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Functional Ink Formulation for Individualized Smart Tags

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Abstract

Smart Tags are functional elements that combine 2D bar codes and environmental sensing into a cost effective tag that can be attached to e.g. product packages, where additional elements should not increase the product costs. Because the Smart Tags are sensitive to environmental conditions, they are dynamic thus enabling context aware services. The enabling technology behind these Smart Tags are functional inks, such as thermochromic and photochromic inks. Functional inks are available commercially for analog printing technologies, but availability to digital printing is limited. In this paper we have shown that it is possible to formulate functional inks also for inkjet printing.

Introduction

2D bar codes have been available for almost 30 years, but during the recent years, their popularity has increased. 2D bar codes, such as QR Codes and Data Matrix codes consist of black and white squares called cells. They provide a large information capacity, even up to 7336 numbers or 4464 alphanumeric characters per code. A sophisticated error correction algorithm is included, which means that information is readable even if up to 30 % of the code is destroyed. 2D bar codes can serve as a link to a database similar to linear bar codes, but they can also serve as an independent database. The physical size of the code is scalable without affecting the information capacity. This means that the cell size of a particular code can be scaled. QR Codes can be easily detected and read with many mobile phones [1] thus providing a link to a digital media and additional information.

The use of functional inks reacting to different environmental conditions in code printing enables that novel digital services are created for the consumers and other stakeholders [2]. Functional ink technologies, such as thermochromic, hydrochromic, fluorescent and photochromic inks, or oxygen and time-temperature indicators [3], make it possible to create dynamic 2D bar codes i.e. Smart Tags that enable changing the achieved information content by scanning the codes by mobile phone.

In the context of this investigation reported in this paper Smart Tags mean visible or electronic markers (2D codes, NFC) with environmental sensing functions (functional ink, sensors, indicators) combined with software intelligence (user information, location, etc.) in order to provide context aware services to end users. There are many commercially available functional inks for printing these Smart Tags.

The most popular and readily available functional ink technologies are thermochromic (changing colour with temperature) and photochromic (changing colour with ultraviolet / sun light). Other commercially available ink technologies include invisible fluorescent inks (seen under UV or IR light), phosphorescent inks (glow in the dark after exposure to a source of light), hydrochromic inks (changing colour after contact with water), and touch'n smell inks (aroma released when rubbed with a finger), among others. However, these ink technologies are mainly for analog printing methods and only a few - mostly fluorescent inks - are available for digital printing methods. The commercial inkjet printable functional inks are targeted for marking applications with continuous inkjet with no candidate for drop-on-demand inkjet. In this paper ink formulation for inkjet printable functional inks - thermochromic and photochromic inks - is reported and the focus is on piezoelectric inkjet technology in order to enable application areas outside coding and marking. Inkjet printable functional inks are essential when the end use scenario requires personalized Smart Tags.

The concept for using functional inks in enhancing dynamic nature of 2D bar codes is that parts (e.g. some of the cells) of a 2D bar code are printed with a functional ink that reacts to the surrounding environment, e.g. temperature, humidity or light conditions. In this paper the complete 2D bar code has been printed with the functional ink, but, as mentioned, the eventual idea is that only parts of the code are printed with the functional ink (Figure 1). In this way, the scanning result of the code changes dynamically when the state of the functional part changes i.e. some parts of the barcode are visible or not. Thereby, the environmental conditions have an effect on the scanning process and resulting digital service. The services can also take into account the other user and context related data, such as user profile on the smartphone and GPS location of the smartphone. These context-aware features will further improve the value and quality of the services provided. [4]

Figure 1. *Options for using functional inks as part of QR codes. From left: (red and grey) cells printed with functional inks, (green) area printed at the bottom of the code with functional ink, and OCR (yellow letter "L") combined with QR codes.*

The benefits of using Smart Tags include consumer engagement through personalized and context-aware services, direct personal contact for brand owners with consumers, increase in product quality and safety, product authenticity and integrity as well as reduction of waste. Since mobile based code scanning is used, the user does not have to understand what the different colours on Smart Tags mean. The mobile app interprets the colour in a correct way and returns the service, accordingly. TagItSmart research project has defined several use case scenarios for Smart Tags [4,5]. In one use case the Smart Tag gives information on life-cycle of the item and indicates a correct consumption temperature as well as gives advice on recycling of the package. The consumer can also be rewarded after recycling is completed. In another scenario the product authenticity is checked with the Smart Tag based on an ink reacting to mobile phone flashlight. In a third scenario the price of the product is determined at the cash register based on state and traceability history of the Smart Tag. Consumers, the potential users of these services, evaluated the TagItSmart use cases to be very interesting for them and emphasized their interest towards interactive relationship with service provider [2]. In addition, consumers are willing to use these kinds of novel services if they feel that they get additional value from them.

Materials and methods

Three inks were formulated for inkjet printing: 1) thermochromic reversible ink changing from red to clear when temperature exceeds +47ºC (ink 1), 2) photochromic irreversible ink permanently changing from clear to red when exposed to sunlight (ink 2), and 3) photochromic reversible ink temporarily changing from clear to magenta when exposed to sunlight (ink 3) and returning back to clear when the light source is removed.

The colorants were thermochromic Chameleon pigment dispersion from LCR Hallcrest originally designed for flexography printing (ink 1), dye based Lumi Inkodye RED (ink 2), and photochromic RED#19 pigment from LCR Hallcrest (ink 3). Solvents used were propyl acetate, 1,2-propandiol and water. Additives used were non-ionic surface active agent Dynol 604, and binders Reactol^{TM} 1717E (polyketone resin) and PVP (polyvinyl pyrrolidone).

The substrates were 1) 100 g/m^2 copy paper for colour printing (copy paper), 2) label paper for laser and inkjet printing (label), and 3) 254 µm thick photographic paper from Intelicoat Technologies (photo paper).

Laboratory scale multinozzle inkjet printer based on single use printhead cartridges (DMP-2850 from Fujifilm Dimatix) with 10 pl drop size was used for printing the inks with 1270 dpi resolution. Printing layout consisted of QR codes of different size: cell size between 0.25-1.00 mm with intervals at 0.25 mm. The QR code contained url "www.tagitsmart.eu/brandprotection" encoded.

Surface tension was measured with Aqua Pi Instrument from Kibron Inc. Viscosity was measured with Anton Paar MCR-301 rheometer at +20oC. Digital USB microscope Dino-Lite and Dino Capture software with 45x magnification was used to image the printed areas. For photochromic inks the light from the microscope caused challenges, because the inks react to even small amounts of UV light, and the images were not of perfect quality. Mobile phone (Nokia Lumia 625) with a suitable 2D bar code scanning software was used for decoding the printed QR codes.

Results

The different inks were evaluated for their inkjet printability, compatibility with paper substrates, visual quality and functional performance. The latter means how well the printed Smart Tags can be scanned with mobile phone and how fast and accurate the colour change of the functional part of the Smart Tag is.

For thermochromic ink formulation (ink 1) a commercial flexographic ink was used as a starting point. The ink was diluted to a lower viscosity of 5 wt-% with a suitable water-based solvent mixture consisting water and 1,2-propandiol in a ratio of approximately 2:1. 0.05 wt-% of surface active agent Dynol 604 was added for adjusting the surface tension and 1 wt-% of binder PVP for avoiding excessive agglomeration. The ink was mixed by 30 min. sonication and 18 hours of mixing, and filtered with 2.7 µm plastic filters. Sonication was used for achieving the required ink stability and decrease in particle size as proved in earlier studies [6]. The resulting surface tension was 33.4 mN/m and viscosity 4.75 cP thus making the formulation suitable for inkjet printing. The ink was inkjet printed on the different substrates at a substrate temperature of +40ºC to fasten the ink drying. For achieving dark enough codes for mobile phone reading, 10 ink layers were printed on each code. Jettability wasn't perfect, but samples were successfully printed (Figure 2). On all the substrates the QR codes with cell size down to 0.50 mm were successfully decoded with a camera phone (Figure 3). On all substrates the print quality is good except with the smallest cell size (0.25 mm) where ink spreading causes the cells not be decoded by mobile phone. However, even with the second smallest cell size (0.50 mm) the physical size of the QR code is only 14.5 mm making it suitable for many applications where only small area is available for the code.

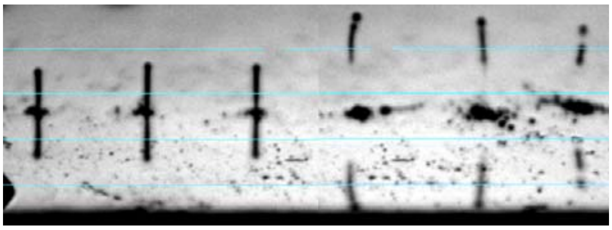

Figure 2. *Drop formation of the thermochromic ink (ink 1).*

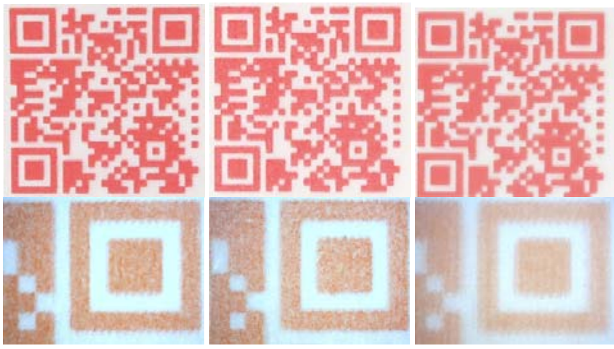

Figure 3. *QR codes with 0.75 mm cell size printed with the thermochromic ink (ink 1) on different substrates: from left copy paper, label and photo paper. Pictures are taken with a camera (above) and with microscope (below).*

Irreversible photochromic ink (ink 2) was mixed with the same solvent mixture as ink 1, but without the binder, because the colorant was a dye based one and no agglomeration was expected. Colorant concentration was 5 wt-% and the ink was mixed with sonication for 30 minutes. The surface tension was 30 mN/m and viscosity 5 cP. The ink was inkjet printed on the different substrates with 10 ink layers for achieving sufficient colour intensity. The ink has good jettability characteristics (Figure 4) and the codes were decodable down to 0.50 mm cell size on photo paper and on label (Figure 5). On copy paper there was too much ink spreading and no codes of good quality were achieved.

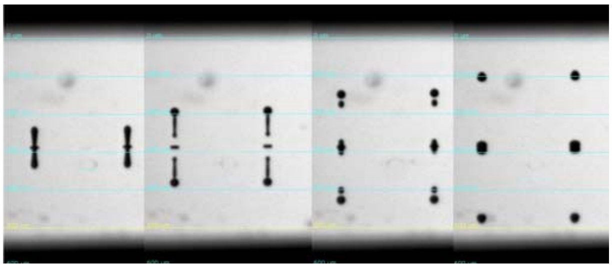

Figure 4. *Drop formation of the irreversible photochromic ink (ink 2).*

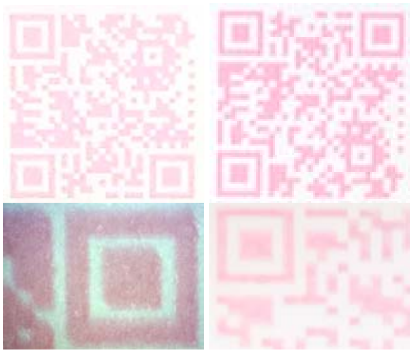

Figure 5. *QR codes with 0.75 mm cell size printed with the irreversible photochromic ink (ink 2) on label (left) and photo paper (right). Pictures are taken with a camera (above) and with microscope (below).*

Reversible photochromic ink (ink 3) was solvent based with a mixture of propyl acetate and 1,2-propandiol in a ratio of 3:2. The pigment concentration was 5 wt-% and 5 wt-% of binder ReactolTM 1717E was added. The ink was mixed with sonication for 30 minutes and filtered with 1 µm plastic filters. The surface tension was 26 mN/m and viscosity 3.5 cP. The drops contained long tails during printing probably due to the low viscosity (Figure 6) resulting in lots of ink spreading on porous substrates, and only on photo paper sufficient print quality for code scanning was achieved (Figure 7). However, with ink 3 only one ink layer was enough for high intensity codes. Microscopic images were not possible to be taken, because the colour was reversible i.e. returned to clear stage too fast under the microscope. Instead a microscope software installed on mobile phone was used.

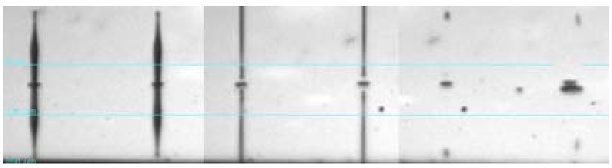

Figure 6. *Drop formation of the reversible photochromic ink (ink 3).*

Figure 7. *QR code with 0.75 mm cell size printed with the reversible photochromic ink (ink 3) on photo paper. Pictures are taken with a camera (left) and a with a mobile phone microscope (right).*

Conclusions

To conclude, it is possible to formulate functional inks for inkjet printing in order to print individualized Smart Tags required for context-aware services. Although the formulation of the functional inks presented in this paper has been successful, there is still room for improvement and fine-tuning the ink recipes, specifically use of additives for improved wetting. The intensity of the resulted colour needs further improvement in order to avoid the need to print multiple ink layers, which might cause issues in industrial scale printing processes. One possibility is to increase pigment or dye concentration in the inks. The results presented here are, however, a good starting point for further development and prove that it is possible to print functional inks, such as thermochromic and photochromic inks, with piezoelectric inkjet technology. This opens up a huge potential for brand owners to develop novel services for consumers and all the stakeholders.

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