorant solvent black 29. For a simplified application the layers where generated by pipetting the layers onto a glass substrate. To observe the variation of layer thickness during drying the pipetted layers are measured by utilizing a confocal microscope. Drying of droplets are measured in a period from 15 minutes up to 36 hours. The results show new aspects of profile characterization and provide insights into the major impact of solvent composition due to the final film uniformity and their formation during the drying process. On the basis of gained 3D pictures the phenomenon of non-moving, called pinned, and moving, called unpinned, of the three-phase contact line can be visualized. To quantify this pinning or unpinning a measure, so called three phase contact line movement, was introduced. The resulting drying characteristics of each solvent ratio together with the examination of thermal gradients indicate that the uniformity of the layer thickness is strongly affected by the ratio of solvents and not by Marangoni Convection. The Coffee-Stain Effect can be observed with pinned and unpinned contact line movement.**

## Introduction

Aside from good solubility of the colorant or a stable dispersion of particles, the most important parameters for the inkjet ink chemistry are viscosity (8-12 Pa·s) and surface tension (~28mN/m) (Magdassi, 2010). These parameters ensure that the ink can pass the nozzle, build a drop in the air and adhere on the substrate without spreading or dewetting. It is well known that the parameter window is small and the variation of solvents is limited. To guarantee an optimized fluid flow in the printing head and a good wettability on the substrate, other quantities like the uniformity of the dry layers are often insufficient and less controlled. Next to the ink formulation, the surface energy of the substrate, the temperature and the ambient atmosphere also have a strong impact on the uniformity of the layer. As a result, ink formulation often bases on an empiric time-consuming approach.

The functional printing applications demand new specifications in comparison to conventional inkjet printing. Smaller dimensions in thickness and width, uniform layers and new substrates are only a few examples. Especially the uniformity on nonporous substrates like glass or foils is becoming increasingly important. In this paper a homogenous thickness is defined as dome-profile.

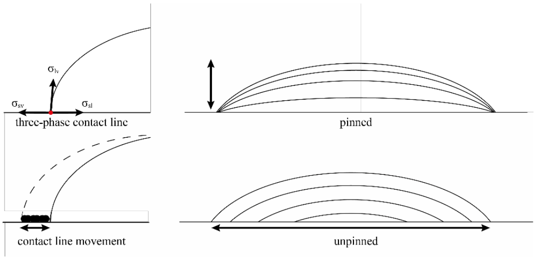

Figure 1: Overview of the different drying characteristics. The three-phase contact line is the contact line between the ink, substrate and air. The three-phase contact line can be pinned and the volume loss gets compensated by a decreasing of contact angle. The three-phase contact line can be unpinned. The volume loss gets compensated by a decreasing contact radius. If the contact line is unpinned a contact line movement can be measured. It is the distance between the origin of the contact line and the current contact line.

There are three interfacial tensions if a fluid is in contact with a solid substrate: $\sigma_{LV}$ (liquid-vapor), $\sigma_{SL}$ (solid-liquid) and $\sigma_{SV}$ (solid-vapor). The three-phase contact line is the contact line between the liquid phase (ink), solid phase (glass substrate) and the vapor phase (air) (Brutin, 2015). At the three-phase contact line the contact angle can be measured. During drying of a fluid on a nonporous substrate the volatile portions like solvents evaporate. The loss of volume in the liquid phase leads to a decrease of the contact angle (pinned contact line) or decrease of the wetted area with constant contact angle (unpinned contact line). If the contact angle gets smaller the height of the fluid gets smaller and the radius is constant. The three-phase contact line does not move and is pinned. If the contact radius gets smaller the height of the fluid is changing slightly as well as the contact angle. The three-phase contact line moves and is unpinned. (Figure 1)

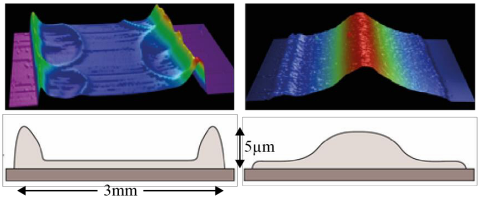

Figure 2: Two different conductive inkjet inks printed and dried on glass. The left structure shows high agglomerations at the three-phase contact line (Coffee-Stain Effect). The right structure shows high agglomerations at the center.

A specific profile of a Coffee-Stain Effect is shown in figure 2. The printed lines are 3mm in width and have a maximum height of 9µm. The cross section has a characteristic shape of a M. In this paper the Coffee-Stain will also be described as M-profile. The Coffee-Stain Effect provokes a non-uniform layer thickness. During the evaporation of solvents, the Coffee-Stain Effect causes aggregations of particles at the three-phase contact line. The dispersion evaporates faster at the three-phase contact line than in the center of the liquid. The different losses of solvent at the outer regions of the fluid cause a compensating flow of solvent towards the three-phase contact line driven by a gradient in solvent concentration. For homogeneity in the ink the remaining solution flows toward the contact line. Particles can stream outward along the solvent flow and aggregate at the contact line (Deegan et al., 1997). It is known that, among others, different shapes (Yunker et al., 2011) and sizes of particles (Weon & Jung, 2010), the drying parameters (Janßen & Jung, 2015) the solvent-mixture (Park & Moon, 2005), electrowetting (Eral et al, 2011) or changes of the atmosphere (Majumder et al., 2012) have an influence on the Coffee-Stain Effect. Those solutions do not homogenize the printed layer ideal. It is assumed that, to generate Coffee-Stain Effects, the solvent needs to evaporate very fast, the temperature gradient needs to be latent and the three-phase contact line needs to be pinned (Park & Moon, 2005).

In addition to the Coffee-Stain Effect, high agglomerations at the center of the printed ink can also occur (Fig.1). In this paper high agglomerations in the center are defined as hill-profile. In literature, these structures are often accounted as Marangoni Convections. While drying inkjet ink, the evaporation of solvent can cause concentration or temperature gradients in the ink which lead to gradients of surface tension (Hu & Larson, 2006). This effect is also known as "tears of wine" (Fournier & Cazabat, 1992). In some cases, the Marangoni Convection is also called "Reversed Coffee-Stain Effect" (Innocenzi, 2013). This leads to the impression that the shape of the profile is only driven by Coffee-Stain Effects and Marangoni Convection. A homogenous thickness is defined as dome-profile.

In this paper it is shown that

- the Coffee-Stain Effect can also be observed for unpinned contact line
- the Coffee-Stain Effect can also occur for low evaporation rates
- high agglomerations in the center can arise without gradients in solvent concentration and temperature
- both structures can occur in one solvent mixture by changing their ratio

## Methods

In an extensive study by Janßen (2012) conductive inks where printed, dried and subsequently measured by utilizing a profilometer. Most inks had an M-profile caused by the Coffee-Stain Effect as evidenced by agglomerations of particles at the outer region or showed a hill-profile by agglomerations of particles in the center. In the present study, a solvent mixture of a conductive copper ink, which has higher agglomerations of particles in the center than at the three-phase-contact line (Fig.1, right), is chosen as a reference. The copper ink is solvent based on ethylene glycol, 1-butanol and 1-methoxy-2propanol. In this paper it is assumed, that the most impact of the uniformity of the layer thickness is the evaporation rate and the surface tension of the solvent. Therefore, the complexity of the copper ink was reduced. For the examination of the drying mechanism a model ink is used, based on two solvents and one colorant.

In table 1 the surface tension and the evaporation rate of the three solvents are listed.

| Solvent | Surface Tension [mN/m] | Evaporation Rate |
|---|---|---|
| Ethylene glycol | 47,3 | 0,01 |
| 1-butanol | 26,2 | 0,46 |
| 1-methyoxy-2-propanol | 27,7 | 0,71 |

Table 1: Surface tension and evaporation rate of the solvents

A model ink consisting of 1-butanol and ethylene glycol in the ratios 1:0, 3:1, 2:1, 1:1, 1:2, 1:3, 0:1 is mixed with 10% colorant solvent black 29 (Valifast Black 2808). To get an understanding of the solvents the model fluid is as simple as possible and a conscious decision to work without binders and additives is given.
A drop of 1µl volume gets pipetted on a glass substrate. The glass substrates are cleaned with Isopropanol and clean room grade wipers.
Next, the liquid drop is observed during drying with a 3D laser scanning microscope. A moderate magnification of 10x has been chosen. This magnification enables a maximum scanning speed and shows the largest image section. The image section has a size of 1,4x1mm$^2$. Fast laser scanning is important due the fact that the ink is measured while drying. Higher evaporation rates lead to faster drying times and a faster change in layer thickness and uniformity. The faster the fluid dries, the more likely it is that a blurring in measurements might appear. One 3D image with the 10x-objective takes about 20 seconds. Depending on the drying time a 3D-image is made every 40seconds for up to 15 minutes.
The resulting images are evaluated in terms of drying characteristics, drying time and profile of the dried drop. The color area of the 3D-images is leveled to the same vertical range. The color already provides an insight as to how the height of the drying fluid changes over time. The 3D images and the microscope images are transformed to video-files. Therefore, videos of the drying fluid exist.

## Results and Discussion

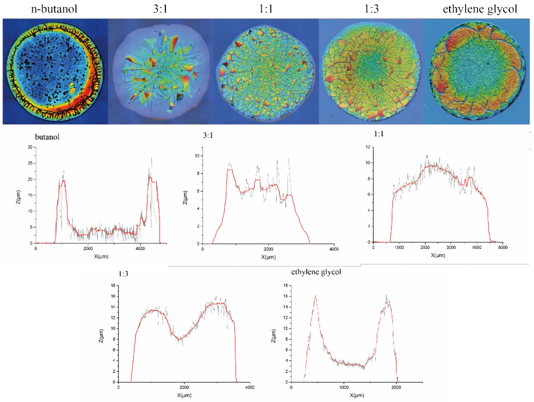

Figure 3: Overview of the variation of 1µl butanol- ethylene glycol mixtures on glass which show different profiles of height. Coffee-Stain Effect: 1-butanol, 1:3 and ethylene glycol; aggregation at the center: 3:1; uniform profile:1:1

An overview of the variation of 1-butanol with ethylene glycol is given in figure 3 and gives an insight into the sensitivity of the drying behavior of different solvent ratios. 1-butanol, 1-butanol- ethylene glycol 1:3 and ethylene glycol show different characteristics of an M-profile which is the result of the Coffee-Stain Effect. 1-butanol-ethylene glycol 3:1 shows a hill-profile due agglomerations in the center. And 1-butanol-ethylene glycol 1:1 shows a uniform profile like a dome shape. Different shapes are only achieved by different ratios of the solvent mixture. With the butanol-ethylene glycol mixture it is possible to influence the shape of the profile from non-uniform layer thickness to uniform layer thickness only by changing the ratio. This demonstrates that the solvent ratio can be used to optimize the uniformity of the layer thickness and should not only be used to adjust the optimal surface tension. It is to expect, that the uniformity varies with different substrates and has to be tested and adapted with new substrates.

While the profiles of 1-butanol and ethylene glycol are quite similar, the formations developed quite differently. The drying time of 1µl 1-butanol specimen takes 15 minutes while the drying time of the 1µl ethylene glycol specimen takes 2300 minutes (Table 2).

| Solvent Ratio | Drying Time [Min] |
|---|---:|
| butanol | 15 |
| butanol:ethylene glycol 3:1 | 180 |
| butanol:ethylene glycol 2:1 | 300 |
| butanol:ethylene glycol 1:1 | 480 |
| butanol:ethylene glycol 1:2 | 840 |
| butanol:ethylene glycol 1:3 | 1080 |
| ethylene glycol | 2300 |

Table 2: Drying time of 1µl fluid.

In figure 4 the drying fluid of butanol and ethylene glycol in a ratio 3:1 is shown and serves a good understanding of the efficacy of the 3D measurement over the drying time and the visualization of the moving contact line. The grey area of the microscope picture represents wet areas, the lighter areas represent dry areas. The distance between the three-phase contact line at one minute and the current three-phase contact line is described as contact line movement. In this example the three-phase contact line is unpinned. While the contact line moves from the outer region to the inner region, a film of dried ink with a thickness of about 8µm is left behind. This can be seen in the images of the microscope as a brighter grey and in the 3D images in blue. The size of the dried ink is not affected. After the fluid is dry, it is not detectable if the three-phase contact line was pinned or unpinned. After t > 180 minutes the model ink is dry and has higher thickness in the center than in the outer region (hill-profile). The ink dries uniformly from the outer to the inner region.
The higher agglomeration in the center might not be affected by gradients in concentration. While the butanol evaporates faster at the outer region than in the inner region, the fluid is unbalanced and higher surface tensions at the outer regions might occur caused by the lower surface tension of the more volatile butanol than the less volatile ethylene glycol. If the gradient of surface tension is big enough a flow from regions of lower surface tension towards regions of higher surface tension should arise. Because the outer region might have a higher surface tension the flow should be from the inner to the outer regions and this would strengthen the M-profile instead of hill-profile. According to this reason it can be assumed that the influence of gradients of concentration are not dominating this scenario.

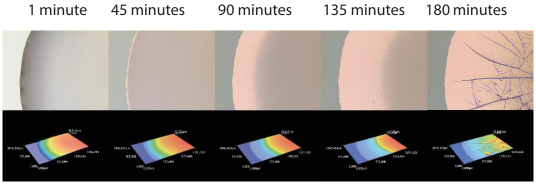

Figure 4: Moving Contact line can be seen during the drying process. (e.g. butanol: ethylene glycol 3:1) While the contact line moves a film of dried ink is left over. The moving contact line does not affect the size of the dried area. The layer thickness is higher in the center than in the outer region. (Image size: 1,4x1mm²)

In figure 5 a 1µl 1-butanol drop is presented. The time dependence measurement gives an insight into the drying behavior of the droplet. In picture 1 a typical drop shape of a dome can be seen. The center (red) of the fluid is higher than the outer region (blue). Only a few seconds later the fluid has changed to a M-profile. The layer is thicker at the three-phase contact line (light blue) than in the center (darker blue). A typical Coffee-Stain can already be predicted. After 15 minutes 1-butanol is dry. The dried profile is a Coffee-Stain. This drying behavior is consistent with the theory of Coffee-Stain Effects.

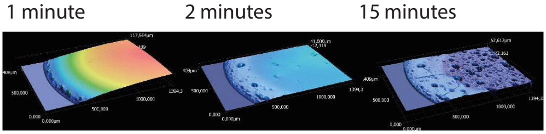

Figure 5: Time dependence images from the laser scanning microscope of a drying 1µl 1-butanol drop on glass after 1, 2 and 15 minutes. (Image size: 1,4x1mm²)

Ethylene glycol and 1-butanol have higher agglomeration of particles at the three- phase contact line then in the center (M-profile). The drying behavior from ethylene glycol has different characteristics then the drying behavior from 1- butanol. In the first minute of drying the model fluid ethylene glycol has the shape of a dome. The noticeable edge and the rough section between three-phase contact line and center are expected to be a measurement error caused by the weak signal of the laser at steep flanks (Figure 6). This can be also seen in the microscopic image. The black area does not give any signal. The high flanks are likelycaused by the high contact angle of ethylene glycol. After 12 hours the contact angle is at its lowest point. Until this point the three-phase contact line is pinned. The loss of ethylene glycol due to evaporation can only be seen in the height of the fluid and the contact angle. After 12 hours the drop starts to build dry edges and the three- phase contact line moves from the outer to the inner region. The contact line is unpinned. The distance between the first 3-phase-contact-line and the last three- phase contact line is about 150µm, which is very small. With the moving of the contact line the contact angle decreases too and the combination provokes a smoother Coffee-Stain Effect than the 1-butanol.

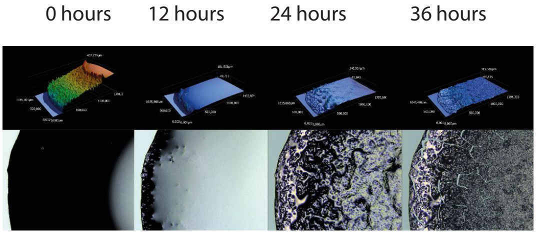

Figure 6: Time dependence images from the laser scanning microscope of a drying 1µl ethylene glycol drop on glass after (Image size: 1,4x1mm$^2$)

The moving three-phase contact line is much stronger with the mix ratio of solvents than with 1-butanol or ethylene glycol. In figure 7 the moving contact line is presented for each mix ratio of solvent. Because 1-butanol has a pinned contact line and the unpinned contact line from ethylene glycol is very small, they are not listed in figure 7. The more 1-butanol in the mixture and the faster the evaporation time is, the faster the border of the three-phase-contact line moves. The contact line moves for all three kinds of profiles – M-profile, uniform layers, and hill-profile. Which kind of profile the dried fluid has cannot be predicted by the pinned or unpinned contact line. A Coffee-Stain Profile can exist while the three-phase contact line is unpinned. Probably the velocity of the contact line movement might give an idea of the characteristic of the profile.

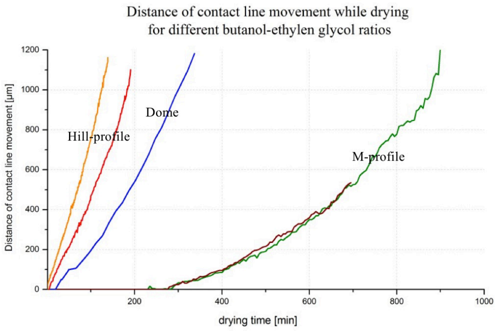

Figure 7: Distance of the moving 3-phase-contact-line from the outer region to the inner region.

Beside the contact line movement thermal gradients inside the fluid while drying might also lead to higher agglomerations at the center. To determine the influence of thermal gradients measurements of surface tension at different temperatures were performed. The surface tension of three different model fluids was measured from 15°C to 30°C (Figure 8). Two fluids show the characteristics of a Coffee- Stain and one shows agglomerations in the center (butanol: ethylene glycol 3:1). The temperature has nearly the same effect on every model fluid. All three mixtures have a decrease from 1,5 mN/m from 15°C to 30°C. If the model fluid has a large gradient in temperature, high gradients in surface tensions can occur and the fluid can flow from low surface tensions to high surface tensions. Because M-profiles and hill-profiles have the same small temperature gradient the temperature gradient might not affect the drying behavior of butanol: ethylene glycol -mixtures.

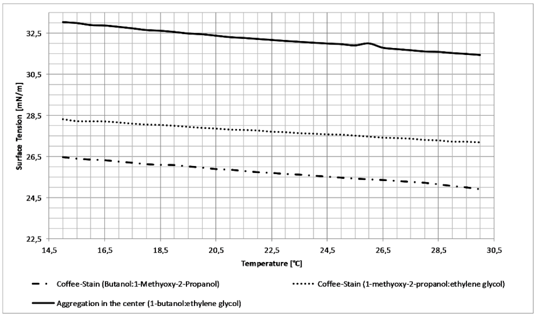

Figure 8: Influence of temperature on surface tension.

## Conclusion

In this paper it is presented that one solvent mixture can result different characterizations in layer thickness just by changing the ratio of solvents. To distinguish the drying characteristics three different variations of layer thickness, called profiles, where postulated. The M-profile with high agglomeration of particles, e.g. colorant, at the outer region, the hill-profile with higher agglomeration of particles at the center and the dome-profile with a uniform layer thickness. To observe the contact line movement a 3D laser scanning microscope is used to measure the layer thickness at different drying times. This new method of measuring the layer thickness of fluids during drying period results in an extended observation of the three-phase contact line movement. This leads to differentiation between the determination of pinned and unpinned contact lines during drying time. Therefore, the 3D scanning microscope is an appropriate tool as an extended in situ method for observation of the drying behavior.

The major influence of solvent composition on the layer thickness could be demonstrated by an example of the solvent system of 1-butanol and ethylene glycol with different ratios. In one combination of solvent three different shapes can be found only by varying the ratio. The final layer thickness after drying of butanol:ethylene glycol in a ratio of 3:1 shows a hill-profile, the butanol:ethylene glycol of a ration 1:1 shows uniform layer thickness (dome-profile) and the butanol:ethylene glycol mixture with ratio of 1:3 shows M-profile. All 3 different layer variations occur with a movement of 3 phase contact line, called unpinned contact line. This is in contradiction to other surveys where the pinned status is described as on precondition for Coffee-Stain like M-profiles.

An example of 3 model inks based on different solvents with different types of layer variation (two M profiles and one hill profile) have similar thermal gradient of surface tension below 0.1mN/m K indicates the minor importance of Marangoni convection to the final dried layer thickness.

The results show how difficult ink formulation is relating to the uniformity of layer thickness. Beside the major parameter of viscosity and surface tension the uniformity of dried layer thickness should become more important for functional printing applications. It might be necessary for uniform layer thickness that the ink formulation need to be adapt for every substrate.

In further works extended mixtures of solvents are suggested to be observed by 3D Scanning observation. A better understanding of solvents and their impact on homogeneity of layer thickness is crucial for the application of inkjet inks in the functional printing industry.

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# UV-VIS spectral analysis of fluorescent brightening agents in combination with carrier substances for inkjet based substrate white-point simulations

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**Keywords:** fluorescent brightening agents, fluorescence, whitepoint, inkjet

**Abstract**

**In this study, colorimetric as well as chemical studies of commercially available fluorescent brightening agents (FBAs) were conducted. Thereby, special attention is given to polyethylene glycol (PEG) with varying molar masses, which is a known carrier for "boosting" or "activating" fluorescence. While the colorimetric analysis focused on printed laboratory FBA-inks containing liquid FBAs and in selected cases PEG, the chemical analysis is performed detached from the chemical environment "paper".**
**It is shown, that the chain-length of PEG has a significant impact on the obtainable quantum yield and therefore emission intensity. Based on spectral analysis, it is concluded that PEG decreases the reaction rate of the isomerization reaction (due to a hindering of the twisting of the C=C double bond) resulting in longer periods in which the excited state of the trans-isomer can exist. This leads to an increased amount of fluorescence from the excited trans-isomers. Hence, the obtained quantum yield is increased. Quantum yield increases from 33% $Q_{eff}$ (in pure water) to 60% (in 30% PEG 1000) are reported.**

## Introduction

One of the key goals in producing paper and cardboard in the paper industry is to achieve a high whiteness degree. This is often realized by the addition of FBAs (Fluorescent Brightening Agents) to the paper pulp and coating (Champ, 2001). The increasing use of FBAs in production substrates, in contrast to proof-substrates that contain often a very limited amount of FBAs, result in serious difficulties in any color management process, especially in terms of white point corrections.
In a preceding journal article, the authors of this study presented a method to achieve an illumination independent colorimetric and visual match between a single proof substrate and most production substrates. This has been accomplished by printing area coverage variable defined amounts of a liquid FBA using inkjet (Bohn, 2016). This preceding research will be briefly reviewed in the section "State of the scientific knowledge & resulting questions"

The key to successfully implement this new type of white-point modification is the possibility to achieve an intense FBA-emission even with minor FBA-ink area coverages to e.g. not negatively affect the total ink volume of the used proof-substrate.

Therefore, this study focuses on the interaction of FBA-inks and carriers on a chemical level with special respect to observed quantum efficiencies of typical FBAs and carriers. Especially the influences of carrier chain lengths on the quantum efficiencies due to effects on the photo isomerization process of stilbene will be discussed in detail.

### State of the scientific knowledge

In this chapter a brief overview about fluorescence in general and relevant properties and mechanics of fluorophores of the type "stilbene" are given.

Fluorescence in general

Fluorescence is the emission of photons by molecules that have absorbed electromagnetic radiation. Emitted photons are typically of longer wavelength, and possess therefore a lower energy, than the absorbed radiation. With other words, the emission of photons by fluorescenting molecules result in a red-shift. Such types of molecules are called "fluorophores".

Many fluorophores absorb invisible UV-radiation and re-emit the absorbed energy in the visible range of the spectra; hence, the fluorescence effect becomes visible to the human eye.

Fluorophores cease to glow immediately after the radiation source stops, unlike phosphorescence, whereby photons are emitted for a significant longer time after (Sauer, 2011).

### FBAs and Carriers in the print- and media Industry

In practice, most fluorophores utilized in the print- and paper industry are based upon stilbene-derivates, of the type "4,4'-Diamino-2,2'-stilbene-X-sulfonic acid". The X represents the sulfonation-degree of the molecule, which can be di-, tetra- or hexa-sulfonated. The number of sulfo-groups mainly determines the solubility of the molecules in water.

- Diaminostilbene-disulfonated FBAs have two sulfonic groups. The two other substituents could be hydrophilic groups. These FBAs show a very good affinity to cellulose, but a limited solubility and are mostly used in the wet-end (Holik, 2006).
- The most commonly used FBA is of the tetra-sulfonated type. Tetra sulfonated FBAs are a versatile substance because of their medium affinity and good solubility. They can be used in most stages of papermaking: wet-end, size-press and coating (Holik, 2006).
- Hexa-sulfonated FBAs are especially used in coatings, where high brightness is required (Holik, 2006).
- Please note, most commercially available FBAs are substituted with additional functional groups to achieve special properties such as acid resistance or to gain a defined red shift.

The performance of these FBAs has been subject to intense research on a practical scale, mainly with focus on empirical determination of the highest whiteness gains possible by changing parameters, such as the concentration of the FBA or the addition of known carrier substance.

Carrier substances are molecules that are known to "intensify" or even "enable" fluorescence on an empirical scale. Used and examined carrier substances are for example polyethylene glycol (PEG), methyl cellulose (MC) or polyvinyl alcohol (PVA), with in each case differing molar masses (and therewith chain lengths of the molecule) and hydrolysis degrees (Blum, 2002).

Some studies show that the type of carrier substance, the used concentration, the actual hydrolysis degree or even the point of time at which the carrier has been added to paper pulp during paper production and lead to individual effects. All examinations have been done for actual paper compositions and not detached from the molecular environment "paper" (e.g. Blum, 2002). Therefore, all these studies are to be classified as empirical.

Paltakari (2009) and Blum (2002) postulated two theories about the operating principle of carriers. While Paltakari postulates that carrier substances and FBAs form "some kind of complex", Blum suggests that carrier enable a monomolecular distribution of the FBAs in one layer on paper substrates (Paltakari, 2009) (Blum, 2002). In both cases, no further explanations are provided.

### Fluorescence of stilbene

The Jablonski diagram is convenient for visualizing possible processes like photon absorption, internal conversion (IC), intersystem crossing (ISC), phosphorescence, delayed fluorescence, and triplet – triplet transitions in a simple way. Furthermore, fluorescence of stilbene can be visualized easily using Jablonski diagrams as shown in Figure 1. The singlet electronic states are denoted by $S_0$, $S_1$, and $S_{2...}$ Please note that absorption is very fast ( $\approx 10^{-15}$s) with respect to all other processes. The vertical arrows correspond to absorption that starts from the (lowest) vibrational energy level of the $S_{0-}$ ground-state, because the majority of molecules are at room temperature in this level. Absorption of a photon by a trans-stilbene molecule (cf. Chapter "photo isomerization") can excite the molecule to one of the vibrational levels of $S_1$ or $S_2$ depending on the actual energy of excitation. For wavelengths between 250 and 310nm, trans-isomer stilbene dissolved in ethanol are excited from the ground state $S_0$ to the excited singlet state $S_2(v_0, v_1,..., v_n)$. Due to vibrational relaxation (VR) of the molecule $S_2$ $(v_0)$ is reached. From this stage, the molecule undergoes an IC to $S_1$ $(v_x)$. This higher vibrational level in $S_1$, undergoes VR to $S_1$ $(v_0)$.

This higher vibrational level in S1, undergoes VR to $S_1$ $(v_0)$. From this exited singlet state fluorescence can occur, i.e. the molecule reaches $S_0$ $(v_0, v_1,..., v_n)$ and a photon is emitted containing the corresponding energy difference .

For wavelength of 310-370nm the molecule is excited from $S_0$ to $S_1(v_0, v_1,..., v_n)$. Again, because of vibrational relaxation energy is reduced until $S_1$ $(v_0)$ is reached. From this particular singlet state photons are emitted until $S_0(v_0, v_1,..., v_n)$ is reached.

The emitted energy for $S_1 \rightarrow S_0$ is often of lower energy and shows therefore a red-shift. The resulting energy difference is known as STOKE's shift (cf. Gispert, 2008).

The underlying processes lead to a certain mirror image of the absorption spectra (the part that leads to a $S_0 \rightarrow S_1$ transition) and the emission spectra (Kasha, 1950). This mirror like behavior is known as KASHA's rule .

Further, detailed information about the Jablonski diagram in terms of fluorescence are discussed and explained by e.g. Sauer (2011).

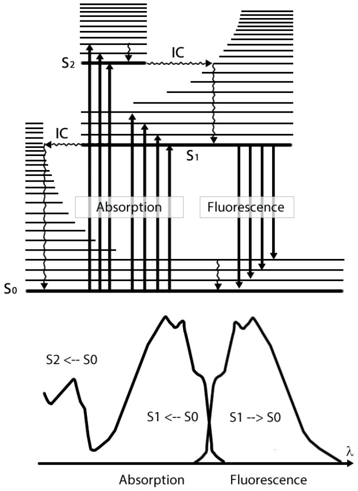

Figure 1: Jablonski diagram of stilbene (absorption and fluorescence). Straight arrows represent radiative processes, whereas wavy arrows stand for non-radiative processes. The orientation of the arrows directly gives information if an absorption is present (up-arrow) or an emission takes place (down-arrow)

### Quantum Yield

One major parameter for characterizing as well as determining whether an FBA is suitable for practical applications or not, is the quantum yield.
The fluorescence quantum yield $\Phi_F$ is the fraction of excited molecules that return to the ground state $S_0$ by emitting photons:

Formula 1: Quantum yield

$$\Phi_F = \frac{k_r^S}{k_r^S + k_{nr}^S}$$

with:

| | |
|---|---|
| $k^S_r$ | as the rate constant of the florescence |
| $k^S_{nr}$ | as the overall non-radiative rate constant |
| $\Phi_F$ | as the quantum yield |

TAs a consequence, the fluorescence quantum yield is the ratio of the number of emitted photons (over the whole duration of the decay) to the number of absorbed photons, hence the qualifier is called "quantum". Because of the Stoke's shift, fluorescence yield expressed in terms of energy is always lower than the energy in total in the case of diamino-stilbene based molecules (Sauer, 2011).
If every photon absorbed results in a photon emitted, the maximum fluorescence quantum yield is 1.0. Substances with quantum yields of 0.10 are still considered fluorescent.

### Parameters affecting Florescence

Several parameters are known to influence fluorescence in terms of observed quantum yields as well as the wavelength and characteristics of fluorescent emission (→ emission shape). Possible parameters are polarity of the solvent, available hydrogen bonds, pH-value of the solvent, pressure, viscosity, temperature, presence of quenchers, electric potential and ions.

E.g., the viscosity of a solvent affects directly the obtainable quantum yield: A higher viscosity leads typically to an increased quantum yield. This relation is described by the FÖRSTER-HOFFMANN law (cf. Formula 3).

In the context of this study, the parameter "viscosity" is considered with special attention (cf. Chapter "Quantum Yield of the tetra-based FBA in dependency of different PEG- concentrations and -molar masses").

### Photoisomerization of stilbene

In chemistry, photoisomerization in general is molecular behavior in which structural changes between isomers are caused by photoexcitation. Both, reversible and irreversible isomerization reactions exist. However, photo isomerization is typically a reversible process as it is found for stilbene.

A simple functional entity, allowing for two different conformations, is the C=C double bond as it is found in the stilbene base structure as it is used in the research conducted for this paper. Based on the arrangement of the two largest ligands, a trans-isomer where both ligands are on opposite sides of the double bond, and a cis-isomer where both ligands are on the same side of the double bond, can be realized (Schmidt-Weber, 2008). Both are shown in figure 2.

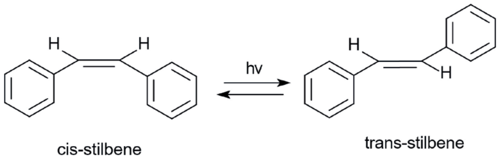

Figure 2: Photon induced photo isomerization of stilbene

Figure 3 shows the absorption spectra of both stilbene isomers, if solved in ethanol (cf. Beale, 1953). It can be seen that a common absorption minimum can be found at 245nm, while the absorption maxima between the cis- and the trans isomer differ significantly (cis-isomer: 280nm; trans-isomer: 305nm). Furthermore, the absorption of the trans-isomer in this wavelength region is much stronger, compared to the absorption of the cis-isomer.

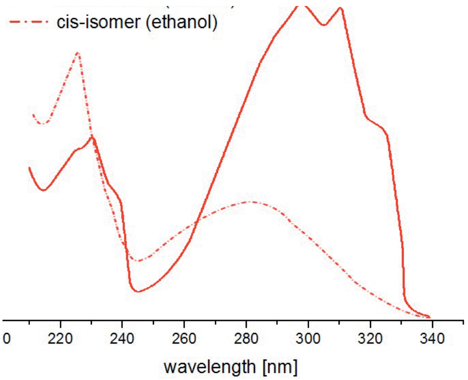

Figure 3: Absorption spectra of the cis- and the trans-isomer solved in ethanol. Differences can be found especially in the wavelength region between 280nm and 340nm (following Beale, 1953)

Abrash and coworkers (2009) elaborated the corresponding energy diagram for the photoreactions of the stilbene isomers based upon the direct excitation into the $S_1$ state (cf. Abrash, 2009). Figure 4 show several possible pathways for structural changes of the cis- and for the trans-isomer form respectively (following Abrash, 2009).

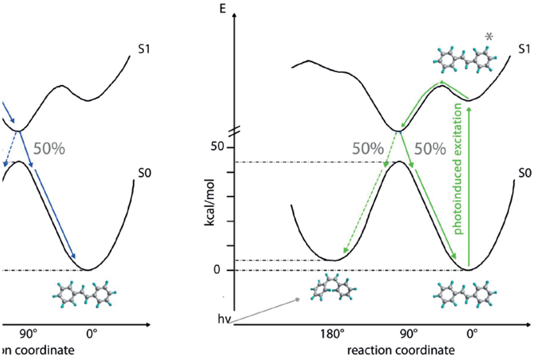

Figure 4: Energy diagram for conversion between stilbene isomers for a cis-isomer initiated isomerization (left) and a trans-isomer initiated isomerization (right)

Figure 4 (left) shows the pathway of a cis-isomer if excited into the excited singlet state $S_1$. Because of this excitation the photoisomerization is initiated and leads to a change of reaction coordinate (abscissa in Figure 4) with regards to the C=C double bonds angle $\Theta$ (cf. figure 5). Following the reaction coordinate, the $S_1$-potential is dropping until an energy of 50 kcal/mol is reached. At this point, the cis isomer relaxes back to the ground state $S_0$ with a 50% - 50% probability of further existing in the cis- or the trans-configuration respectively. The lifetime of the excited cis state is 1ps (Todd, 1998). During this period the isomer is able to emit photons, but mainly at the same wavelength as it has been excited with (absorption = emission).

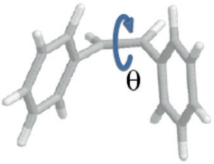

Figure 5: Rotation coordinate $\Theta$ of the C=C double bond of a stilbene molecule

In contrast, Figure 4 (right) shows the pathway of a trans-isomer if excited to the excited singlet state $S_1$. Again, because of excitation, the photo isomerization is initiated and leads to a change of reaction coordinate with regards to the C=C double bonds angle $\Theta$ (cf. figure 4 (right)). Following the reaction coordinate, the $S_1$-potential is dropping again until an energy of 50 kcal/mol has been reached. At this point, the trans-isomer relaxes back to the ground state $S_0$ with a 50% - 50% probability of further existing either in the cis- or the trans-configuration. The main difference is the much longer lifetime of the trans- isomer, which has been determined to be 70ps long (Todd, 1998). The reason for the longer period arises from a local maximum of the potential curve, as it is shown in figure 4 (right). Again, during this period, the isomer is able to emit photons. Thereby, the trans-isomer emits at longer wavelengths (red-shift), what we perceive as fluorescence. Because of the much longer period in which the trans-isomer exists, more photons are emitted from the excited state. Another important implication of the extended lifetime is that more trans-isomers may exist since the photo isomerization is a continuous process.

## Methods

This chapter is split into methods that have been used for colorimetric studies and methods, that have been utilized for chemical studies

Colorimetric studies

For all colorimetric studies, a laboratory UV-VIS-Spectrophotometer of the company Tec5 GmbH with a spectral range of 250-780nm and a spectral resolution of 1nm in combination with a 200-Watt Xenon-high pressure light-source has been used. The readings have been done using a 45:0-degree measurement geometry. Furthermore, several UV-Cut filter have been used to fully or partially suppress the excitation of FBAs that are applied to substrates. Utilizing the principle of printing liquid FBAs using inkjet (cf. Bohn, 2016), three FBAs and (poly-)ethylene glycol ((P)EG) acting as a carrier with differing average molar masses have been applied (cf. Table 1) to three (mostly) un-brightened substrates (cf. Table 3).

Table 1: Overview of used Fluorescent Brightening Agents and their relevant properties

| **Chemical name** | **Short name** | **Molecular mass [g/mol]** |
|---|---|---|
| Di-sulfonated diamino-stilbene acid derivative | di-type | 1036.57 |
| Tetra-sulfonated diamino-stilbene acid derivative | tetra-type | 1165.05 |
| Hexa-sulfonated diamino-stilbene acid derivative | hexa-type | 1513.00 |
| Polyethylene glycol | PEG | 200, 400, 1000, 2000 (average) |
| Ethylene glycol | EG | 62.07 |

Table 2: Used substrates with relevant parameters

| Name | Manufacture | Grammage [g/m$^2$] | FBA | Surface | White point (M1) | | |
|---|---|---|---|---|---|---|---|
| | | | | | L* | a* | b* |
| ProNatur | unknown | 200 | non | Uncoated, matte | 99.31 | -0.34 | 1.65 |
| GMG ProofPaper semi-matte 250 | GMG | 250 | non | Coated, semi-matte | 97.16 | -0.68 | -2.55 |
| EFI BestXpress | EFI | 250 | non | Coated, semi-matte | 96.38 | 0.24 | -2.82 |

Table 3: Overview about printed FBA & Carrier combinations as well as concentration variations

| **Sample number** | **Used FBA** | **Concentration [%]** | **Used Carrier** | **Carrier [%]** | **Water [%]** |
|---|---|---|---|---|---|
| *Without Carrier* | | | | | |
| 1-t | tetra-type | 0.05 | non | 0 | 99.95 |
| 2-t | tetra-type | 0.2 | non | 0 | 99.8 |
| 3-t | tetra-type | 0.8 | non | 0 | 99.2 |
| 4-t | tetra-type | 3.2 | non | 0 | 96.8 |
| 5-t | tetra-type | 6.4 | non | 0 | 93.6 |
| 6-t | tetra-type | 20 | non | 0 | 80 |
| *With Carrier* | | | | | |
| 4-t-1 | tetra-type | 3.2 | PEG 1000 | 1 | 95.8 |
| 4-t-2 | tetra-type | 3.2 | PEG 1000 | 2 | 94.8 |
| 4-t-3 | tetra-type | 3.2 | PEG 1000 | 4 | 92.8 |
| 4-t-4 | tetra-type | 3.2 | PEG 1000 | 8 | 88.8 |
| 20-t-1 | tetra-type | 20 | PEG 1000 | 1 | 79 |
| 20-t-2 | tetra-type | 20 | PEG 1000 | 2 | 78 |
| 20-t-3 | tetra-type | 20 | PEG 1000 | 4 | 76 |
| 20-t-4 | tetra-type | 20 | PEG 1000 | 8 | 72 |

## Chemical studies

Bohn already showed that the chemical environment "substrate" strongly interacts with FBA-inks (Bohn, 2016). Because UV-VIS-reflectance spectrometer based readings (cf. chapter "colorimetric considerations") do not allow readings of the absorption, excitation & emission behavior of FBAs and carries independently from substrates UV-VIS-measurements on a chemical level are needed.

For that reason, to fully understand the occurring interactions of the FBA- and carrier-molecules, absorption spectra of all FBAs and carriers (cf. table 3) have been acquired in an aqueous solution by utilizing a UV-Vis-spectrometer (device name: Cary 50; company: Agilent Technologies; spectral range: 200-900nm; 0:0 geometry). Thereby, this type of spectrometer gathers data from liquids based on transmission readings (in contrast to the UV-Vis-reflectance spectrometer as it is used for substrate measurements (cf. chapter "colorimetric studies).

Next, a fluorescence spectrophotometer (device name: Cary Eclipse; company: Agilent Technologies; spectral range: 200-900nm; 0:90 geometry) is utilized to gain spectral emission and excitation readings of all FBAs with and without carrier dissolved in an aqueous solution.

By utilizing fluorometric readings, substrate related effects are avoided and a reliable base is given to study previously observed effects, like greening and substrate depending emission intensity differences on a chemical founded level.

These readings are used to calculate fluorescent quantum yields of isolated FBAs in pure water and with several ethylene glycol and polyethylene glycols and concentrations acting as solvents. It is important to understand that, in addition to (P)EG, other substances are known to act as a carrier. (P)EG shows no absorption at the excitation wavelength of interest (340nm) nor at wavelengths showing emissions (380-550nm), even for concentrations up to 30%.

The quantum yield of the analyzed FBAs is calculated by utilizing Formula 2. This formula is an easy and commonly accepted way to determine the quantum yield of unknown substances. This method relays on a fluorescence standard with a known quantum yield. For this study the substance anthracene (CAS: 120-12-7), dissolved in ethanol, is utilized as a fluorescence standard. Anthracene is known to possess an average quantum yield of 0.27 in ethanol (Melhuish, 1961). Furthermore, the absorption and emission spectra of anthracene is suitable for the chosen excitation wavelength of 340nm, which has been selected for all excitation analysis in this study. The absorption and emission spectra of anthracene is shown in figure 6.

Formula 2: Used formula to determine quantum yields

$$\Phi_X = \Phi_{ST}\left(\frac{Grad_X}{Grad_{ST}}\right)\left(\frac{\eta_X^2}{\eta_{ST}^2}\right)$$

With

| | |
|---|---|
| $\Phi_X$ | as the quantum yield of an unknown substance |
| $\Phi_{ST}$ | as the known quantum yield of a fluorescence standard |
| $Grad_x$ | as the linear gradient of the unknown substance |
| $Grad_{ST}$ | as the linear gradient of the fluorescence standard |
| $h^2_x$ | as the squared refraction index of the solvent, which has been used to solve the unknown substance |
| $h^2_{ST}$ | as the squared refraction index of the solvent, which has been used to solve the fluorescence standard |

Please note I:
The linear gradient can be calculated from different absorption levels (Absorption <= 0.1) that are plotted against the integrated emission.

Please note II:
Both, the FBAs as well as the fluorescence standard have been diluted until an absorption max of 0.1 had been reached to avoid non-linear effects like inner filter effects. A full description of the for this study utilized approach to calculate the quantum yield is described by (Horiba, 2017).

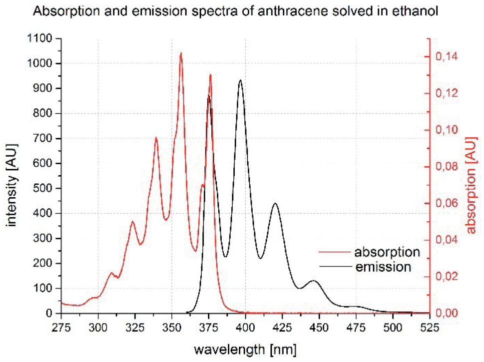

Figure 6: Absorption and emission spectra for anthracene dissolved in ethanol. The emissions spectra is based on an excitation at 340nm

Additionally, obtained spectral absorption and emission readings are used for further analysis.

Finally, the viscosity of all solvents has been determined by utilizing a rheometer (Physika MCR 101), since increasing viscosities are known to have an effect on the obtained quantum yield (cf. chapter "Influences on fluorescence").

## Results

This chapter is divided in colorimetrical based considerations regarding printed FBA-s using inkjet and chemical based considerations of FBAs in the liquid state

### Colorimetrical Consideration

Substrate specific comparison for a single FBA-type & -concentration

Figure 7 shows the a* b*-color coordinates for the FBA-ink "t-5" (cf. table 3) with (nominal) area coverages starting from 0% (whitepoint of the substrate) up to 100% in 10% steps (Frequency modulated).,The green mark equals a 0% area coverage and the red mark equals a 100% area coverage in each case.

In the case of the substrate "GMG ProofPaper semimatte 250" a strong negative increase of the b*-value ($b^*_{0\%\text{-AC}}$ = -2.5 → $b^*_{100\text{-AC}}$ = -19.1, with AC as the area coverage of the applied FBA) can be observed, while the a*-value only slightly increases ($a^*_{0\%\text{- AC}}$ = -0.85 → $a^*_{100\text{-AC}}$ = 3.1). The a*b*-shift shows a linear behavior for all area coverages. Please note that this linear behavior is known to be a typical FBA-emission behavior without any greening.

The substrate "BestXpress" behaves comparable to the substrate "GMG-Semimate". Only the whitepoint differs right from the beginning (GMG-Semimate: a*: -0.85; b*: -2.5 / Best-Xpress: a*:0.1; b*: -1). Apart from that, the same linear a*b*-behavior is observed.

In the case of the substrate "ProNatur" a moderate increase of the negative b*-value ($b^*_{0\%\text{- AC}}$ = 2 → $b^*_{100\text{-AC}}$ = -8.3) is found, while the a* value shows a significant decreases ($a^*_{0\%\text{-AC}}$ = -0.43→ $a^*_{100\text{-AC}}$ = -1.9). The a*b*-shift shows a non-linear behavior for high area coverages (90% & 100%). Divergent from the already discussed substrates, this papers whitepoint shifts towards coordinates of the Lab-system that are associated with the color impression "green". This can be interpreted as significant greening.

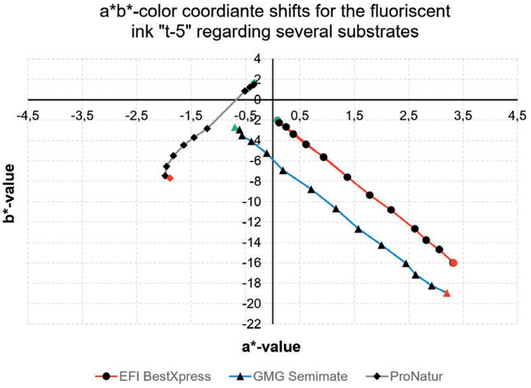

Figure 7: a*b*-color coordinate shifts of a tetra-based FBA-ink (6.4% concentration) for area coverages of 0% - 100% regarding three differing substrates without carrier

To outline these effects, Figure 8 shows the spectral response of all three substrates once with an area coverage of 0% (actual paper whitepoint) and once with 100% FBA-ink area coverage.

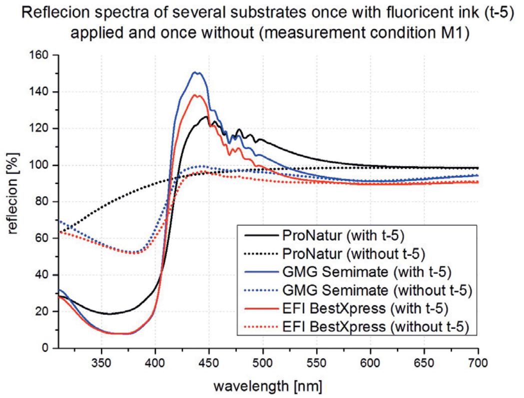

Figure 8: Total radicance factor of three substrates once with FBA-ink (type: t-5; 100% area coverage) and once without (0% area coverage) applied to three substrates and once without (measurement condition: M1)

In conclusion, it can be argued that the chemical environment "paper" has a significant influence on the performance of applied FBAs using inkjet.

*Influence of different FBA-concentrations*

Figure 9 shows the influence of several FBA-concentrations (0.8%, 3.2%, 6.4% & 20%) on the a*b*- coordinates for several area coverages. For concentrations of 0.8%, 3.2% & 6.4% an increase of the negative b*-value is observed and therefore an increase of emission. The a*-value is slightly increasing in an comparable way. For a concentration of 20%, the b*-value is lower than for the 6.4% concentration. Furthermore, the a*-value is in comparison significantly decreased. This leads to a significant greening. In conclusion, an increase of absorption leads to intensified blue emissions until a certain point is reached and the blue emission becomes greenish. This may occur because of inner filter effects or quenching.

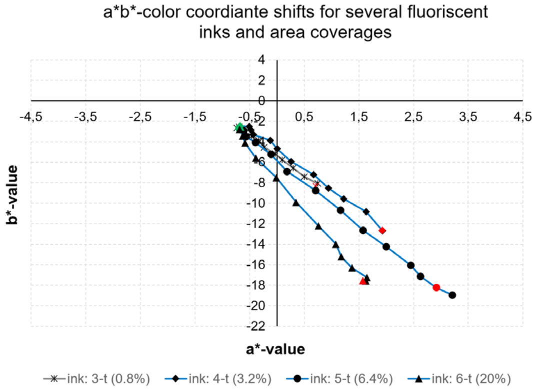

Figure 9: a*b*-color coordinate shifts of several tetra-based FBA-inks varying in their concentration (0.8%, 3.6%, 6.4% & 20%) for area coverages of 0% - 100% without carrier regarding the substrate "GMG ProofPaper semimatte 250"

Figure 10 shows the influence of polyethylene glycol with an average molar mass of 1000 g/mol in a concentration of 8% added to 3.2% & 20%-FBA-inks. For the 3.2%-ink, the b*-value is nearly doubled from -12.7 to -24.01. Therefore, the obtained blue emission is also nearly doubled. For the 20%-ink, the greening is prevented.The b*-value is decreases from -17.9 to -16.

In conclusion, it is shown that the addition of PEG enables stronger fluorescent emissions on substrates while greening is prevented. The presented colorimetrical analysis does not allow conclusions about the way PEG interacts with FBAs. Because substrates are complex, in terms of their molecular structure, it is difficult to derive interpretations of observed effects.

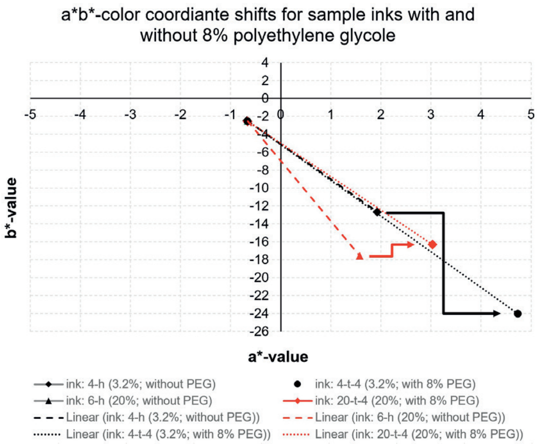

Figure 10: a*b*-color coordinate shifts induced by the FBA-inks 4-h, 6-h (without carrier) 4-t-4 and 20-t-4 (with carrier) regarding the substrate "GMG Semimate"

Hence, in the next chapter "Chemical Considerations" FBAs and Carriers are studied detached from the molecular environment paper in the liquid state.

## Chemical Considerations

### *Quantum Yield and spectral analysis of used FBAs without carrier in solution*

Figure 12 shows the obtained absorption values of all FBAs & anthracene plotted against the integrated emission intensity for an excitation wavelength of 340nm. It can be seen, that all measurements of a diluting series show linear gradients with very good correlation coefficients ($R^2$) of 0.9967 up to 0.9902. Furthermore, all gradients run through the zero point of the diagram. This is a strong evidence that no impurities of the solutions distort the obtained quantum yields.

The obtained values are used to calculate individual quantum yields (cf. Figure 11) by utilizing Formula 2.

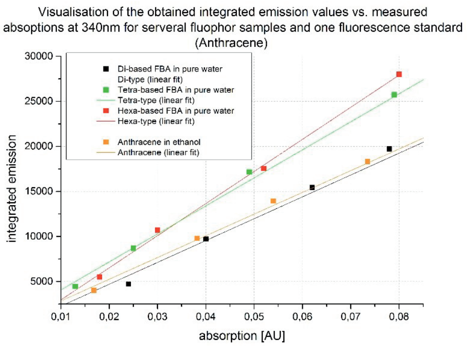

Figure 11: Visualization of obtained emission values plotted against measured absorptions at 340nm for the FBAs "di-type", "tetra-type" and "hexa-type". The linear dependency obtained for each sample-series show very good $R^2$-values. Furthermore, all grades run through the 0-point of the diagram, indicating that no impurities or measurement errors have compromised the results.

Table 4: Details about used FBAs and the fluorescence standard "anthracene" with obtained quantum yields

| Name | Used solvent | Average molar mass $[g\cdot mol^{-1}]$ | Quantum yield $\Phi$ [%] |
|---|---|---|---|
| Di-type | $H_2O$ | 1036.57 | **26%** |
| Tetra-type | $H_2O$ | 1165.05 | **33%** |
| Hexa-type | $H_2O$ | 1513.00 | **38%** |
| Anthracene | Ethanol | 178.23 | **27%** |

For the FBA "tetra-type" a quantum yield of 0.33 was found, while the FBA "hexa-type" shows a slightly higher quantum yield of 0.38. The FBA "di-type" shows the lowest quantum yield of 0.26.

Figure 12 shows the normalized absorption and emission spectra of all three FBAs.

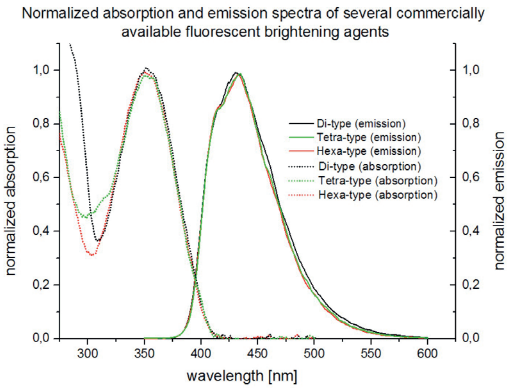

Figure 12: Normalized absorption and emission spectra of several FBAs solved in $H_2O$. Common emission maxima at 435nm and common absorption maxima at 350nm are obtained. Differences in local minima are found in the range of 275-325nm

It can be seen, that the normalized emission spectra of all three FBAs (di-, tetra- and hexa-sulphonated) correlate very well. This is also true for the main absorption at 350nm, which is very relevant for practical applications in the print and paper industry. Only the secondary absorptions (for wavelengths <= 325nm) show significant differences.

It can be stated that the number of sulphonic-groups do not affect the relevant absorption wavelength area (320-420nm) as well as the shape of the emission spectra (380 – 570nm). Furthermore, it can be derived that most likely existing functional groups, that are able to change the wavelength of absorption and emission, are present in a comparable manner in all three types of FBA. This assumption is derived from the molar mass of the diaminostilbene base molecule and the molar masses of the commercially available FBAs. The assumption that functional groups are in fact influencing e.g. the emission wavelength is derived from the fact that the base stilbene shows absorption and emission wavelengths of lower energy (cf. figure 3).

*Quantum Yield of the tetra-based FBA in dependency of different PEG- concentrations and -molar masses*

The FBAs "di-type", "tetra-type" & "hexa-type" have been studied, only when dissolved in pure water acting as a solvent. In this chapter the tetra-based FBA is examined with regard to its interaction with (P)EG, which is known to be a suitable carrier to "activate" and "intensify" the emission. The used molar masses of (P)EG are presented in table 3. in chapter "Methods".

Table 5 shows the obtained quantum yields of the tetra based FBA for several solutions which are composed out of poly- (ethylene glycol) with different molar masses (and therefore different chain lengths) and concentrations. The rest of the solution is substituted with pure water in each case. The prepared combinations of (P)EG and water are acting as solvents.

Additionally, the measured solution specific refractive indexes as well as measured viscosity values are shown.

Table 5: Obtained viscosities, refraction indexes and quantum yields for several (P)EG solutions (see next page)

| Name | Added substance | Average molar mass [g·mol$^{-1}$] | (P)EG [%] | $H_2O$ [%] | Viscosity [mPa*s$^{-1}$] | Quantum yield | Refraction index |
|---|---|---|---|---|---|---|---|
| EG 10% | Ethylene glycol | 62.07 | 10 | 90 | 1.34 | 0.373 | 1.347 |
| EG 30% | Ethylene glycol | 62,07 | 30 | 70 | 2.64 | 0.441 | 1.381 |
| EG 50% | Ethylene glycol | 62.07 | 50 | 50 | 3.95 | 0.496 | 1.401 |
| EG 100% | Ethylene glycol | 62.07 | 100 | 0 | 10.1 | 0.60 | 1.451 |
| PEG 200, 2.5% | Polyethylene glycol | 200 | 2.5 | 97.5 | 1.08 | 0.374 | 1,335 |
| PEG 200, 5% | Polyethylene glycol | 200 | 5 | 95 | 1.27 | 0.417 | 1.338 |
| PEG 200, 10% | Polyethylene glycol | 200 | 10 | 90 | 1.66 | 0.511 | 1.342 |
| PEG 200, 30% | Polyethylene glycol | 200 | 30 | 70 | 4.08 | 0.580 | 1.377 |
| PEG 400, 2.5% | Polyethylene glycol | 400 | 2.5 | 97.5 | 1.25 | 0.436 | 1.336 |
| PEG 400, 5% | Polyethylene glycol | 400 | 5 | 95 | 1.4 | 0.486 | 1.334 |
| PEG 400, 10% | Polyethylene glycol | 400 | 10 | 90 | 1.75 | 0.548 | 1.344 |
| PEG 400, 30% | Polyethylene glycol | 400 | 30 | 70 | 5.1 | 0.607 | 1.376 |
| PEG 1000, 2.5% | Polyethylene glycol | 1000 | 2.5 | 97.5 | 1.56 | 0.535 | 1.339 |
| PEG 1000, 10% | Polyethylene glycol | 1000 | 10 | 90 | 2.04 | 0.594 | 1.345 |
| PEG 1000, 30% | Polyethylene glycol | 1000 | 30 | 70 | 8.32 | 0.599 | 1.391 |

Please note, that PEG and EG have been chosen for further analysis since all variants of this substance show no absorption at the excitation wavelength at 340nm and in the wavelength area 380- 570 where the emission takes place. Hence, direct comparisons of the obtained quantum yields become possible.

Figure 13 shows the logarithmically plotted quantum yield against the logarithmically plotted viscosity for all solvents in combination with the tetra-based FBA (5-t).

For the solvents based upon the substance ethylene glycol (EG) with concentrations of 10%, 30%, 50% and 100% a linear dependency can be identified. The obtained quantum yield is growing for increasing viscosities. This behavior is in accordance with the FÖRSTER-HOFFMANN law (cf. formula 2).

Formula 3: Förster-Hoffmann law

$$\log\Phi = C + x\log\eta$$

with:
$\Phi$ as the quantum yield
$\eta$ as the viscosity of the solvent
C as a temperature dependent constant
x as a substance specific constant

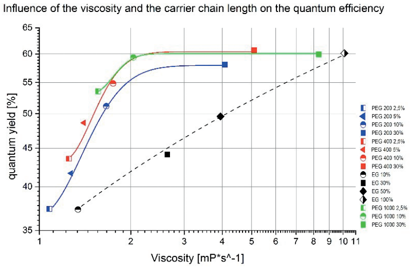

Figure 13: Influence of the solvents viscosity and carrier chain-lengths on the quantum yield

For all other solvents that base on PEG (concentration >10%) this law seems to fail. E.g., in the case of PEG 200 with an average molar mass of 200g/mol no linear dependency can be observed for concentrations of 2.5%, 5%, 10% and 30%. In particular, low concentrations of PEG 200, PEG 400 and PEG 1000, and therefore low viscosity changes (PEG 200 2.5% →1.1mPa→PEG 200 5% →1.2mPa → PEG 200 10%→1.4mPa), result into dramatic higher quantum yield gains compared to EG solutions (10% → 1.06 mPa).

A comparable behaviour can be observed for PEG 400 & PEG 1000 based solvents. If only moderate high concentrations of PEG are used (e.g. PEG 200 2.5%, 5% and 10%) a linear behavior can be identified (cf. figure 14).

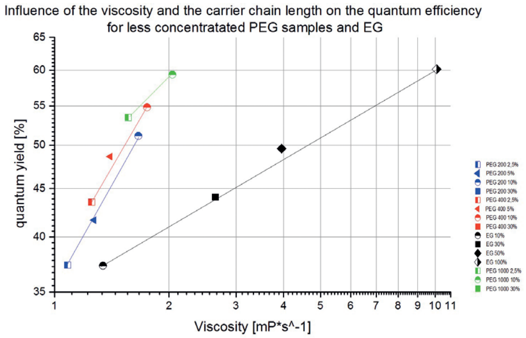

Figure 14: Influence of the solvents viscosity and carrier chain-lengths on the quantum yield for selected concentrations of EG and PEG in $H_2O$. A linear dependency is found in accordance to the "Förster-Hoffmann-Law"

It can be concluded that this behavior results from a maximum quantum yield that can be achieved by slowing down the inversion reaction (C=C double bond twist). Other non-fluorescent deactivation reactions are not affected, so the quantum yield cannot be increased beyond this value (cf. figure 5). Therefore, the period in which especially the trans-isomer exists is extended. Because the only difference between all solvents can be found in the chain length of the molecules (which only moderately increases the viscosity) this parameter seems to influence massively the obtainable quantum yield even for low concentrations of PEG compared to EG.

To outline this behavior Figure 15 shows a reduced dataset. Again, all EG based solvents with 10%, 30%, 50% & 100% are shown, while only the 10% concentration variant of the PEG 200, PEG 400 and PEG 1000 solvents are plotted. Even the 30% EG solution, which shows a comparable low viscosity of 2.64 compared to the viscosities of 10% PEG 200 (viscosity: 1.66), PEG 400 (viscosity: 1.75) & PEG 1000 (viscosity: 2.04), shows a significant lower quantum yield of 37% compared to the quantum yields obtained from the other solutions (PEG 200 10%: $Q_{eff}$: 0.551, PEG 400 10%: $Q_{eff}$: 0.548, PEG 1000 10%: $Q_{eff}$: 0.594).

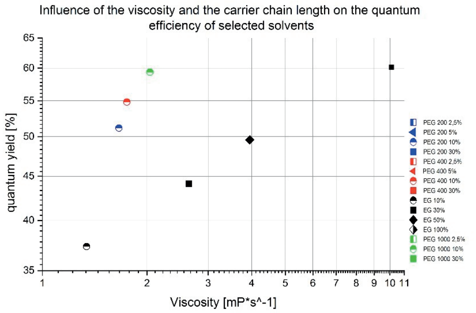

Figure 15: Influence of the solvents viscosity and carrier chain-lengths on the quantum yield for selected chain-lengths of PEG in comparison with EG in $H_2O$. The parameter chain length leads to higher quantum yields for lower viscosities.

These data indicate that not only the viscosity affects the quantum yield but especially the chain length of the molecules, which can be interpreted as a substance specific parameter, as it is considered by the FÖRSTER-HOFFMANN law. One possible explanation is that the chains lead to a certain "physical" hindering of the isomerization. This effect is possibly intensified due to in one another cross-linked chains, increasing the physical boundary of the C=C double bond twist of the isomerization and thus reduces the reaction speed of the isomerization itself.

With figure 4 in mind, it can be assumed that the lifetime of the excited trans-isomer is further extended by this effect (viscosity and chains), leading to a higher ratio of the fluorescent trans-isomers compared to the less fluorescent cis-isomers. This in conclusion results in an increased quantum yield compared to non-chained-molecules such as ethylene glycol.

To give further proof, a spectral analysis of the absorption spectra of the tetra-based FBA shows a significant red-shift for all 30% PEG-solutions compared to pure water (10nm shift) and the EG-based solutions with concentrations of 50% and 100% (4nm shift) (not shown).

As shown in the chapter "State of the scientific knowledge" the absorption spectra of the cis- and the trans-isomers differ significantly (cf. figure 3). More precisely, the trans-isomers absorption shows a significant red-shift in the wavelength region of 290-340nm compared to the cis-molecules absorption (cf. figure 16).

If these spectra are compared with the absorption spectra of the tetra-type FBA once solved in pure water and once solved in 30% PEG 1000, it can be seen, that the local absorption minimum of 310nm remains the same, while the peak at 345nm (pure water) shifts to 355nm (30% PEG 1000) (cf. figure 16).

Against this background, it can be assumed that the shift of wavelength results from a higher ratio of trans-isomers that have a higher fluorescence quantum yield in PEG and are therefore changing the isomer ratio, benefiting the trans-isomer. As already shown (cf. figure 13), this effect occurs also of increasing viscosities but much less distinct compared to solutions containing PEG (and therefore longer chains). In conclusion, this gives another indication that the quantum yield is increasing due to higher numbers of trans-isomers that are exited for an extended time-frame.

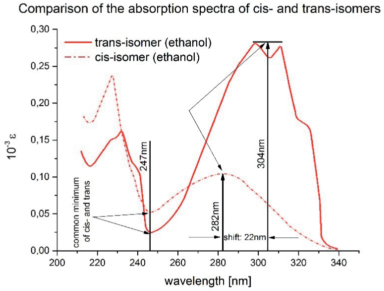

Figure 16: Absorption spectra of cis- and trans-isomers solved in ethanol

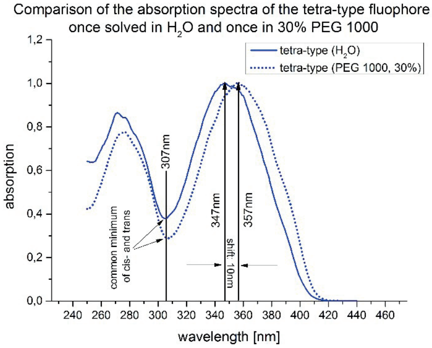

Figure 17: Absorption spectra of the tetra-based FBA once solved in pure water and once in 30% PEG 1000

Figure 18 shows the absorption as well as the emission spectra of the tetra-based FBA once solved in PEG 1000 (30%) and once solved in pure water. Next to the already shown red-shift of the absorption, a blue-shift of the emission is obtained. Furthermore, the blue-shifted emission (tetra-FBA in 30% PEG 1000) shows a "double peak", if compared to the FBA solved in pure water. This double peak is also found for the pure trans-isomer (cf. Figure 16). Hence, the "mirror-rule" applies very well.

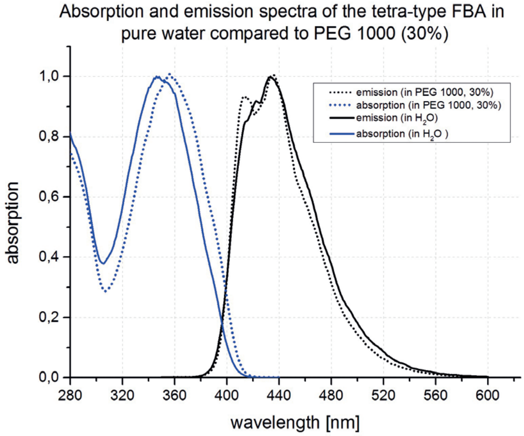

Figure 18: Absorption and emission spectra of the tetra-based FBA once solved in pure water and once in 30% PEG 1000

## Discussion

The presented results show that the quantum yield of commercially available FBAs can be increased by the addition of carrier substances. It was found that the obtainable quantum yield directly correlates with the actual chain-length of used carrier-molecules.

The correlation between chain length and emission intensity was also found empirically for printed FBA-ink-layers on unbrightened.

Figure 19 shows the obtained emission spectra of FBA-ink samples printed on the unbrighened substrate „Epson SPP 205". With Figure 16 and Figure 17in mind, it can be concluded that the obtained second peak at 415nm for the 5%-PEG, 6.4%-tetra-type FBA-ink result out of a higher ratio of the trans-isomer. Hence, PEG-chain-length related effects do not only occur while in the liquid state and detached from the molecular environment "paper" but also in the non-liquid state, e.g. if applied using inkjet or applied during paper-production.

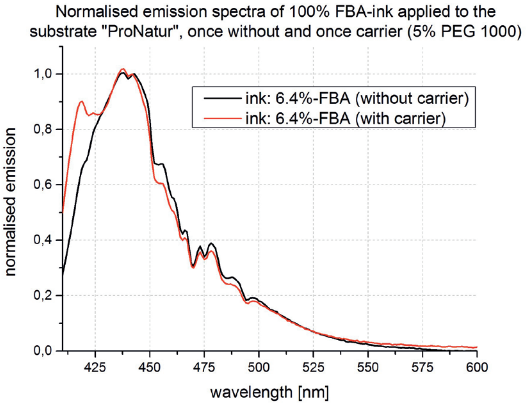

Figure 19: Normalised emission spectra of 100% FBA-ink applied to the substrate "ProNatur", once without and once carrier (5% PEG 1000). A blue-shift is found for the carrier containing sample

Against this background, the theories of Paltakari and Blum seem to be unlikely:

- Blum assumed that carriers promote a monomolecular distribution of FBAs in one layer on a paper-surface. Since in this study observed effects also occur while in the liquid state no monomolecular distribution can be realized.
- Paltakari suggested that FBAs and carriers create "some kind of complex". Out of a chemical perspective, a complex is typically related to metal components. This is very unlikely for the given substances. In this study it is assumed, that long-chained PEGs are linked together for high concentrations, intensifying this way the steric hindering of the C=C double bond. This can be interpreted as some kind of complex.

## Conclusions

In this study it is shown, that the chain-length of carriers such as PEG has a very significant impact on the quantum yield. Already low concentrations (10%) of PEG in the liquid state, result in a boost from 33% quantum yield up to 60% (in the case of the tetra-type FBA). The actual chain-length of the carrier (derived from the actual average molar mass) is the driving factor for increased quantum yields. Spectral analysis indicate that this increase in quantum yield results mainly from higher numbers of trans-isomers compared to the number of cis-isomers (cis-trans ratio). It is shown, that this shifted ratio towards the trans-isomer results probable not only from viscosity related effects on the quantum yield but especially the chain length of the molecules, which can be interpreted as a substance specific parameter as it is considered by the FÖRSTER-HOFFMANN law. One possible explanation is that the chains lead to a certain "physical" hindering of the isomerization. This effect is possibly intensified due to cross-linked chains, increasing the physical boundary of the C=C double bond twist of the isomerization and thus reduces the reaction speed of the isomerization itself.

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# Identification of skills gaps in cross-media design and production in the creative industries at the national level

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Keywords: Cross-Media Design and Production, Creative Industries Sector Skills Councils, Policy Initiatives Future Skills

## 1 Introduction

This second of two initial reports into the developing requirements of the Creative Industries Cross Media Design and Production sector will focus on national strategies of the four CIGN participating nations (Belgium, Germany, UK/Scotland and Sweden) and observations from the silent partner, Ryerson University in Toronto, Canada.
These approaches vary. Not all of the partner's home countries have a cohesive national strategy for gathering data on the emerging Creative Industries sector in Europe and beyond. Geographically, the home countries and communities differ greatly in the scale and composition of regional and national governance. In some cases, they adopt a National Sector Skills Council approach to gather data on emerging Cross Media Design and Production areas. Others rely on a close relationship with key industrial partners as a way of communicating, sharing best practices and identifying future labour and market trends and requirements.
It is the intention of this report to identify these varying national strategies, investigate the main findings from each partner's research and identify key areas for future curricular development within a shared pan-European, and future global networks.

## 2 Country Strategies

A questionnaire, based on findings from the initial research was distributed to key national agencies/strategic partners, and once collated, form the basis of curricular development in the emerging area of Cross Media Design and Production

## 2.1 Belgium

### 2.1.1 Background information

In Belgium, many initiatives are carried out for matching skills demand and supply. Many of these initiatives are undertaken at regional levels, as this task is the responsibility of the regions and not of the Federal Government. Education is the responsibility of the linguistic communities of Belgium (Dutch-speaking, French-speaking and German-speaking) and continuing vocational training is the responsibility of the Regions (Flanders, Wallonia and the bilingual Brussels-Capital). Sectorial bi-partite agreements (commissions paritaires), which set the employment and continuous training frameworks, are signed at the national level but are generally executed at regional/community levels. As the University College Artevelde resides in the Flemish region, this document will limit its research scope to this region.[1]

### 2.1.2 Main findings of the study

In Flanders, there are sector commissions in the following sectors: goods transport, metal and technological industry, textile and confection, welfare and health care, timber and construction, and tourism. These commissions formulate policy proposals regarding socio-economical issues in specific sectors for the Flemish Government. Their composition and competence are similar to the Social and Economic Council, but limited to a specific sector. The sector commissions are made up of employer and employee representatives.

In 2004 the Flemish Government established the Flanders District of Creativity. The main aim of this organization is to stimulate creativity in industries in order to create new jobs and to maintain a healthy economic environment. Within this framework a position paper [2] was published in 2011 by the 26 Flemish Creative organisations united in the Flanders Creative Industries Platform. In this paper they formulated six policy priorities for further follow-up by the Flemish government. One specific policy recommendation urges the Flemish government to further the integration of business and entrepreneurship skills training among higher arts education and other education courses that prepare students for a career in the Creative Industries.

[1] This country report refers to data presented in the report: Sector Councils on Employment and Skills at EU level [1]

There is no single body responsible for skills identification for the Creative Industries in Flanders. However, there are a number of sectoral training funds (STFs) monitoring skills identification for various segments of the creative industries, but not for the creative industry as a whole. In particular, GRAFOC[2] and CEVORA[3] are of interest for the identification and training of new competences for professional profiles in media design and production. Additionally, there is mediarte.be. This sector training fund deals the audio-visual field. The board is composed of employers' and employees' representatives. Thus, education or training bodies are not represented on those boards.

All the STFs are run by bipartite and joint boards, which have equal representation from employees and employers. In general, both private and public training centres and consultants provide training and other supported activities to the STFs. Both promote training programmes and employment opportunities. For the implementation of training programmes, they cooperate with a network of specialized partners for which they can contract educational institutions and professional trainers. In addition to the two organizations mentioned above, there is also the SERV[4]. The Competency Team of SERV is working on development and implementation of the occupational profile database, Competent in close co-operation with the VDAB (Flemish Employment and Training Service). The
team is working with Flemish employer and employee organizations and the various sectors. Competent is an occupational profile database. It contains profiles with the details of occupations, the activities employees are expected to perform, required competencies and expertise, and how the work is organized. The profiles cover the entire labour market. They are classified into domains and clusters, which makes the information easy to search. SERV ensures that the profiles remain up-to- date and that they are approved by the social partners. In the area of education and training, the content of Competent serves as the prime source for the Flemish Qualification Framework. Over time, in Flanders we will also be working in this policy domain with a 'common' competence language. Competent is able to support sectors, companies and organizations with their HR policy, job classifications, etc. Based on the data in Competent, they can develop instruments linked to those used by providers of labour market services and training.
All three organizations mentioned run their study centre that monitors employment development in the sectors and undertakes studies on several issues such as hard-to-fill occupations, professional and qualification profiles, and training needs. Studies are undertaken in cooperation with other research centres, federations, social secretariats, and outsourcing agencies. Extensive contacts are maintained with companies for identifying and monitoring training needs. As CEVORA covers a number of sectors as opposed to GRAFOC it is the larger of the two and it employs a greater number of professional staff.

Besides the activities of the above-mentioned organizations, many activities are undertaken in Flanders and Belgium to identify skills demand and supply and to enhance skills. An example is a joint project of the Flemish Government and social partners known as Competence Agenda 2010 [3]. The project has a budget of 38 million Euros, which is being used for competence development in the period 2007 to 2009[5]. To form the agenda, an external research company was commissioned to undertake research on future skills, amongst others. The project develops the talents and capacities of students, teachers, jobseekers and employees so that more people are employed[6].
Since there is not an active sector council for the creative industries, the Belgian partner of the CIGN- project took the initiative to contact potential and possible partners of such a creative skills council and to propose a meeting. At this meeting the questionnaire regarding future skills for the creative industries will be discussed. The following organizations are contacted: CEVORA, Mediarte.be, GRAFOC, Flanders DC and SERV.

## 2.2 Germany

### 2.2.1 Background information

In Germany education, professional training, culture and media are not competences of the Federal Government but of the federal states. The Ständige Konferenz der Kulturminister der Länder is the coordination body of cultural and education ministers of the federal states. It has different committees and subcommittees including committees on higher education, professional training, and culture. The main national organisation concerned with vocational education is the Federal Institute for Vocational Training (BIBB). Social partners sit in its governing body and are directly involved in the development of the curricula of regulated professions taught in the dual system (a combination of

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[2] GRAFOC is the sectoral training fund for labourers (blue collar workers) in the print media industry. http://www.grafoc.be/

[3] CEVORA is a transversal training fund for employees (white collar workers) in a range of sectors. http://www.cevora.be/generic/wiezijnwij

[4] SERV: In the Flanders Social and Economic Council (SERV), Flemish employers and employees discuss and consult about issues falling within the scope of Flemish authority.

theoretical and on-the-job learning). In addition to the dual system (mostly for technical occupations), professionals active in audio-visual sectors graduate from arts and research universities (performers and other artistic occupations, journalists, etc.), universities of applied sciences (sound engineers, senior technicians, producers, etc.), and in private education and training bodies.

Continuous training is less developed but ad-hoc schemes are managed by educational institutions, employers' dedicated institutes (e.g. ARD, ZDF Medienakademie or RTL School of Journalism) and professional organizations (Deutscher Bühnenverein, German Association of Orchestra, German Theatre Technical Society, etc.).

### 2.2.2 Main findings of the study

There is no equivalent to National Sector Skills Councils in Germany. Dialogue and co-operation between the world of education and training and the labour market are decentralised, except for regulated professions (dual system, negotiations under the umbrella of the Federal Institute for Vocational Training). Many participants, (public institutions, employers, trade unions, professional associations, networks of schools and universities, etc.) are active in the education and training fields, and produce occupational standards, education and employment data, etc. Information is not centralised however at the sector level in the perspective of monitoring trends in employment and skills needs. Education and training bodies (especially universities) have developed specific projects (i.e. the Nexus project or dedicated Career centres) to support students' insertion in the labour market.

### 2.2.3 Assessment of and participation in (a) European Sector Skills Council(s)

Interests from German stakeholders in seeing the set up of (a) European Sector Skills Council(s) in the audio-visual field are mixed for reasons of opportunity (solid German vocational and educational landscape), representation (no equivalent bodies to Sector Skills Councils, decentralized decision making processes at federal state level), and perspective (resistance to a potential harmonization of educational and training systems). Interest in an enhanced exchange of information and best practices at European level between education and training providers and labour market stakeholders has been expressed but only if implemented in a light and flexible way.

The specific objectives of a European body, and the representation of German stakeholders in such a structure will need to be further discussed with German social partner and education representatives.

## 2.3 Scotland/United Kingdom

### 2.3.1 Background information

In the UK, the generally accepted definition of the creative industries is: 'Those industries which have their origin in individual creativity, skill and talent which have a potential for wealth and job creation through the generation and exploitation of intellectual property'. (UK Department of Culture, Media and Sport[7])

The Scottish Government describes the Creative Industries as: 'those which have their origin in individual creativity, skill and talent. They include industries that have the potential to create wealth and jobs through the development, production or exploitation of intellectual property' [4]. Research has shown that the UK has the largest creative sector in the EU and possibly the largest in the world relative to Gross Domestic Product [5].

Internationally, a UN report found that between 1996 and 2005, that global trade in creative goods grew at an annual rate of 8.7% [6]. The creative industries in Scotland generate more than £5 billion of turn-over in the Scottish economy and in March 2011, the Scottish Government made a commitment to build on this potential – 'The creative industries, including digital content and technologies, is one of these sectors. Research has shown that the UK has the largest creative sector in the EU and possibly the largest in the world relative to GDP' [4]. The creative industries sector in Scotland experienced significant growth over the last decade. In 2008, turnover in the creative industries stood at £5.7 billion, while GVA was £3.0 billion [4]. Between 2000 and 2010 GVA in the sector increased by 25% in real terms, compared to 14% in the economy as a whole.

Scotland's cultural development body, Creative Scotland[8] was formally established on July 1, 2010 as a single, national body for arts, culture and creative industries. Its aim is to modernize the network of investment, build new relationships and support Scottish talent and creative enterprises to empower them to succeed at home and internationally and help realize the potential contribution of creativity in every part of society and the economy.

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[5] http://www.esfagentschap.be/uploadedFiles/Voor_ESF_promotoren/Nieuwe_oproepen/Fiche%20oproep%20Lerende%20Netwerken%20 Competentiemanagement

[6] http://www.acw.be/content/view/905/400/

[7] https://www.gov.uk/government/policies/media-and-creative-industries

### 2.3.2 Sector Skills Councils

The UK has a very well developed model of Sector Skills Councils. Two national Sector Skills Councils deal with, among other subsectors, the areas covered by the CIGN project.

Sector Skills Councils in the UK are independent, employer led UK wide organizations that aim to develop skills standards with employers to support productivity and profitability growth and enhance competitiveness in UK and overseas markets. There are 18 sector skills councils and 5 sector skills bodies in the UK who work with over 550,000 employers to define skills needs and standards in their industry.

There are 2 main Sector Skills Councils in the UK pertaining to the Creative and Cultural Industries (herein CCIs): Creative Skillset[9] (TV, Film, Radio, Interactive Media, Animation, Computer Games, Facilities, Photo Imaging, Publishing, Advertising and Fashion and Textiles) and Creative and Cultural Skills[10] (Craft, Cultural Heritage, Design, Literature, Music, Performing, and Visual Arts), both of which have Scottish departments as an integral part of their structure.

Creative & Cultural Skills, primarily focus on the areas of music, theatre, design and cultural heritage and also provide opportunities for employment, training and apprenticeships in each of these convergent sectorial areas.

Creative Skillset focus on the areas of Advertising and Marketing Communications, Animation, Fashion and Textiles, Film, Games, Photo-Imaging, Publishing, Radio, Television and VXF and are therefore very well served to assist the CIGN project in the area of Cross Media Design and Production. CSS cover the four countries that make up the United Kingdom, (England, Northern Ireland, Scotland and Wales). Regional centres are located in each country and address specific local as well as national requirements.

Both organisations have dedicated full time staff and run large-scale research projects in the fields of labour market intelligence and apprenticeships, among other initiatives: The CCIs in the UK can also be influenced by other Sector Skills Councils, in particular e-Skills UK[11] (Software, Internet and Web, IT Services, Telecommunications and Business Change). It is important to note the increasing blurring of boundaries and interdisciplinary fusion between the various elements and platforms that make up the creative industries in the UK.

In 2010 a CIHE report stated senior BBC technical staff, producers, engineers and technologists will increasingly converge into teams working together to deliver interface, service and content – as one product – rather than different teams working in isolation and then hoping to tie the solution together. This led to e-Skills, Skillset and Creative & Cultural Skills consistently identifying development of hybrid skills – 'technical, business, creative, and interpersonal – as the vital pre- requisite of monetizing content and services' [7].

### 2.3.3 Characteristics of the CCIs in Scotland

CCIs in Scotland are characterized as being/having:

- Small businesses
- A high proportion of work is self-employment/freelance work.
- The Labour Force Survey 2010 showed around 20-25% of the creative industries workforce is self-employed – more than double the average for all industries across Scotland
- Overall, 25% of those working or available for work in the Creative Media Industries are 'freelance'[12] and the remaining operate on an 'employee' basis [14]
- For the Creative and Cultural Skills footprint 44% describe themselves as 'self-employed'.
- Excluding self-employment, although there has been a steady increase in employment e.g. from 38,500 people in 1998 to over 63,000 in 2012
- In 2008 there were 8,485 registered enterprises operating in the CI sector in Scotland (5% of all registered business in Scotland); 97% of the enterprises are small, Scottish owned and account of 69% of employment, 60% of which have 0 employees)
- The Employer Survey report indicates that 75% of employers recruit through personal contacts
- Project/ad-hoc work
- Informal hiring/work experience
- Lower pay but higher satisfaction?
- Portfolio career?
- Adaptable and resourceful
- Creative networks are key
- Strong work ethic
- Aware of competition
- High levels of resilience

### 2.3.4 Main findings of the study

UK sector skills councils are responsible for the live performance, design and cultural heritage; (Creative & Cultural Skills) and audio-visual sectors (Creative Skillset). They have developed strong ties with the industry through their governance structures, their consultations schemes, and other ad hoc co-operations implemented in the context of specific projects.

They are employers' led bodies but they also involve trade

[8] www.creativescotland.com
[9] www.creativeskillset.org
[10] www.ccskills.org.uk
[11] www.e-skills.com

unions and further and higher education sectors in their strategic decisions. Stakeholders confirmed the representative voice of those organizations in skills discussions.
The UK sector skills councils have developed sophisticated models to gather labour market intelligence in the audio-visual and live performance sectors. They also offer on-line information portals for career development in those sectors. Apprenticeship and the development of quality training schemes have been one of the key focus areas of both organizations in the recent years.
Creative & Cultural Skills and Creative Skillset have already been involved in numerous European and international activities. Transfer of good practices from the UK to other countries has been one of the main focuses of those partnerships.

### 2.3.5 Assessment of and participation in European Sector Skills Council(s):

Creative and & Cultural Skills and Skillset are the relevant UK participants to future European Sector Skills Council(s). Both organizations have expressed a strong interest in such a structure, even if the Council(s) to be set up cover only part of their respective remit.
Both councils are representative of national stakeholders involved in skills discussions. Direct involvement of national participants should be considered on an ad-hoc basis.
Both councils could share a vast amount of labour market and future skills intelligence. They could also transfer qualitative experience and know how in many aspects of skills forecasting, qualification developments, information portals, apprenticeship frameworks, etc.

## 2.4 Sweden

### 2.4.1 Background information

There are no Sector Skills Councils in Sweden. Training issues are dealt with at the company level in social dialogue frameworks or in the context of sector initiatives. However there are professional advisory bodies, to the Creative and Cultural Industries below.
The Swedish Employment office has a dedicated culture and media department offering specific support to unemployed workers in those sectors, including access to training. It produces regular data on unemployment trends in the culture and media field, and convenes several times a year a consultation group made up of professional organisations and education providers. Focusing on an exchange of information, this group is not developing overall strategies on skills anticipation or skills matching.
Several other public institutions (Arts Council, Arts Grant Committee, etc.) address the topics of employment and working conditions in the sector, and produce data and statistics.

### 2.4.2 The Agency for Higher Vocational Education

The main mission of this agency is to be responsible for matters relating to the Polytechnic in Sweden and to ensure that training meets the needs of working life skills.
They analyze the social needs of education in the Polytechnic, deciding which courses are to be included in the UAS and oversee government grants for the training. They check and also assess the quality of programs and results. In addition to this, they are responsible for matters relating to two forms of education that are outside the Polytechnic - arts and cultural education and interpreter training programs in adult education.

The Authority oversees the training requirements and programs that are within their remit, and manage comments and complaints on education. They are also responsible for coordinating a national structure for validation of training and professional skills, and they are the national focal point for the EQF (European Qualifications Framework).

### 2.4.3 The Public Employment Service

Labour market related institutions have experienced a long history in Sweden. The Public Employment Service (AF - Arbetsförmedlingen), was founded at the turn of the 19th century. Over time, it evolved from a private organization into a public one. Sweden also has a long tradition concerning the involvement of the social partners in labour market related councils, although more for continuing than in initial training.

### 2.4.4 Sector and Transversal Councils

*Initial vocational education and training*

Up to now, upper-secondary education was divided into 14 vocationally oriented sectors (e.g. health care, technology) and 3 academic national programs. The main features of this structure were approved by Parliament some 15 years ago. To ensure that the various programs matched requirements of, on the one hand higher education and on the other, of the labour market, temporary committees were set which prepared curriculum outlines (aims, subjects, exams, etc.).
The tri-partite working groups (representatives from the

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[12] 'Freelance' = contract of less than 365 days and „employee"=contract of 365 days or more.

branches / sectors, the trade unions, and the school system) prepared the programs in close cooperation with the world of work. The national level Agency of Education is responsible for ensuring that the aims and outlines of the various programs keep matching the changing requirements of higher education and the labour market. Whenever this is no longer the case, a new temporary working group is formed to revise the curriculum outline.

Currently, a reform of upper-secondary education is being proposed. The new upper secondary structure will have three tracks: the academic and vocational tracks will be modernized and a new apprenticeship system be added. For each of the programs, an advisory board will be set up to develop the program outlines. In the law, the tri-partite advisory boards will be given a permanent status. This status creates the conditions for a better contact between the training system and the world of work.

*Continuing Vocational Training*

The Public Employment Service (AF - Arbetsförmedlingen) is divided in 68 labour market regions. Each region has a Regional Branch / Skills Committee including representatives from the business sectors and from a host of public bodies. It influences decisions concerning the scope and orientation of the supply of labour market training, i.e. training for workers and job seekers.

In contrast to some other member states, although Sweden has Sectoral Training Funds in some sectors, they do not play a significant role with regards to the planning and provision of continuing vocational training. CVT arrangements are made, in very general terms in the collective labour agreements, and, in specific terms at the level of individual firms.

### 2.4.5 Forecasting of jobs and skills needs

The main providers of information on qualitative and quantitative trends in the labour market, from a long to a short-term perspective, include:

Statistics Sweden (SCB - Statistika Centralbyrå) provides with 'Trends and forecasts' an overview of demographic developments and trends in education and training and on the labour market. On the basis of detailed projections of labour market supply and demand, areas of mismatch (excess/shortage) are identified. In the years when 'Trends and forecasts' is not issued, a complementary forecast is published in 'Education and work', which makes predictions for the next five to ten years. The publication comprises assessment about potential mismatches between the supply and demand for education by educational groups.

A third forecast is the 'Labour market tendency survey'. It presents short-term forecasts based on a sample of firms whose employees represent those educational groups that are considered most relevant. There are several SCB surveys about 'on the job training'. It has to be emphasizes that many of the SCB surveys cover both quantitative and qualitative aspects, e.g. the survey on working conditions. Almost all of the statistical data is presented at both national and regional levels.

The Public Employment Service (AF - Arbetsförmedlingen) is since January 1, 2008 the new Swedish labour market authority. It combines the National Labour Market Board and the County Labour Boards. The AF is engaged in short-term forecasts based on regular surveys and on-going contacts with employers' organizations, trade unions and other key stakeholders. The AF also carries out surveys in specific branches/sectors, e.g. in relation to temporarily layoffs and the mismatch between supply and demand. The surveys, which are mostly occupation-based, are a minor activity within the AF.

The National Institute of Economic Research (KI - Konjunkturinstitutet) performs analyses and forecasts of the Swedish economy and conduct-related research. Besides monthly broad economic forecasts, KI regularly asks a minimum of 3,000 firms in the private sector for their assessment of the development of the economy (output, new orders, employment, labour shortage etc.). The objective is to provide a quick qualitative indication of actual outcomes and expectations regarding central economic variables for which no quantitative data is yet available. These surveys cover manufacturing, the building sector, and part of the private services sector.

### 2.4.6 Assessment of and participation in (a) European Sector Skills Council(s)

All participants consulted during the study visit expressed an interest in accessing European-level information on employment and skills needs trends in the live performance and audio-visual sectors, and in developing European collaborations. As there is no formal sector body dealing with employment and skills, Swedish participation to a European structure would need to be further discussed with social partners.

## 2.5 Canada

The participation of Canada in this committee grew from pre-existing relationships between the School of Graphic Communications Management and the European partners. These relationships included student and faculty cooperation in research projects and education.

### 2.5.1 Background information

As the world's second-largest country by landmass, Canada faces new challenges when it comes to the assessment and delivery of skills-based education for Creative Industries and cross media producers. The geographic size of the country is such that it could encompass all of the European CIGN partner countries within its boundaries. Canada is subdivided into ten provinces and three northern territories. Canada's population includes only 35 million persons. The cities of Toronto, Montreal and Vancouver each have more citizens than some of the provinces and territories. Outside of the major cities, the country is one of the most sparsely populated in the world, with the majority of citizens living and working along a shared border with the United States. Canada is an officially bilingual country (English and French) with the majority of the French-speaking population living in the province of Quebec.

Canada exhibits a population bulge in the baby boom generation – a group that will exit the workforce over the next ten years. The country, in anticipation of this situation, has aggressively welcomed immigrants from many other countries. Both geographic and demographic factors require innovative thinking with regards to educating a new and renewed workforce.

Although the bulk of cultural activities and cross media production are found in relative proximity to Canada's shared border with the United States, cultural activities are valued in all parts of the country. In the report Creativity Unleashed the worth of the Creative Industries was described thus "In Canada, the cultural sector was worth $84.6 billion in 2007, or 7.4% of Canada's total real GDP – more than the insurance industry ($20.8 billion), the hotel and restaurant industry ($28 billion), or the agriculture, forestry, hunting and fishing industries ($26.4 billion) combined."[8] A report by the Conference Board of Canada indicated that in 2007 the Cultural sector employment exceeded 1.1 million jobs.

In other words the economic definition of Creative Industries is that it is a sector of the global economy that is focused on creating as well as exploiting intellectual property products such as films, music, games, fashion designs, etc. and/or at providing creative services. Typically the list would include areas such as:

- Advertising
- Architecture
- Art and Antique Markets
- Crafts
- Design (objects, furniture, etc.)
- Designer fashion
- Emerging Medias (New media)
- Film and Video
- Interactive leisure software (Wii, video games…)
- Interior Design
- Music
- Performing Arts (Theatre, Dance, Musicals…)
- Photography
- Publishing
- Software and computer services
- Television and Radio

The term Cross-Media is may be defined as a design created and distributed in a variety of media and formats. In Canada this could be demonstrated by a marketing campaign that runs in print media and television, and is then supplemented by apps, web sites, and magazines. These media crossovers are often perceived as being new, however they combined use of traditional media with emerging technologies. In the current media-landscape[13] consumers control the use of media; they decide when and where they wish to access specific media and content. The cross media sector itself defines the term as follows:

"The cross media-sector provides multimedia products and services by using radio, television, Internet, mobile devices, print and events simultaneously along each other." [9]

Education and training in Canada is organized and provided by publicly funded universities and community colleges, as well as industry organizations, labour unions, and private educational institutions. In addition, some larger corporations provide their own on-the-job training and education solutions. Each of the ten provinces and three northern territories assume responsibility for public education. Funding is provided from the government sources, from tuition fees, and from donations and endowments.

Education is a provincial jurisdiction means that curricula and research specialties are focused on the provincial or regional level. The Canadian federal government funds agencies that provide grants to artists and cultural workers, the provincial (and territorial) governments are involved in the funding and regulation of community colleges and universities, and the provincial and municipal governments oversee events related to cultural industries. Cultural industries activities are also funded by not-for-profit and private sector organizations. In the appendix of this report, please find an annotated listing of provincial and territorial references to the Creative Industries. Few mention policy, and links to formal education providers are scant.

Skills assessments are becoming increasingly important. In 2013, Employment and Social Development Canada published the report "Skills in Canada: first results from the Program for the International Assessment of Adult Competencies (PIAAC)". This report compares "literacy, numeracy and problem solving skills in technology-rich environments (TRE)" across the Canadian provinces along with OECD member countries.

### 2.5.2 Assessment of and participation in (a) Canadian Sector Skills Council(s)

Sector Skills Councils exist in Canada and predominantly serve trades and service sectors of the economy. "The Sector Council Program (SCP) in Canada is guided by four principal objectives:

- Increased industry investment in skills development to promote a quality workforce;
- A learning system that is informed of, and more responsive to, the needs of industry;
- Reduced barriers to labour mobility, leading to a more efficient labour market; and
- Enhanced ability of industry to recruit and retain workers and to address human resources issues." [10]

The Sector Council Program states that each council "…provides information regarding employer expectations; hiring practices; how training is planned, developed and delivered; and, labour market conditions within that sector. They also provide information on career opportunities for the sector; apprenticeship programs; assessing foreign credentials; integrating immigrants into the workplace; developing occupational standards and certification programs; and, advancing a 'learning culture' in Canada for employers and workers alike." [11]

The list below shows different sector councils by industry. Unfortunately, few of these have a direct relationship with the Creative Industries or cross media production:

- Aboriginal Human Resource Council
- Apparel Human Resources Council
- BioTalent Canada
- BuildForce Canada
- Canadian Agricultural Human Resource Council
- Canadian Apprenticeship Forum
- Canadian Automotive Repair and Service Council
- Canadian Council for Aviation & Aerospace
- Canadian Council of Professional Fish Harvesters
- Canadian Printing Industries Sector Council
- Canadian Steel Trade and Employment Congress
- Canadian Supply Chain Sector Council
- Canadian Tourism Human Resource Council
- Canadian Trucking Human Resources Council
- Child Care Human Resources Sector Council
- Cultural Human Resources Council
- Environmental Careers Organization of Canada
- Electricity Human Resources Canada
- Food Processing HR Council
- Forest Products Association of Canada
- Forum for International Trade Training
- HR Council for the Non-profit Sector
- Information and Communications Technology Council
- Mining Industry Human Resources Council
- Motor Carrier Passenger Council of Canada
- Petroleum Human Resources Council of Canada
- Police Sector Council
- Wood Manufacturing Council[14]

*The Canadian Printing Industries Sector Council*
This sector council was established in 2006 in response to concerns among employers related to education and training, marketing the services of the industry. In 2012 the federal government indicated that Sector Council that funding would be reduced, and then withdrawn, and it was left to individual industry groups to decide whether they could or would support the work of the councils on an on-going basis. As a result, the Canadian Printing Industries Sector Council was disbanded in 2013. The HR Toolkit develop by the Canadian Printing Industries Sector Council was later absorbed
into the Canadian Printing Industries Association[15] representing the pre-press, press, bindery and
allied industries, where it is still available. "Among the tools and resources CPISC developed are national skill standards lists, occupational profiles, labour market information, a roadmap of industry technology, an online HR toolkit, and the Career Focus Program that co-chair Jeff Ekstein said has helped companies attract new people to the industry." The only strong provincial Sector Council in Canada at present is situated in the province of Manitoba.

*Growing Awareness of Creative Industries and Cross Media production in Canada*
Schawk™ promotes cross-media services to benefit customers who are concerned about brand protection across various media. Schawk's services include (among others), retail catalogues, product packaging, digital production, POP displays, store circulars, brand advertising and marketing collateral.
At the upcoming Design Educators forum (part of the Design Thinkers conference to be held in Toronto in November 2015), proposed themes include:

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[13] https://cmidm4.files.wordpress.com/2009/11/social-media-landscape.jpg

[14] success.ca/index.php/partner-engagement/sector-councils

[15] www.cpia-aci.ca/en/

- How design curriculum can respond to the external pressures of evolving technologies, labour market demands and professional practices?
- How design schools are moving beyond traditional disciplinary boundaries and modes of communication to embrace new models of collaboration and holistic education?

Outside of the education system, there is increasing interest in cross media production. Based on a survey of topics presented at the Merging Media conferences in 2012, 2013, and 2014 it clear that the cross-media field (or as it is sometimes referred to in the promotional brochures, "trans media"), is only partially "cross" or "trans". Premedia, print and post-media processes are rarely referred to. The majority of participants are involved in fields utilizing by not referred to including web development, gaming, television and video production.

In Canada, there is one university and over eight community colleges offering programs related to the printing industry. Numerous others offer programs in graphic design and other digital processes. Similar to post-secondary educational institutes the United States, several post-secondary educational institutions in Canada view presses (and pressroom operations as being high cost (equipment, consumables, supplies and technical staff).

*Cross Media Skills Education*

It is important to recognize the link between cross media skills and cross media production. Although the term "cross media" is rare for course offerings in Canada, it is not an indication that courses related to the principles of cross media production do not exist. Marketing courses are strongly promoted in almost all business-related degrees in Canada. Courses in real-time personalization and variable-data printing (VDP) are also promoted, both in business schools and in technical courses related to the printing of VDP documents.

Where cross media production and Creative Industries leadership appears to be burgeoning is in educational institutions. University of Toronto hired Richard Florida at the Rotman School of Business; Sheridan College launched a bachelor's degree in interaction design in 2014. Ryerson University launched a bachelor's degree in a modular-based Creative Industries program in 2013. OCAD University launched The School of Graphic Communications Management at Ryerson University has recently revamped its curriculum, launching in fall 2015 and will introduce the course GCM 362[16]: Web and Cross Media.

Other areas where cross media, and cross media education are emerging include the following:

- The American owned Shawk corporation is promoting itself on it's Canadian website as "Schawk! is a Global Cross-Media Production Agency[17]
- Interactive Advertising Bureau of Canada (IAB Canada) "IAB Canada's Cross-Media Optimization Studies (CMOST) programme has, to date, conducted ground-breaking research for nine major Canadian advertisers with the help of Dynamic Logic. These studies include the following clients: Molson, RBC Insurance, General Motors, Canadian Tire, Unilever, AIM Trimark, Kal Tire, Red Bull and Tetley Tea.
- The key objectives of IAB Canada's CMOST programme are to help Canadian advertisers understand how to utilize interactive advertising within a media mix, by providing fact-based proof of how the internet works within various multi-media campaigns; and, to create a continuous ad effectiveness learning program which engages leading Advertisers, Publishers and Agencies across multiple industries, and using various types of ad creative, messaging, formats, media, timing, etc.[18]

Canada Post offered the following in 2013, in partnership with Xerox, the Lowe Martin Group (private commercial printing company) and XMPie: "The Cross-Media Campus is an industry initiative, championed by Canada Post and sponsored by industry leaders who have pledged their financial support, their influence and their expertise to expand the relationship marketing and cross-media skillsets of marketing, advertising, digital and social agencies in Canada" [12]. Sessions were targeted to Production staff, as well as an executive forum. Recent offerings include cross media optimization.

- A Cross Media Conference was held at Graphics Canada 2015, Canada's Largest Showcase for the Graphic Communications and Printing Industries Apr 16-18, 2015 Toronto International Centre
- The Journalism program at Ryerson University, in it's program overview (Calendar for 2015/16, states, "Students are introduced to journalism as practised across all forms of media within the first two years, after which they may choose courses to concentrate in specific media (online, newspaper, magazine and broadcast) or gain expertise in a cross- media skill such as editing, or in a specific beat in journalism (including sports, business or international reporting)." [13]

Although there are many engaged in Creative Industries and Cross Media design in Canada, the appearance of these terms is relatively recent.

- Creative Industries are widely accepted as being of importance for cultural, social and economic benefits across the country
- Cross media not a widely recognized term in Canada, even though many companies are producing or working in cross media environments

[16] http://www.ryerson.ca/calendar/2015-2016/pg3897.html#328597

[17] r.search.yahoo.com/_ylt=A0LEVjURKGdVmZcA.C8nnIlQ;_ylu=X-3oDMTE0czFxOTFnBGNvbG8DYmYxBHBvcwMyBHZ0aWQDRkZYVUkyN18xBHNlYwNzcg--/RV=2/RE=1432852626/RO=10/RU=http%3a%2f%2fwww.schawk.com%2f/RK=0/RS=Xz6qizndZ-ylkziTd0EfrZ0fmexc-

[18] iabcanada.com/research/cmost/

- There needs to be some organization to link the fields of Creative Industries, cross media production and education together.

## 3 Conclusions

The country participants in this project have identified the following conclusions from the research conducted for this report:

- The participating countries all identify the importance of the Creative Industries for their economic, social and cultural benefits
- The development of sector skills councils related to the Creative Industries is non-existent in Sweden and Germany, disappearing in Canada, disguised as sector funds in Belgium and strongest in Scotland/United Kingdom.
- It should be noted that one of the most valuable assets of a strong sector skills council is the ability to gather labour market intelligence about the sector(s) they represent. In the countries where Sector Skills Councils are non-existent, it remains to various unconnected federal/regional or industry-based agencies to gather information and create forecasts.
- In some countries the terms "cross media" are not yet fully understood, particularly in the context of job skills.

In addition, the partners determined the following:

- The need for a better, globally accepted definition and understanding of cross media production and what it entails.
- The need for a global description of what a cross media curriculum includes (goals, projects outcomes) and discussion about how this is delivered (on site or online), and how it is administered.
- There is a strong need for government agencies (SSCs), industry, educational institutions and labour unions to work together to identify cross media jobs of the future, and to decide how to educate, train and cross-train graduates as well as current employees, to fill them.

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[8] Dr. Daniel Doz, President, Alberta College of Art and Design, speech to the Calgary Chamber of Commerce, Creative Industries Committee, Wednesday 16 February, 2011.

[9] Reynaert, Indira; Dijkerman, Daphne (2009) Basisboek Crossmedia Concepting. Den haag: Boom Onderwijs.

[10] National Qualifications Systems Forum (2009). Sector Councils in Canada. http://www.resultsthroughintegrity.com/nqsf/2009/07/sector-councils-in-canada.html.

[11] Canadian Immigrant Integration Program (2015). Sector Councils, http://www.newcomersuccess.ca/index.php/newcomer-resources/sector-councils.

[12] Canada Post Cross (2013). Cross-Media Campus – Education, Awareness & Hands-On Training for Agency Professionals. http://www.canadapost.ca/cpo/mc/assets/pdf/business/dm/trainingguide.pdf.

[13] Ryerson University (2013). 2013-2014 Undergraduate Calendar. http://www.ryerson.ca/calendar/2013- 2014/pg651.html.

[14] Skillset (2009) Employment Census, Skillset/UK Film Council (2008) Feature Film Production Workforce Survey and LFS, ONS July 2009 – June 2010.

## Appendix

British Columbia

- Creative BC, British Columbia's Creative Catalyst, http://www.creativebc.com/, The only mention of education refers to the film/movie industry.

Saskatchewan

- Association of Creative Industries of Saskatchewan, http://www.culturalindustries.sk.ca/
- Moving Saskatchewan's Creative Industries Forward -Building a Long-term Strategy, http://www.pcs.gov.sk.ca/MovingSaskatchewanFoward
- Saskatchewan funds a new creative industries agency, signalling an end to SaskFilm: http://www.theglobeandmail.com/arts/film/saskatchewan-to-fund-new-creative-industries-agency-signalling-an-end-to-sask-film/article8676463/

Manitoba

- Economic Development Winnipeg: http://www.economicdevelopmentwinnipeg.com/key-industries/creative-industries

Newfoundland

- Government of Newfoundland Entrepreneurship and Innovation – Cultural Industries, http://www.government.nl/issues/entrepreneurship-and-innovation/investing-in-top-sectors/creative-industry
- Creative Industries fund NL, http://www.stimuleringsfonds.nl/en/

New Brunswick

- Creative Futures—A Renewed Cultural Policy for New Brunswick: http://www2.gnb.ca/content/dam/gnb/Departments/thc-tpc/pdf/Culture/2014CulturalPolicy.pdf
- Brief from the New Brunswick Arts Board (artsnb), http://www.parl.gc.ca/Content/HOC/Committee/411/FINA/WebDoc/WD5138047/411_FINA_PBC2011_Briefs%5CNew%20Brunswick%20Arts%20Board%20E.html

Nova Scotia

- Film and Creative Industries Nova Scotia Act, http://nslegislature.ca/legc/statutes/film%20and%20creative%20industries%20nova%20scot ia.pdf
- Nova Scotia CAN: Building the Creative Economy in Nova Scotia, http://www.creativecity.ca/database/files/library/ns_can.pdf

Prince Edward Island

- http://www.culturepei.ca/pdfs/Andrew_Terris_CulturePEI_Sept_24th_Forum.pdf
- The Creative Economy and the English Speaking Communities in Quebec (ESCQ), https://www.ic.gc.ca/eic/site/028.nsf/eng/00040.html, (Note: This web site also includes links to a number of relevant policy papers
- LES INDUSTRIES CRÉATIVES: catalyseurs de richesse et de rayonnement pour la métropole http://www.qftc.ca/uploads/files/PDF/btmm-creative-industries.pdf

Yukon Territory

- Cultural Industry Training Fund: http://yukonartscentre.com/programs/cultural_industry_training_fund

Canada

- Strengthening Canada's Digital Advantage, Quarterly Monitor of Canada's economy http://www.ictc-ctic.ca/wp-content/uploads/2014/02/ ICTC_SCDA_Winter2014_EN.pdf

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