Original scientific paper UDC: 655.3.026

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 shown that microcapsules cause small color differences while perceptive analyses gave very interesting results.

KEY WORDS

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

Raša Urbas,
Urška Stankovič Elesini

University of Ljubljana, Faculty of Natural Sciences and Engineering, Ljubljana, Slovenia

Corresponding author:
Raša Urbas
e-mail: rasa.urbas@a.ntf.uni-lj.si

First recieved: 11.04.2015.
Accepted: 13.05.2015.

Introduction

Raised printing is nowadays used for different purposes – for purely esthetic reasons or particular intentions e.g. printing for visually impaired or blind people. This type of printing with sufficient height of prints can be achieved with different printing techniques (engraving, screen printing, flexo printing, inkjet printing, etc.) (Nomura et al., 2014; Christian, 2001; Meola et al., 2000; Stankovič Elesini et al., 2014), application of multiple layers of printing ink (Bethune et al., 2002; Willfahrt, 2010), special surface treatment (Torii, 1997) or use of special 3D expanding inks or varnishes (Yonezava, 1981; Wilkinson, 2012; Rygas et al., 2014; Wang, 2014; Urbas et al., 2014). Depending on the purpose, height of printed elements e.g. their thickness varies. When printing for purely esthetic reasons printing height depends on the designer or producer's wish. But when printing for those who can't see or those with impaired vision printed elements must achieve adequate height according to the requirements in different standards, legislations and national documents, which specifically define printed parameters (DIN 32976, 2007; Directive 2001/83/EC, 2001; Oouchi, 2004; Graeme et al., 2008; Fajdetič, 2011). Few expert and scientific papers are written on the area of raised prints (Nomura et al., 2014; Bethune et al., 2002; Koch, 2003; Delmerico, 2013), and almost all are focused on achieving the appropriate height. In our previous researches (Stankovič Elesini et al., 2014; Urbas et al., 2013; Urbas et al., 2014), height of raised prints was achieved by special printing inks with incorporated expandable microcapsules. By use of those microcapsules, prints were high enough even with just one layer of ink. On the other side, we were looking for an addition value, by which blind and visually impaired people would be able to recognized printed objects like pictures. Printing different type of textures are known for long time (Yonezava, 1981; Dupont, 1994; Torii, 1997; Rygas et al., 2014) and also printing with fragrances (Ladds et al., 1971; Spector, 1981; Sweeny, 1985; Stanislav, 1998), but not in the case of raised prints for blind and visually impaired people, as it was one of the objectives in our research. Prints with fragranced microcapsules were successfully performed (Urbas et al., 2013; Stanković Elesini et al., 2014) however some interesting observation were also made on the colour change and tactile performances, on which is the focus of this article.

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/m^2 (in this research indicated as SP), and*
- *two-side coated, wood-free Biomatt paper, with high whiteness (bright white) and declared grammage (weight) 120g/m^2 (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 Elesini 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 1

Properties of unprinted printing substrates SP and BM with their calculated color difference.

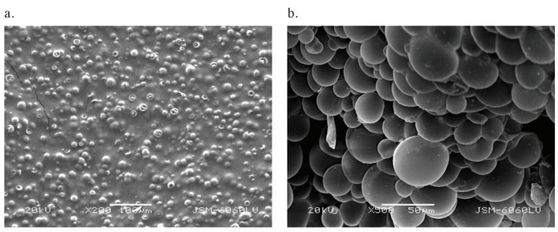
Sample / Property	SP	BM
Height of capillary rise [mm] **MD / CD**	19 / 17	13 / 12
Roughness [ml/min] **Side A / Side B**	148.6 / 138.0	64.2 / 102.0
Color values **L*** **a*** **b***	 94.29 1.01 -2.54	 94.35 0.96 -3.30
Color difference ΔE [/]	0,42	

Printing inks

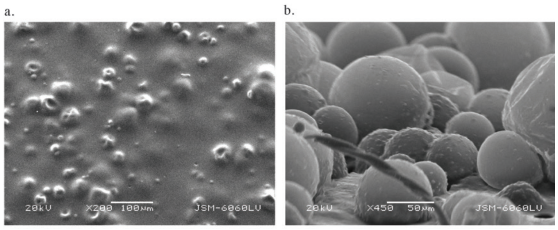
Printed samples were made with three different commercially prepared (ready-to-use) printing inks – two 3D expandable and one ordinary printing ink (with no expandable components), all from Achitex Minerva Spa (Italy):

- *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/m^3, 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/m^3, viscosity 110dPa·s and pH value 9.1;*
- *Elastil 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/m^3, 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 rubbery 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 unexpanded (a) and expanded (b) printing ink MF-SR (SEM, 200x (a) and 500x (b) magnification).*



» **Figure 2:** *Microscopic images of unexpanded (a) and expanded (b) printing ink MF-FL (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 (0 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.

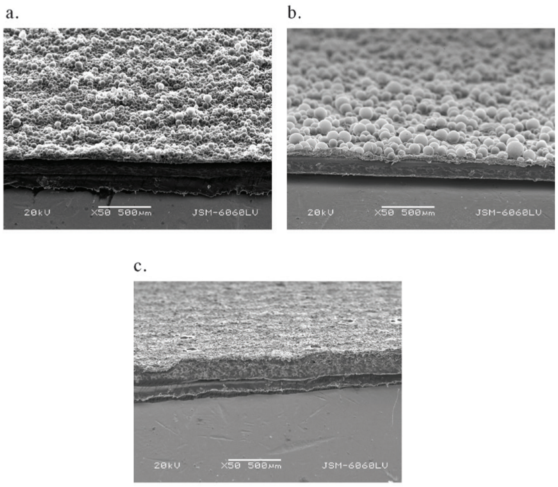
Testing methods

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/cm^2, on sample area 1cm^2 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. Color differences are calculated between samples with and without fragranced microcapsules.

Property / Sample	Grammage [g/m²]	Thickness of prints [mm]	Color values L*a*b* [/]	Color difference ΔE [/]
SP	146.45*	/	L*=94.29 a*=1.01 b*=-2.88	/
SP – MF-SR 0	164.47	0.113	L*=87.15 a*=-3.90 b*=-9.33	1.39
SP – MF-SR 15	152.81	0.052	L*=86.99 a*=-5.21 b*=-8.88	
SP – MF-FL 0	159.15	0.061	L*=82.89 a*=-3.39 b*=-12.70	4.88
SP – MF-FL 15	156.25	0.037	L*=87.29 a*=-4.64 b*=-11.00	
SP – EC 0	163.97	0.008	L*=88.39 a*=-5.63 b*=-8.15	1.18
SP EC 15	158.59	0.004	L*=89.22 a*=-5.18 b*=-7.45	

** measured value was slightly different as declared by paper producer*

Table 3

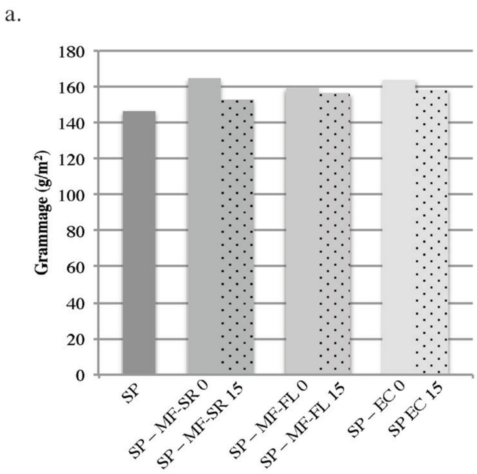
Measured properties of unprinted and printed substrate BM with MF-SR, MF-FL and EC printing ink. Color differences are calculated between samples with and without fragranced microcapsules.

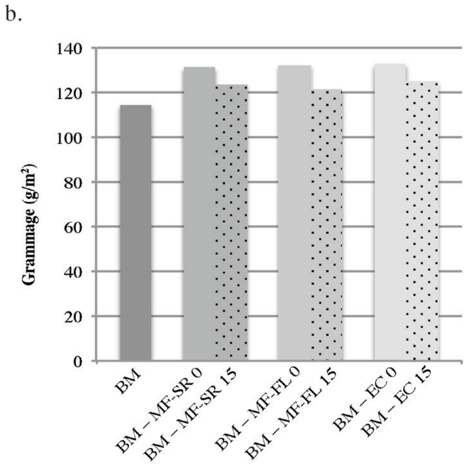
Property / Sample	Grammage [g/m²]	Thickness of prints [mm]	Color values L*a*b* [/]	Color difference ΔE [/]
BM	114.55*	/	L*=94.35 a*=0.96 b*=-3.30	/
BM – MF-SR 0	131.21	0.165	L*=86.71 a*=-3.68 b*=-8.76	2.86
BM – MF-SR 15	130.75	0.104	L*=86.14 a*=-5.79 b*=-10.61	
BM – MF-FL 0	132.17	0.122	L*=86.19 a*=-3.77 b*=-13.99	3.35
BM – MF-FL 15	121.17	0.098	L*=87.40 a*=-4.31 b*=-10.91	
BM – EC 0	132.65	0.062	L*=88.89 a*=-5.51 b*=-8.01	0.57
BM – EC 15	124.68	0.056	L*=89.26 a*=-5.64 b*=-7.60	

** 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.

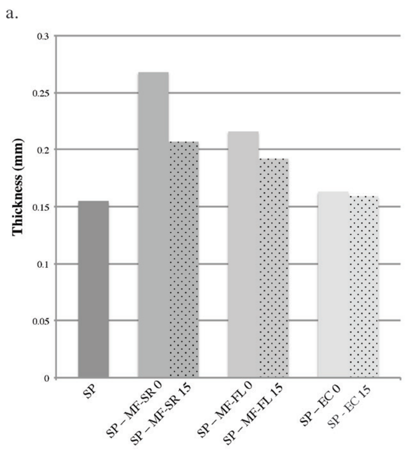
Similar results were obtained for the **thickness** of prints. Lower values of thickness were achieved for SP printing substrate with more opened surface and higher adsorption properties (Table 1) and thus higher penetration of printing inks into the substrate.

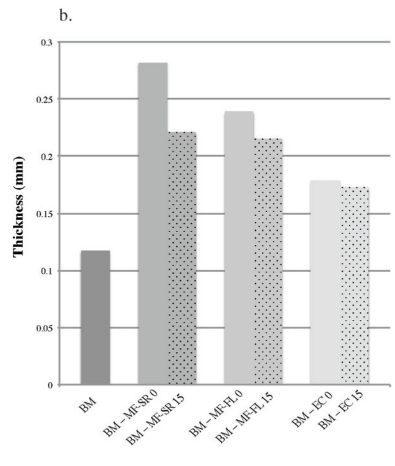




» **Figure 4:** *Grammage of unprinted paper substrate SP (a) and BM (b) and printed with MF-SR, MF-FL and EC printing ink.*

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).

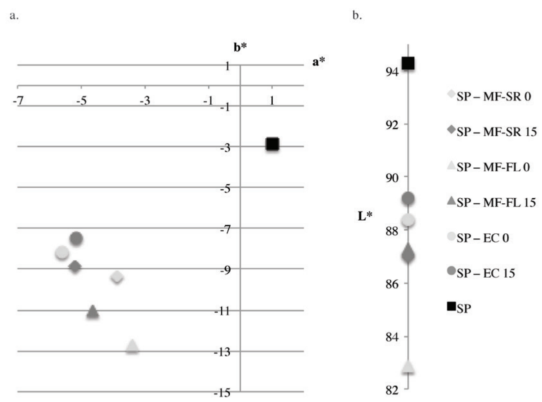




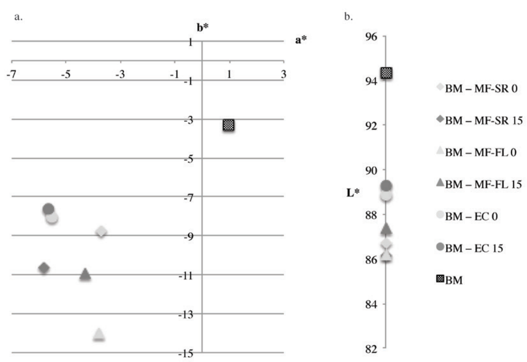
» **Figure 5:** *Thickness of unprinted paper substrate SP (a) and BM (b) and printed with MF-SR, MF-FL and EC printing ink.*

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.

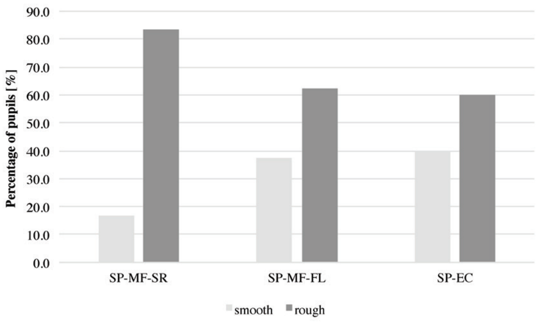


» **Figure 6:** *a*b* color values (a) and values of lightness L* (b) of paper substrate SP printed with MF-SR, MF-FL and EC printing ink.*



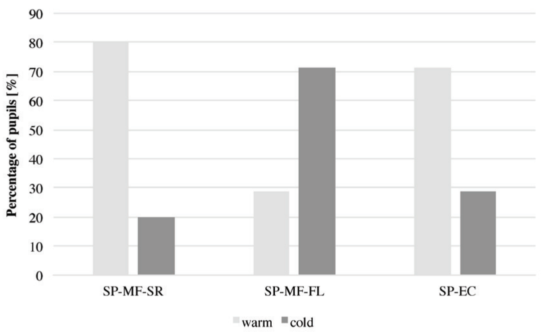
» **Figure 7:** *a*b* color values (a) and values of lightness L* (b) of paper substrate BM printed with MF-SR, MF-FL and EC printing ink.*

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).



» **Figure 8:** *Perception of smooth and rough surfaces of samples by pupils printed on SP paper substrate*

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 warn/cold fillings of surface probably also had some small influence on results.



» **Figure 9:** *Perception of warm and cold surfaces of samples by pupils printed on SP paper substrate.*

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

1. Bethune, A., Vayrette, S. H. (2002) Method of applying material to a substrate. Patent US 2002/0142106 A1.
2. Christian, S. (2001) Printing process combining conventional and braille printing with the aid. Patent EP 1 153 756 A1.
3. Delmerico, R. (2013) Printed image for visually-imapired. Patent US 20130293657 A1.
4. DIN 32976 (2007) Braille – Requirements and dimensions.
5. Directive 2001/83/EC (2001) Article 56a – Guidance concerning the Braille requirements for labelling and the package leaflet.
6. Dupont, G., Tissot, P., Manceaux, J. (1994) Method for the maufacture of objects having superficial relief patterns. Patent US 005325781A.
7. EN ISO 536:2012 (2012) Paper and board – Determination of grammage.
8. Fajdetić, A. (2011) Standardization of Braille in the EU and other European Countries. World Congress Braille. Leipzig, Germany, pp. 8.
9. Garner, J. L., Tiffany, P. A. (1979) Method for expanding microspheres and expandable composition. Patent US 4179546 A.
10. Graeme, D., Wilkins, S. M., Robinson, D. (2008) Braille dot height research: Investigation of Braille Dot Elevation on Pharmaceutical Products. [Online] Available from: http://www.birmingham.ac.uk/Documents/college-social-sciences/education/victar/braille-dot-height.pdf [accessed 20th February 2015].

11. Harper, C. A. (2006) Handbook of Plastics Technologies: The Complete Guide to Properties and Performance. New York: McGraw-Hill Professional.
12. ISO 543:2011 (2011) Paper abnd Board – Determination of thickness, density and specific volume.
13. ISO 6588-1:2012 (2012) Paper, board and pulps – Determination of pH of aqueous extracts – Part 1: Cold extraction.
14. ISO 8787:1996 (1996) Paper and board – Determination of capillary rise- Klemm method.
15. ISO 8791-2:2013 (2013) Paper and board – Determination of roughness/smoothness (air leak methods)- Part 2: Bendtsen method.
16. ISO 11664-4:2008 (CIE S 014-4/E:2007) (2008) Colorimetry- Part 4: CIE 1976 L*a*b* Color space.
17. Koch, T. (2003) Method for fabricating printed products with a profiled surface and printed products fabricated with said method. Patent WO 2001 DE 03295 20010823.
18. Ladds, J. S., Emerson, M. H. (1981) Teaching apparatu. Patent US 3570139.
19. Meola, J. J., Strousland, G. R. (2000) Three-dimensional raised image screen printing. Patent US 6.092.464.
20. Nomura, K., Ushijima, H., Mitsui, R., Takahashi, S., Nakajima, S. (2014) Screen-offset printing for fine conductive patterns. Microelectronic Engineering 123, pp. 58-61.
21. Oouchi, T. W. A (2004) Study of Legible Braille Patterns on Capsule Paper: Diameters of Braille Dots and Their Interspaces on Original Ink-printed Paper. [Online] Available from: http://202.237.53.67/kenshuka/josa/kankobutsu/pub_a/nise_a-8/nise_a-8_1.pdf [accessed 10th August 2014].
22. Pesquet, G., da Silva, L. F. M., Sato, C. (2011) The use of thermally expandable microcapsules for increasing the toughness and heal st ructural adhesives. Frattura ed Integrità Strutturale 16, pp. 18-27.
23. Rygas, T. P., Thaurailingam, T., Crisan, S., Chalifoux, N. J. S. (2014) Method and composition for printing tactile marks and security document formed therefrom. Patent US 8.846.778 B2.
24. Spector, D. (1981) Scratch and smell puzzle. Patent US 42432246.
25. Stanislav, L. A. (1998) Scented transferable tattoo. Patent US 5817385.
26. Stankovič Elesini, U., Šumiga, B., Manojlović, S., Urbas, R. (2014) Raised printing with screen printing technique. 7th Symposium of Information and Graphic Arts Technology. Ljubljana: Faculty of Natural Sciences and Engineering, Department of textiles, pp. 187-192.
27. Sweeny, N. P. (1985) Fragrence-releasing microcapsules on a see-through substrate. Patent US 4493869.
28. Šumiga, B. (2013) Informacijski pristopi v načrtovanju kemijskih postopkov mikrokapsuliranja : doktorska disertacija. Ljubljana.
29. Torii, M. (1997) Heat transfer printing sheet for pro producing raised images. Patent US 6.004.416.
30. Urbas, R., Mayik, V., Golob, G., Stankovič Elesini, U. (2014) Printing braille with expanding 3D screen printing inks. Naukovo-tekhnichna konferentsia profesors'ko-vykladats'koho skladu, naukovykh pratsivnykiv i aspirantiv. L'viv: Ministerstvo osvity i nauky Ukrainy, Ukrains'ka akademia drukarstva, pp. 56.
31. Urbas, R. (2013) Printing microcapsules on different cellulose based substrates for achieving added value of the products. Proceedings of the COST Training school: printing of bio-based materials in packaging. Budapest, pp. 253-262.
32. Wang, L. Y., Yang, X., Zhang, J., Zhang, C., Hea, L. (2014) The compressive properties of expandable microspheres/epoxy foams. Composites, no. Part B, pp. 724-732.
33. Wang, L. Y. (2014) The compressive properties of expandable microspheres/epoxy foams. Composites 56 (Part B), pp. 724–732.
34. Willfahrt, A. S. (2010) Optimising Stencil Thickness and Ink Film Deposit. International Circle, 17.
35. Wilkinson, P. A. (2012) A method for producing 3-d printed images. Patent WO 2012007563 A2.
36. Yonezava, Y. (1981) Method for producing relief. Patent US 4.268.615.
37. Yushi-Seiyaku, T. M., Yushi-Seiyaku, I. M., Yushi-Seiyaku, Y. M., Yushi-Seiyaku, K. M. (2005) Heat-expanding microcapsule and use thereof. Patent EP 1508604-A1.