Color differences and perceptive properties of prints made with microcapsules

ABSTRACT

The aim of the research was to establish whether addition on fragranced microcapsules influences on color values and perceptive properties of prints. For this purpose, three types of printing inks were used on two sets of the paper substrate. Color properties were measured by standard methods while perceptive properties were determined by subjective method. Research has showed that microcapsules cause small color differences while perceptive analyses gave very interesting results.

KEY WORDS
expandable inks, microcapsules, color change, color, screen printing, perception

Materials and methods

Influence of microcapsule addition into different printing inks on the color properties of prints was studied on two printing substrate, which were printed with three
different printing inks all containing the same type and amount of microcapsules and pigment. Properties of used materials are presented in the continuation.

**Paper substrates**

Paper substrate properties can play a significant role on the color properties of prints. Therefore for the purpose of the research prints were made on two different paper substrates:

- uncoated, wood-free Superprint paper, machine-finished and surface sized, with declared grammage (weight) 150g/m² (in this research indicated as SP), and
- two-side coated, wood-free Biomatt paper, with high whiteness (bright white) and declared grammage (weight) 120g/m² (in this research indicated as BM).

According to declared values, coated BM printing substrate had lower grammage. Paper substrate SP had more opened structure compared to BM, which was determined by SEM in previous research (Stankovič Elesni et al., 2014). As it can be seen in Table 1 SP paper substrate had a rougher surface than coated BM paper substrate, which had smoother more uniform surface with micropores. Measured values of capillary rise indicated that both SP and BM printing substrates were very hydrophilic, thought SP uncoated substrate showed higher absorptiveness that was, according to its surface, expected. Measured color values showed that both paper substrates had very similar properties of lightness (L*) and color opponent dimensions (a*, b*). Calculated color difference has shown that the color difference of both selected paper substrates was minimal (0.42).

<table>
<thead>
<tr>
<th>Property</th>
<th>Sample</th>
<th>SP</th>
<th>BM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Height of capillary rise [mm]</td>
<td></td>
<td>19 / 17</td>
<td>13 / 12</td>
</tr>
<tr>
<td>MD / CD</td>
<td></td>
<td>138.0</td>
<td>138.0</td>
</tr>
<tr>
<td>Roughness [ml/min]</td>
<td></td>
<td>148.6 / 138.0</td>
<td>64.2 / 102.0</td>
</tr>
<tr>
<td>Side A / Side B</td>
<td></td>
<td>138.0</td>
<td>64.2 / 102.0</td>
</tr>
<tr>
<td>Color values</td>
<td></td>
<td>94.29</td>
<td>94.35</td>
</tr>
<tr>
<td>L*</td>
<td></td>
<td>1.01</td>
<td>0.96</td>
</tr>
<tr>
<td>a*</td>
<td></td>
<td>-2.54</td>
<td>-3.30</td>
</tr>
<tr>
<td>b*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Color difference ∆E [/]</td>
<td></td>
<td>0.42</td>
<td></td>
</tr>
</tbody>
</table>

**Printing inks**

Printed samples were made with three different commercially prepared (ready-to-use) printing inks – two 3D expandable and one ordinary printing ink (with no expandable components), all from Achitex Minerva Spa (Italy):

- **Minerfoam SR** contains acrylic polymer and expandable microcapsules and is composed of vinylidene chloride-acrylonitrile copolymer (in this research indicated as MF-SR). MF-SR properties: density 1.05g/m³, viscosity 110dPa∙s and pH value 8.5;
- **Minerfoam FL** contains acrylic polymer and expandable microcapsules and is composed of acrylonitrile copolymer (in this research indicated as MF-FL). MF-FL properties: density 0.95g/m³, viscosity 110dPa∙s and pH value 9.1;
- **Elastic Comprente** (in this research indicated as EC), which was highly elastic water-based paste with acrylic binders, without expandable microcapsules. EC properties: density 0.95g/m³, viscosity 110dPa∙s and pH value 8.2.

EC is an ordinary screen printing ink, with no expandable properties, which was used for the comparison with two other selected printing inks. MF-SR and MF-FL printing inks are inks, which expand due to the presence of thermally expandable microcapsules, which consist of flexible wall and liquid expanding agent core material (low boiling hydrocarbon or other volatile material) (Garner et al., 1979). At elevated temperature the core of microcapsules vaporizes and the pressure inside the microcapsules increases thus causing the expanding of the wall by several times (Harper, 2006; Wang 2014). The degree of expansion is time and temperature (above 130°C) depending, but also the amount of printing ink and properties of paper substrate must not be overlooked (Yushi-Seiyaku et al., 2005; Pasquet et al., 2011). Both expandable printing inks distinguished in their properties as well as their printed appearance: MF-SR exposed rubbbery effect while MF-FL exposed velvet effect. EC gave smooth surface.

Before printing, all three inks were analyzed by SEM. Image analyses have shown that MF-SR printing ink had a lot of smaller expandable microcapsules (the average diameter was 11.6μm) (Figure 1a), while MF-FL printing ink had a bit larger and not so numerous expandable microcapsules (the average diameter was 30.7μm) (Figure 2a). In the case of EC printing ink expandable microcapsules were not present. Therefore its surface was clearly most even. The average diameter size of expanded microcapsules in MF-SR varied from 30μm to 92μm (Figure 1b) and for MF-FL from 50μm to almost 100μm (Figure 2b).

**Figure 1:** Microscopic images of unexpand ed (a) and expanded (b) printing ink MF-SR (SEM, 200x (a) and 500x (b) magnification).
In all three printing inks the same amount of pigment Royal Blue R (Achitex Minerva Spa, Italy) was added in the mass concentration 3%.

**Fragranced microcapsules**

For the purpose of the research in all three selected printing inks, the same 15% by mass of fragranced microcapsules was added. Microcapsules were prepared as an aqueous solution with “in situ” polymerization in industrial 200-L reactor system (Šumiga, 2013). Though they were colorless, the aqueous solution appeared white due to the relatively high concentration of microcapsules in it (approx. 30-35%). These fragranced microcapsules differed from the expandable ones in printing ink – they were much smaller in size (average size was 4.3μm), their shell was made from melamine-formaldehyde and their core was made of a mixture of essential oils (in this research indicated as fragranced microcapsules). These fragranced microcapsules were not expandable. The viscosity of an aqueous suspension of microcapsules was 2.07dPa∙s, and the amount of free formaldehyde was under 0.2%. Fragranced microcapsules were selected because of their distinguished properties. Firstly they show very good resistance to mechanical forces, therefore their melamine-formaldehyde shell doesn’t crack during printing and secondly they have very good resistance to higher temperature of drying and expanding processes. Since the fragrance is released only by scratching and rubbing of the surface, we have used this property in the research for subjective testing the presence of fragranced microcapsules after printing.

All samples were printed with screen printing technique on an automatic machine (SD 05 RokuPrint, GmbH), with one squeegee passage. Prints were made with PET screen printing mesh of 43 threads/cm in density and 80μm in diameter of monofilament.

For the purpose of the research two sets of sample prints were made:

- samples, which were printed with selected printing inks in which only pigment was added, and
- samples, which were printed with the addition of pigment and fragranced microcapsules.

In selected printing inks the same amount of fragranced microcapsules and pigment was added, 15% and 3%, respectively. Samples were designated as follows: firstly type of printing substrate (SP or BM), secondly type of printing ink (MF-SR, MF-FL or EC) and thirdly amount of added microcapsules (O or 15%).

After printing all samples were dried for 40 seconds at 100°C in a drying tunnel (Shrink machine BS-B400). Afterwards (within one hour) samples printed with expandable printing inks had to be temperature treated in a heating oven (Binder FD 115) for 3 minutes at 150°C, so that the expansion of microcapsules could occur.

**Testing methods**

For the purpose of the research following methods for measuring properties of material as well as printed samples were used: grammage was determined in accordance with standard EN ISO 536:2015 (EN ISO 563:2012, 2012); thickness was measured on Mitutoyo apparatus (No. 2050 F-10), with load 500cN/cm², on sample area 1cm² in accordance with standard ISO 543:2011 (ISO 543:2011, 2011); height of capillary rise was measured in machine and it’s cross direction (MD and CD) by Klemm method in accordance with standard ISO 8787:1996 (ISO 8787:1996, 1996); roughness of paper substrates was determined with Bendtsen method, described in standard ISO 8791-2 (ISO 8791-2:2013, 2013); L*a*b* color values were measured in accordance with standard ISO 11664-4:2008 (CIE S 014-4/E:2007) (ISO 11664-4:2008, 2008) and from those values color differences between samples printed with and without fragranced microcapsules were calculated. Beside listed measurements image analyses was performed by scanning electron microscope (SEM, JSM 6060 LV, Jeol).

For determination of perceptive properties of prints all printed samples were tested in a group of 33 pupils (6-8 years old) with tactile analyses. Analyses were performed by pupils with normal eyesight, therefore they were blindfolded so that during testing they could not see the samples. Analyses consisted of a set of questions with which we could determine whether pupils find surface smooth or rough, warm or cold and whether all samples can be distinguished by any other differences.

**Results and discussion**

Image analyses of printed samples, printed with all three selected inks showed that there is a significant difference in printed surface of prints (Figure 3). Different type of expandable microcapsules gave different printed surface; in the case of smaller and numerous expandable microcapsules MF-SR the surface had rubbery effect, while in the case of larger and fewer expandable microcapsules of MF-FL the surface was...
velvet-like. EC printing ink gave smooth surface with the plane, silky touch. Fragranced microcapsules, incorporated into inks were in the cross section of prints observed on the surfaces of expandable microcapsules.

**Figure 3**: Microscopic images of longitudinal cross-section of printed SP paper substrate with printing ink MF-SR (a), printing ink MF-FL (b) and printing ink EC (c) without the addition of fragranced microcapsules (all SEM, 50x magnification).

Beside image analyses other measurements were performed according to previously mentioned testing methods on unprinted and printed samples. Results of sets of samples were compared in their properties and are presented in Table 2 and Table 3

**Table 2**

Measured properties of unprinted and printed substrate SP with MF-SR, MF-FL and EC printing ink.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Grammage [g/m²]</th>
<th>Thickness of prints [mm]</th>
<th>Color values L<em>a</em>b*</th>
<th>Color difference ΔE [l]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP</td>
<td>146.45*</td>
<td>/</td>
<td>L*=94.29 a*=1.01</td>
<td>b*=2.88</td>
</tr>
<tr>
<td>SP – MF-SR 0</td>
<td>164.47</td>
<td>0.113</td>
<td>L*=87.15 a*=3.90</td>
<td>b*=9.33</td>
</tr>
<tr>
<td>SP – MF-SR 15</td>
<td>152.81</td>
<td>0.052</td>
<td>L*=86.99 a*=5.21</td>
<td>b*=8.88</td>
</tr>
<tr>
<td>SP – MF-FL 0</td>
<td>159.15</td>
<td>0.061</td>
<td>L*=82.89 a*=3.39</td>
<td>b*=12.70</td>
</tr>
<tr>
<td>SP – MF-FL 15</td>
<td>156.25</td>
<td>0.037</td>
<td>L*=87.29 a*=4.64</td>
<td>b*=11.00</td>
</tr>
<tr>
<td>SP – EC 0</td>
<td>163.97</td>
<td>0.008</td>
<td>L*=88.39 a*=5.63</td>
<td>b*=8.15</td>
</tr>
<tr>
<td>SP EC 15</td>
<td>158.59</td>
<td>0.004</td>
<td>L*=89.22 a*=5.18</td>
<td>b*=7.45</td>
</tr>
</tbody>
</table>

* measured value was slightly different as declared by paper producer

**Table 3**

Measured properties of unprinted and printed substrate BM with MF-SR, MF-FL and EC printing ink.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Grammage [g/m²]</th>
<th>Thickness of prints [mm]</th>
<th>Color values L<em>a</em>b*</th>
<th>Color difference ΔE [l]</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM</td>
<td>114.55*</td>
<td>/</td>
<td>L*=94.35 a*=0.96</td>
<td>b*=3.30</td>
</tr>
<tr>
<td>BM – MF-SR 0</td>
<td>131.21</td>
<td>0.016</td>
<td>L*=86.71 a*=3.68</td>
<td>b*=8.76</td>
</tr>
<tr>
<td>BM – MF-SR 15</td>
<td>130.75</td>
<td>0.014</td>
<td>L*=86.14 a*=5.79</td>
<td>b*=10.61</td>
</tr>
<tr>
<td>BM – MF-FL 0</td>
<td>132.17</td>
<td>0.012</td>
<td>L*=86.19 a*=3.77</td>
<td>b*=13.99</td>
</tr>
<tr>
<td>BM – MF-FL 15</td>
<td>121.17</td>
<td>0.009</td>
<td>L*=87.40 a*=4.31</td>
<td>b*=10.91</td>
</tr>
<tr>
<td>BM – EC 0</td>
<td>132.65</td>
<td>0.062</td>
<td>L*=88.89 a*=5.51</td>
<td>b*=8.01</td>
</tr>
<tr>
<td>BM – EC 15</td>
<td>124.68</td>
<td>0.056</td>
<td>L*=89.26 a*=5.64</td>
<td>b*=7.60</td>
</tr>
</tbody>
</table>

* measured value was slightly different as declared by paper producer

Results have shown that after printing grammage of samples increases, as expected. However, the addition of aqueous suspension of fragranced microcapsules into inks causes a slight decrease in grammage of all printed samples, regardless to the used paper substrate (Figure 4). Added aqueous suspension of fragranced microcapsules replaced one part of the printing ink and thus caused a decrease in ink share and increase of water share. Later, during printing water evaporated, while grammage was lower than in the case of ink without fragranced microcapsules.

Similar results were obtained for the thickness of prints. Lower values of thickness were achieved for SP printing substrate with more opened surface and higher adsorption properties (Table 1) and thus higher penetration of printing inks into the substrate.
After the aqueous suspension of fragranced microcapsules was added, the viscosity of printing inks decreased, and thus penetration of ink was even higher into the substrate as in the case of ink without fragranced microcapsules (Figure 5).

Consequently, thickness decreased after the addition of fragranced microcapsules. The decrease of thickness after added fragranced microcapsules was lowest with EC printing ink and highest with MF-SR printing ink, which had smaller but numerous expanding microcapsules.

**L*a*b* measurements** have showed that both paper substrates had almost the same color values, therefore all color changes, which would occur in comparison of the samples, could be contributed to the properties of printing inks and its additions of pigment and fragranced microcapsules. Measurements of L*a*b* values have shown that the highest color differences occurred with MF-FL printing ink, slightly smaller with MF-SR and the smallest with EC (Figure 6 and 7). In the case of expanding printing inks, calculated color differences (ΔE) (Table 2 and 3) showed that these were noticeable but nevertheless still permissible after added microcapsules. In the case of EC ink, differences were small and almost negligible.

**Sets of samples were in the tactile analysis presented to the group of pupils to establish whether differences in prints made with different printing inks exist and whether pupils can distinguish perception**
differences among them. Results have shown that pupils noticed differences between samples printed with three printing inks. They have determined that in all three inks, surfaces were rougher than smooth (Figure 8) and that surface of MF-SR (which gives rubbery surface) felt rougher than the surfaces of MF-SR (with fluffy surface) and EC (with smooth surface).

Since MF-FL has a velvet-like surface, our opinion was that the surface of this sample will be assessed as “worm” by pupils. Contrary, it was assessed as cold and unexpectedly samples with MF-SR and EC ink were specified to be warmer to touch (Figure 9). The color of prints was gentle blue and as it is well known that blue belongs to cold colors, the influence of color on warm/cold fillings of surface probably also had some small influence on results.

At the end of small but interesting tactile test performed by pupils, we were also impressed by the last following results. In answering the question on what the surface resembles them pupils attributed MF-FL to fur and hair-like touch (e.g. bear, caterpillar, kiwi, peaches, etc.) while MF-SR was associated with smooth fruity-like surfaces (e.g. apple, orange, lemon, etc.). Similar results as for MF-SR were obtained for EC. Those results were a little bit in contrary to the results of the first question on smooth/rough surface. According to the fact that test was made on small group of pupils, which were faced with “virtual blindness” for the first time, deviations in results were expected and were taken only as a starting point for the following researches.

Conclusions

From the presented results, it could be concluded that microcapsules have small but not negligible influence on prints. Since microcapsules were originally in aqueous suspension, they were added as such to three different types of printing inks of which viscosity changed immediately. Consequently, grammage of prints slightly decreased, while thickness decreased significantly, especially for the expandable inks used in this research. Color change of prints without and with fragranced microcapsules was noticed, but it was still in the permissible range event at 15% of added microcapsules. Subjective testing of applying pressure (scratching and rubbing) to the surface also confirmed that fragranced microcapsules were still presented in final prints. By tactile analysis, surfaces were recognized as rough/smooth or as warm/cold.

References


