Development of “micrograna” synthesis methodology for application in e-paper applications, Review of current technologies and Prospects

N.K. Kakizis[2], M. Tsigonias[1, 2], A. Politis [1,3], E. Nils [3], S. Nomikos [1], A. Kanellopoulou [4], C. C. Trapalis [4] and N.K. Kanellopoulos [2]

1. *1. Faculty of Graphic Arts Technology, Athens Technological Educational Institute, Ag. Spyridonos, 12210, Egaleo, Athens, Greece*
2. *2. Micro-porous Materials and Membranes for Environmental Applications Laboratory, Institute of Physical Chemistry, National Centre for Scientific Research ‘‘Demokritos’’, Terma Patriarchou Grigoriou & Neapoleos, 15310, Ag. Paraskevi, Athens, Greece*
3. *3. College of Engineering, Royal Research Institute of Sweden (KTH), Valhallavägen 79, Stockholm, Sweden*
4. *4. Institute of Materials Science, NCSR “Demokritos”, Agia Paraskevi, Athens, Greece*

Abstract

As the proliferation of modern information and nanomaterials-related technologies has substantially transformed the interaction methods between people, the development of electronic paper technology (e-paper), has intrigued research groups and questions the usability of one of the most well-established means of communication. Possible applications for e-paper include robust-light-weight and low-power consuming matrix display assemblies integrated in multi-layer, thin, and flexible polymer media carriers. E-paper and electronic display elements and e-inks that are currently being developed include microencapsulated electrophoretic fluid dispersions of nanoparticles, Gyricon beads, and liquid crystals. As e-paper is a non-disposable media and information can be updated and superimposed on the same e-paper/device by restructuring the position of the e-ink micrograna, it contemplates a strong ecological approach. E-paper technologies hold different qualities with substantial variation of technical specifications. The development and optimization of a microgranulated electrophoretic medium solves the lifetime issues of e-paper and permits the fabrication of a bistable electronic display solely by means of printing. In the current paper the change of the geometry of the micrograna is partially investigated and optimised. Finally, this paper reviews the current e-paper technologies and discusses the potential usability of the e-paper and the future of the traditional paper.

Keywords

Electronic paper development, microsynthesis, information proliferation, new imaging methods and systems

1. Introduction

In the year 2000 the Nobel Prize in Chemistry was awarded Alan J. Heeger , Alan G. MacDiarmid and Hideki Shirakawa for the discovery and development of conductive polymers [1]. Conductive polymeric systems gave us the great opportunity to watch our lifes differently. With the use of flexible, conductive and transparent polymeric films, flexible multilaminated displays and E-paper solutions are able to be constructed.

2. Methodological approach

This paper has been based on both literature study, focusing on the investigation of e-paper technological solutions and relevant technologies and also on the preliminary findings of a new methodological approach for the encapsulation of e-ink dyes.

3. Background and literature review

3.1 e-paper technologies

Electronic paper or similar technologies has been a very active field of research during the past 3 decades or so. A number of different approaches and technological solutions have been followed towards the development of electronic paper and relative applications and the results obtained varied significantly [2], [3], [4], [5], [6], [7].

However, all the approaches that have been followed have resulted in the development of multilayer assemblies, usually comprised by one active and two substrate layers. The active layer, which lies in-between layers of conductive polymeric material, is comprised by microspheroids, i.e. microcapsules, microspheres, micro-grana or other similar formations. In most cases, the microspheroids have the ability to change their inherent color by means of the application of an electric voltage. Two are the major approaches in e-paper synthesis and implementation, which at the same time have reached a certain level of technological maturity, Gyricon Beads [8] and electrophoretic ink [9], which has been originally developed by the E Ink Corporation. The basic operational principles of Gyricon (Fig. 1) are based on the properties of a monolayer of charged microspheres that exhibit two different colour sides, black and white. The microspheres active monolayer is constrained between two carrier substrate layers. Electrode grids integrated in both substrate layers are used to develop and apply an electric field. Upon application of the electric field, the charged microspheres present – on-demand – their black or white semisphere as the microsphere rotates freely under the applied forces, thus allowing the black or the white semisphere of the microsphere to become oriented with respect to the viewing plane.

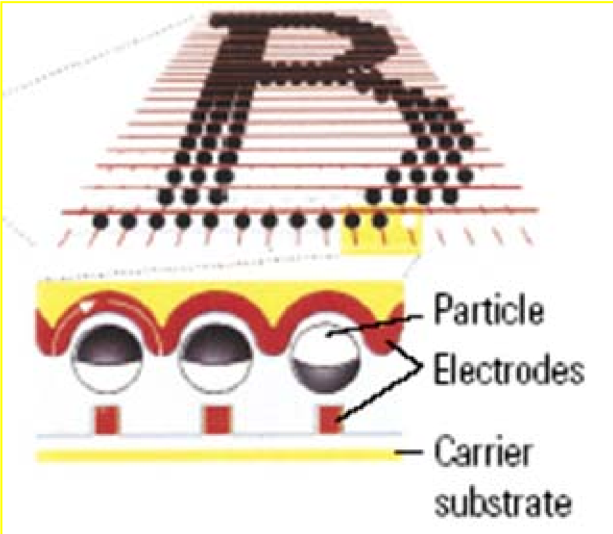

Figure 1: Schematic representation of the principle of operation of the Gyricon beads e-paper*. Source: Xerox Corporation.*

Similar operational parameters are followed by the electrophoretic ink (e-ink) technological approach. Microcapsules with a diameter of about 100μm contain dyes with suspensions of electrically charged white titanium oxide (TiO_2) particles. Under the presence and subsequent influence of an electric current, the particles orientate towards one of the two microcapsule's semispheres. This movement allows the contained dye to be visible or not and thus creating the illusion of color to the viewer (Fig.2).

Both technologies can be used for the creation of monolayers of active microcapsules that can be used for the development of displays and reading devices [10], [11], [12].

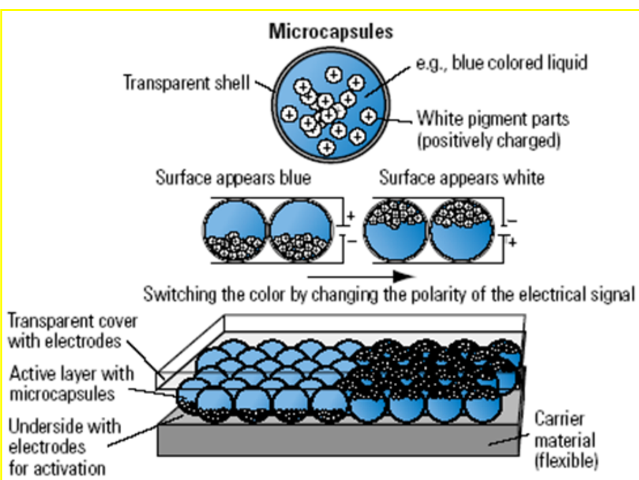

Figure 2: Schematic representation of the principle of operation of the e-ink*. Source: E Ink – Phillips Research.*

3.2 E-paper Characteristics & Technology Appraisal

No matter how promising and full of research and technological prospects the e-paper technologies are, there exist a number of inherent problems and weaknesses in each and any of the involved technological solutions that need to scientifically and technologically addressed and resolved prior to any meaningful or significant large scale application of e-paper technology. These may be summarized under the framework of three main areas: 1) layer and capsule geometry, 2) component miniaturization and 3) display performance and analysis.

Starting from capsule geometry considerations, two are the main factors that affect the performance of both the individual capsules as well as the display monolayer formed, overall capsule size and shape. It has been concluded that the size and shape microspheroid arrangements that are currently used for the encapsulation of the dyes or particles, present a number of problems with respect to the visual and electrical performance of the display as well as with respect to the reliability and operational life of the assembly. In this manner, it has been proposed the transformation of the microcapsule into either a micrograna (discoid) arrangement with a diameter of 50-100 μm and an overall height of 5-10 μm, or into a microfacoid/lenticular geometry with diameter up to 100 μm and of 5-10 μm height. Apart of the transformation of the microsperoid-microcapsule geometry into more efficient but complex geometries, a different approach targeting the significant reduction of the existing arrangements has also been proposed. To this end, the overall microspheroid size (microcapsules and beads alike) needs to be reduced down to around 10 μm. The reduction in the size, apart form the obvious effect on the miniaturization of the display assembly, will have a number of other side-advantages such as: reduction of response time for the same voltage conditions and subsequently lower energy consumption, increase in the display resolution obtained and increase of the expected life-time of the display.

In view of the proliferation of informatics in developing third-world economies and the power requirements that this may involve, the development of reliable displays based on e-paper or similar technologies may be proven to have a positive impact on environmental and socioeconomic conditions. The development of e-paper displays, as demonstrated in Fig.3, presents a significant "indirect" economic motive with respect to the overall power requirements. With respect to currently available LCD displays, e-paper displays may be proven to be more economically attractive in the log-term in developing economies.

Of course the reduction of the size cannot be accomplished without the additional improvement of the substrate materials. This improvement focuses on two areas: the improvement of the physicochemical properties of the substrate materials and the enhancement of the overall display contrast. As it has been investigated (Table 1, Fig.4), contrast plays an important role in the usability and impact of an e-paper technological application as it significantly enhances readability and usability of the media. Table 1 provides a comparison between paper and e-paper characteristics.

The overall improvement of the properties of the encapsulated dye and of the dye-microparticles system is expected to have a positive effect in future e-paper systems and is already attracting significant research efforts. As it has been already stated, most existing e-paper technologies are based on either colored microspheres or on the co-encapsulation, along with a suitable dye, of charged titanium oxide particles are encapsulated. This latter principle is the basis for most e-ink related technology applications. However, titanium oxide particles tend to agglomerate [6]. This agglomeration process usually leads to the particle discharge and to an overall degradation of the display properties and to reduced display life-time.

Finally, the current state-of-the-art in e-paper technology does not allow the attribution of color and colored images through the e-paper displays currently available. This is a direct result of the inherent limitations of the technological approaches followed and may be proven to be in itself a major research and technological objective.

Properties	Paper	Gyricon	E-Ink
Contrast	10:1	10:1	30:1
Reflectance	50%	20%	40%
Reflection Type	Lambertian	Lambertian	Lambertian
Viewing Angle	All	All	All
Flexibility	Yes	Yes	Yes
Color	Yes	No	No
Response Time	N/A	80msec	100msec
Voltage	N/A	90 V (max)	90 V (max)

Table 1. Presentation of paper characteristics in comparison to the two main e-paper technologies. Source: Wall Street Journal Newspaper.

4. Process for the encapsulation of TiO_2 particles & process optimization

Under the scope of the current study and in view of the findings in relation to the microcapsule miniaturization and formation process presented above, a new method has been developed. The process in itself is a combined series of chemical processes aiming to the co-encapsulation of a carrier dye and titanium oxide particles into silica microcapsules and is presented by means of a process/workflow diagram in Fig. 5.

The process in itself may also be carried-out under the framework of two distinguishable versions, named Procedure A and Procedure B.

By initially using 1-Octanol and Hydroxypropyl Ethanol at 80 °C for four hours we develop a solution containing H_2O, PEG (poly-ethylene-glycol) Pluronic Acid and NH_4OH which results tetraethoxysilane (TEOS). The process has been designated as Procedure B. A more complex Procedure A (Fig. 5) results also in the development of TEOS but involves additional intermediate steps. To this end, the use of SPAN 80, which is a sorbitan monooleate ester/non-ionic surface active agent used in food

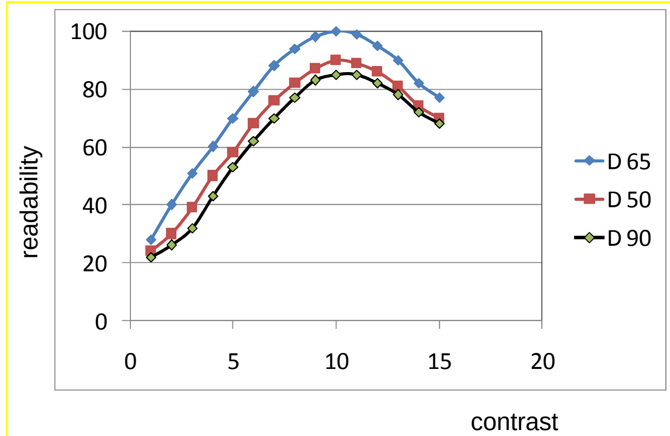

Figure 3: Power consumption of LCD displays Method for the micro encapsulation of titanium oxide particles for use in e-paper applications. Source: KTH

products and oral pharmaceuticals, along with the use of HPC and Tween 20 results in a successful multiple emulsion encapsulating retinol. Tween 20 is a monoionic detergent widely used in biochemical applications (polyoxyethylenen sorbitol ether suitable as a solubilizing agent for membrane proteins and as blocking reagent in blotting applications). Both Span 80 and Tween 20 act as surfactants with the aim of enhancing the emulsion encapsulation process. After the formation of TEOS, the solution is washed with ethanol and followed by processing by means of centrifugation, drying and calcination.

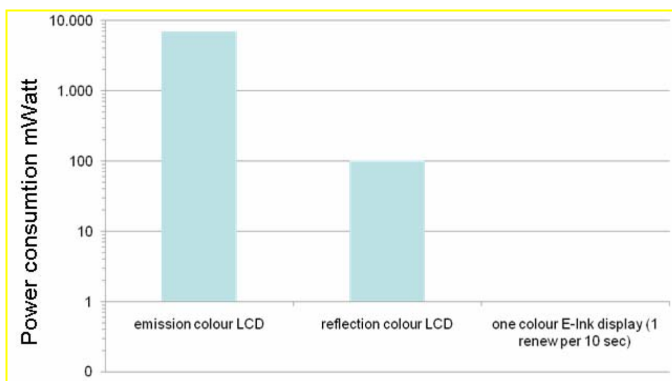

Figure 4: Correlation of the document readability and substrate contrast. Source: KTH

Both variations of the process result in the formation and development of hollow microspheres suitable for the encapsulation of titanium oxide particles and suitable dyes. However, only preliminary results have been obtained so far and a lot of parameters remain to be investigated. One of the main areas of concern is the microcapsule formation process which needs to result a more uniform microcapsule population. During a first stage of optimization, procedure A was devised and two surfactant agents (Span 80 and Tween 20) were introduced. The results obtained (Fig. 7a and Fig 7b for Procedure A and B respectively), exhibited a significant increase in both number of hollow microcapsule formation as well as size uniformity of the developed microcapsules for Procedures A and B.

During a second stage of optimization, currently under development, the experimental arrangement presented in Fig. 6 has been devised and will be used for microcapsule formation and development.

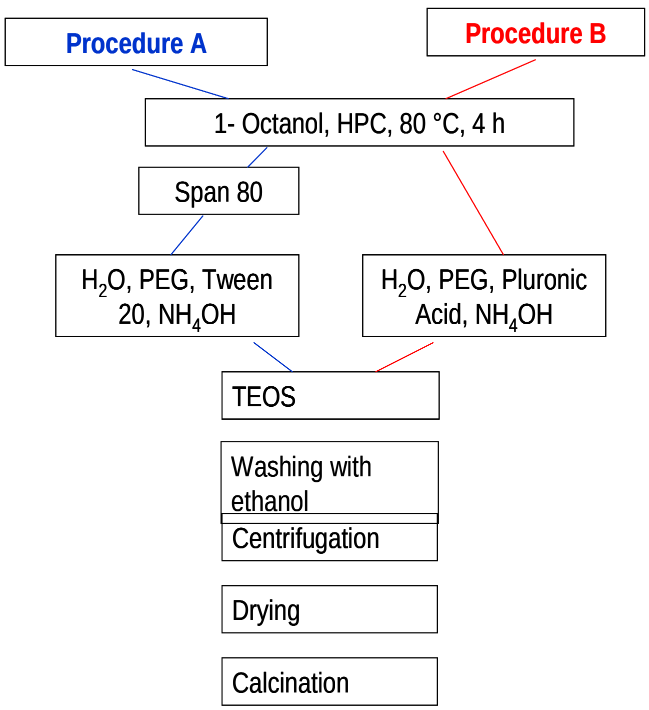

Figure 5: Method for the micro encapsulation of titanium oxide particles for use in e-paper applications.

The device by means of an arrangement of concentric orifices achieves the development of microcapsules in the order of 40-100 μm. Air is used as the carrier medium for the formation and development of the microcapsule, while the arrangement allows a high degree of flexibility with respect to the materials that are going to be used.

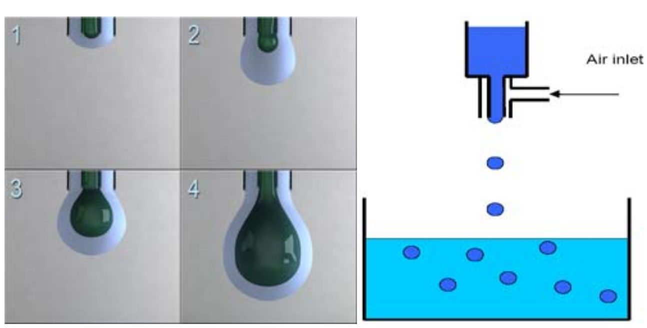

Figure 6: Experimental arrangement for the development of silica microcapsules for e-paper applications

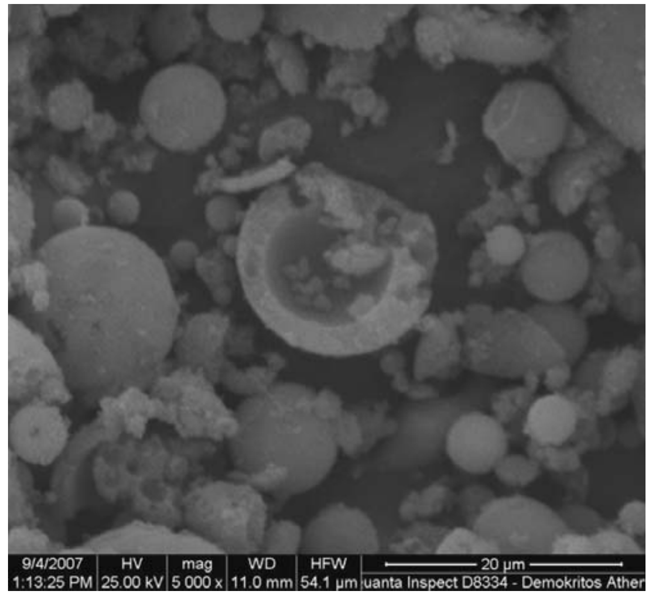

Figure 7a: SEM images of hollow silica microspheres with porous shells – Procedure A

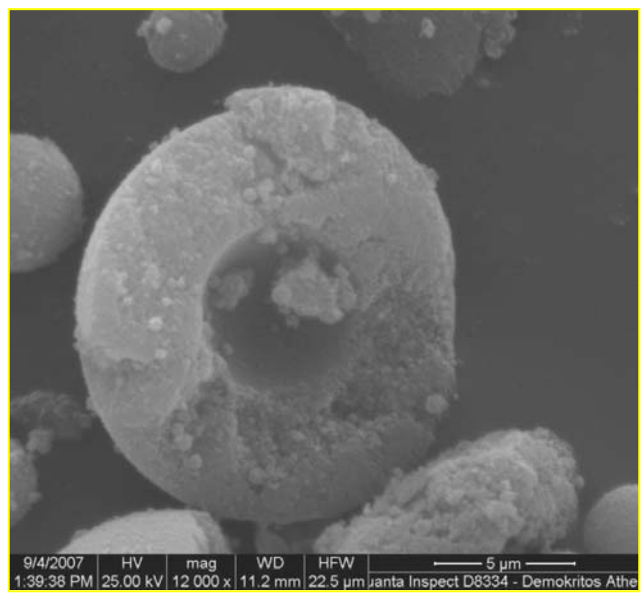

Figure 7b: ***SEM images of hollow silica microspheres with porous shells*** *– Procedure A*

Furthermore, it is expected that during a follow-up phase of the current experimentation process, the formation of microcapsules in the area of 20 μm will become possible.

5. Discussion & future research prospects

E-paper applications and optimization of related technologies are expected to receive significant attention in the next few years and become the object of significant research efforts. In this manner and apart from the necessary miniaturization of the components and the optimization and integration of the involved technologies, it will be of outmost importance the development of a colored e-paper display. Te available technologies exhibit inherent limitations with respect to the attribution of colors other than black and white or white and blue. The RGB color standard of modern LCD displays, or other similar color formats, cannot be reproduced by existing e-paper displays. One solution towards this is the development of a new generation of pigments and inks that will incorporate particles of different chromatic tones. Of course, the main concern is the development of a suitable particle system or model pigment that will incorporate in a single system all three basic colors.

The research team, responsible for the current study, has directed its efforts to both the area of the development and optimization of an efficient encapsulation process and towards the development of a dye that will allow for attribution of basic colors in an e-paper display.

6. Acknowledgements

The authors would like to acknowledge the financial contribution and support of the IN-SItu study and DEvelopment of processes involving nano-PORous Solids - INSIDE-PORES, European Network for Scientific Excellence.

7. References

[1] Heeger A. J., MacDiarmid A. G. and Shirakawa H, "P-Type electrically conducting doped polyacetylene film and method of preparing same", US Patent 4222903, 1978.

[2] Murau, P. & Singer, B., "The understanding and elimination of some suspension instabilities in an electrophoretic display". J. Appl. Phys. 49, 4820–4829, 1978.

[3] Claus, C. J. & Mayer, E. F.in Xerography and Related Processes(eds Dessauer, J. H. & Clark, H. E.) 341–373 (Focal, New York, (1965)).

[4] Fowkes, F. M., Jinnai, H., Mostafa, M. A., Anderson, F. W. & Moore, R. J, in Colloids and Surfaces in Reprographic Technology (eds Hair, M. & Croucher, M.D.) (Am. Chem. Soc), 1982.

[5] Berggren M., Kugler T., Remonen T., Nilsson D., Miaoxiang C. and Norberg, P, " Paper electronics and electronic paper", In: Proceeding of the 1st International IEEE Conference on Polymers and Adhesives in Microelectronics and Photonics, pp. 300-303, Potsdam, Germany, 2001.

[6] Rogers A. J., Bao Z., Baldwin K., Dodabalapur A., Crone B., Raju V.R., Kuck V., Katz H., Amundson K., Ewing J. and Drzaic, P., "Paper-like electronic displays: Large-area rubberstamped plastic sheets of electronics and microencapsulated electrophoretic inks". In: Proceedings of National Academy of Science, vol. 98, no. 9, 4835–4840, 2001.

[7] Wang C., Bos P.J., "Bistable C1 ferroelectric liquid crystal device for e-paper application", Displays 25, 187–194, 2004.

[8] Sheridon N. K. et al, "Method for making microencapsulated gyricon beads", US Patent 6524500, 2003.

[9] Albert J. D. et al, "Process for creating an encapsulated electrophoretic display", US Patent 6067185, 2000.

[10] Comiskey B., Albert J. D., Yoshizawa H. and Jacobson J., "An electrophoretic ink for all-printed reflective electronic displays", Nature 394, p.p. 253-255, July 1998.

[11] Wang L., Fine D., Sharma D., Torsi L. and Dodabalapur, A. "Nanoscale organic and polymeric field-effect transistors as chemical sensors", J. of Analytical and Bioanalytical Chemistry, Springer Berlin / Heidelberg 384 (2): 310-321, 2006.

[12] Chen Y., Au J., Kazlas P., Ritenour A., Gates H. and Goodman J., "Ultra-thin, high-resolution, flexible electronic ink displays addressed by a-Si active-matrix TFT backplanes on stainless steel foil. In: Proceedings of the International Electron Devices Meeting, IEDM '02 (IEEE), 2002.

8. Author Biographies

Nickolas Kakizis received his BSc. in Mech. Eng. & Computer Science, his MSc. in Material Science of advanced Composites and his PhD in Material Science and Sensor Systems Integration from the Univ. of London. He is a Project Manager and Research Coordinator for the NCSR "Demokritos".

Marios Tsigonias received his BSc in Graphic Arts Technology from the Technological Educational Institute of Athens and his MSc in Chemistry (Polymers) from the National University of Athens. He is teaching in the Graphic Arts Technology Faculty in the TEI of Athens and he is working on nanostructured materials and polymers for GA applications in the NCSR Demokritos.

Spyridon Nomikos received his BSc in Graphic Arts Technology from the Technological Educational Institution of Athens and his PhD in Graphic Arts (Polymers) from the University of Aegean. He is teaching in the Graphic Arts Technology Faculty in the TEI of Athens and he is working on the research of the RFID systems.

Anastasios Politis received his BSc in graphic Arts Technology from the Technological Educational Institute of Athens and his PhD in Graphic Arts from the KTH – Royal Institute of Sweden. He is teaching in the Graphic Arts Technology Faculty in the TEI of Athens and he is working on publishing systems, new graphic Arts technologies and packaging applications.

Enlund Nils is a senior researcher and professor at the Royal Institute of Engineering of Sweden (KTH) and has as its primary research interest printing media and digitization of printing processes.

Aggeliki Kanelopoulou is a post-graduate student at NCSR "Demokritos" and responsible for most of the experimental data presented in the current paper.

Christos Trapalis is a research director at NCSR "Demokritos" and its research objectives target mainly the development of a new generation of pigments and inks based on titanium oxide.

Nick Kanellopoulos is a director of research at the NCSR "Demokritos" and in charge of the Microporous Materials and Membranes for Environmental Applications Laboratory and respective research group. He is also the coordinator of the Inside-Pores European Network of Scientific Excellence funded under the 6th Framework Programme for Research & Technological Development of the European Union.