microcup® electronic paper by roll-to-roll manufacturing processes

HongMei Zang & R. C. Liang

A high performance, light-weight, flexible and durable electronic paper/display with low power consumption and affordable cost has been pursued for years to replace paper or book. Bistable electrophoretic display (EPD) based on electrophoresis of charged pigment particles in a dielectric solvent was introduced in the early 1970s.[1-4] It has received extraordinarily attention in the past decade because of its outstanding properties in bistability, power consumption, viewing angle, and reflective contrast ratio. However, until now, no EPD technology in the prior art is capable of delivering all the features and cost structure required to achieve any significant business success.

In this paper, electronic paper manufactured by a roll-to-roll process based on novel Microcup® and top-sealing technologies will be discussed.[5-8] Rolls of ultra thin, ultra light, and flexible EPDs with format flexibility, excellent physicomechanical properties and wide viewing angle have been produced on a continuous plastic web at high speed and low cost.

Microcup® Electrophoretic Displays

As shown in the schematic drawing of a typical Microcup® EPD (Figure 1), a Microcup® array filled with a dispersion of charged pigment (such as TiO_2) microparticles in a colored dielectric solvent is sandwiched between a pair of electrodes. The electrode on the viewing side is transparent. When a voltage difference is applied, the pigment microparticles selectively migrate to the electrode(s). Depending on the polarity of the particle charge and the electrode, either the color of the pigment or the color of the dielectric solvent will be seen by the viewer. Typical dimension of the Microcup® may vary in the range of 60-180 um in width or length, 12-40 um in height, and 5-25 um in width of partition walls (Figure 2).

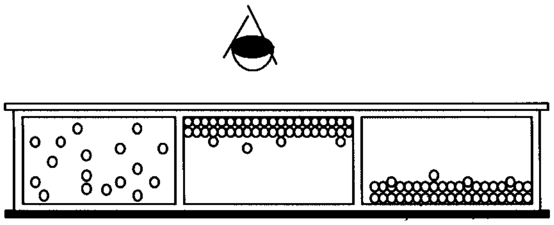

Figure 1. Schematic cross-section of a Microcup® EPD.

The pigment microparticles are submicron in size with a narrow size distribution and are density-matched very closely to the dielectric solvent by incorporating low-density polymer on their surface. Excellent dispersion stability has been observed even after centrifuged at 1000G for more than 30 minutes.

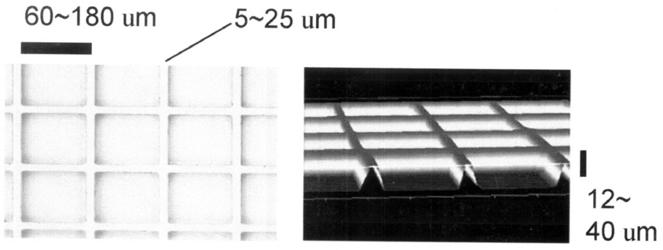

Figure 2. Surface profiles of a typical Microcup® array as measured by Wyko NT1000 Surface Profiler.

Roll-to-Roll Display Manufacturing Processes

The Microcup® array may be fabricated by a roll-to-roll synchronized lithographic process.[9] For example, an electrode film such as ITO/PET may be coated with a radiation curable composition, imagewise exposed with a moving photomask synchronized with the web, and developed with a solvent to form the Microcup® array. Alternatively, the Microcup® array may be manufactured by microembossing.[10,11]

A schematic process flow of a typical SiPix roll-to-roll process for the manufacturing of electronic paper is shown in Figure 3. Rolls of Microcup® EPD panels may be prepared by (1) coating a radiation curable composition on an

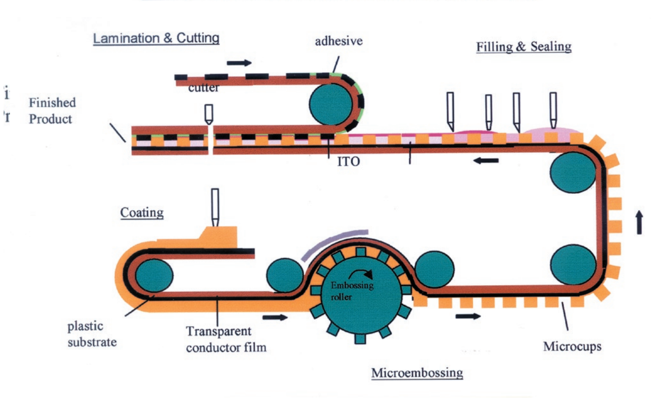

Figure 3. Schematic process flow of the SiPix roll-to-roll electronic paper manufacturing process.

ITO/PET film, (2) embossing the coating with a pre-patterned male mold and hardening the composition, (3) filling the Microcup® array with an electrophoretic fluid and top-sealing the filled array, and finally (4) laminating the sealed array with a second substrate (conductor) film. The throughput of the entire process starting from a bare conductor film to the assembled EPD panel may be realized at a speed of ≥10 ft/min.

The Microcup® composition typically comprises multifunctional monomers and oligomers such as polyester acrylates, silicone acrylates, or polyurethane acrylates carefully selected for optimum mold release and physicomechanical properties. Binder, surfactants, antioxidants and oxygen scavengers may also be added to improve the rheology, coatability, storage stability and the UV curing speed.

The Continuous Filling/Top-Sealing Processes(5,8,12,13)

The steps of filling and sealing a liquid crystal composition into a LCD cell are generally very time-consuming. Depending on the size of the display, the liquid crystal used and the cell gap, 1-20 hours are typically required to reduce trapped-in defects, particularly air pockets. To enable the roll-to-roll manufacturing of Microcup® EPDs, however, each process step in Figure 3 must be accomplished within seconds. The SiPix 1-pass filling and top-sealing process is shown in Figure 4. A sealing composition is pre-emulsified in the electrophoretic fluid containing density-matched pigment microparticles and coated onto the Microcups® (4A). The sealing composition is optimized to allow fast phase separation and creaming of the sealing layer to form a contiguous film with acceptable integrity on the top of the filled Microcups® (4B). The phase-separated top-sealing layer may then be hardened by, for example, UV curing (4C).

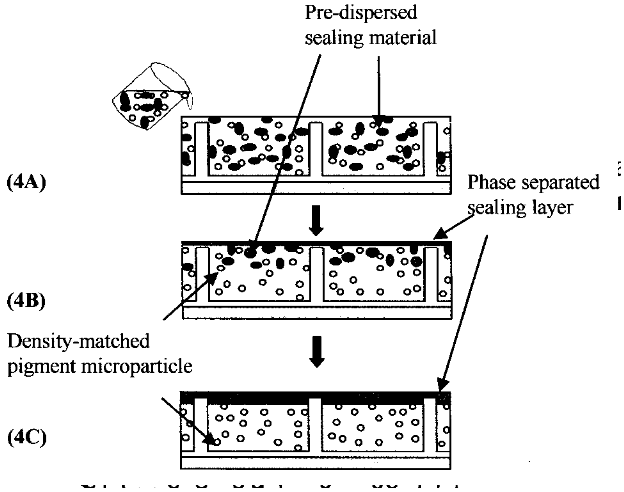

Figure 4. Schematic SiPix 1-pass top-sealing process.
(4A) Filling the Microcup® with an electrophoretic fluid comprising a pre-emulsified sealing composition
(4B) Phase separation and floating of the lighter sealing composition to the top of the fluid
(4C) Hardening the top-sealing layer

Alternatively, the Microcup® array may be filled and top-sealed by a 2-pass top-sealing process. Partially filled Microcups® are overcoated with a top-sealing composition which is then dried and hardened by, for example, interfacial polymerization or crosslinking, moisture, radiation, and thermal curing, or their combinations.

To achieve an acceptable seamless top-sealing by either process, at least six critical parameters must be optimized: (1) the density difference between the sealing composition and the electrophoretic fluid, (2) the degree of incompatibility among the pigment microparticles, the dielectric solvent, and the sealing composition, (3) the surface tension and interfacial tension of all interfaces or surfaces involved, (4) the interaction between the sealing composition and the partition walls, (5) the rheology of both the sealing composition and the electrophoretic fluid, and (6) the integrity and physico-mechanical properties of the sealing layer during and after sealing. The 1-pass sealing process is highly attractive because of its simplicity. However, the 2-pass process is more tolerant particularly when the sealing composition is at least partially compatible with the electrophoretic fluid. High quality Microcup® displays have been successfully produced at high yield with a web speed of more than 30 ft/min. Color displays may also be prepared continuously by sequential filling and top-sealing of, for example, red, green and blue electrophoretic fluids in predetermined areas of the Microcup® array.

Microcup® EPDs

For traditional displays, the manufacturing cost typically increases dramatically as the size of the display increases. The unique Microcup® structure and the innovative top-sealing process allow each Microcup® to be isolated and sealed seamlessly. Displays of different sizes and shapes may be prepared from the same jumbo roll of the Microcup® EPD panel without the risk of leaking out the fluid enclosed therein. Figure 5A shows an optical photograph of a segment Microcup® EPD operating at ±15V while the display was bended at about 120° angle. Figure 5B shows that the segment Microcup® EPD has a near 180° viewing angle and maintains its switching performance even after the display was cut. This format flexibility significantly reduces the scrape rate and in turn the cost since

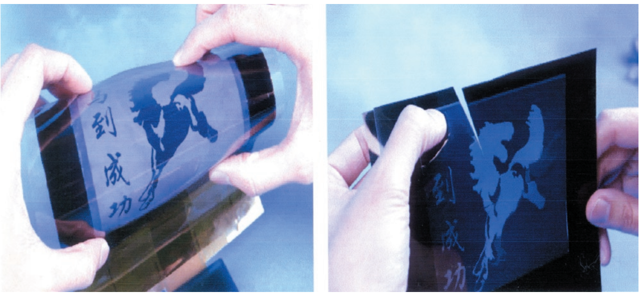

Figure 5. Photographs of a segment Microcup® EPD switched at ±15V; (5A) switched at 120° bend angle, (5B) switched well even after the display was cut.

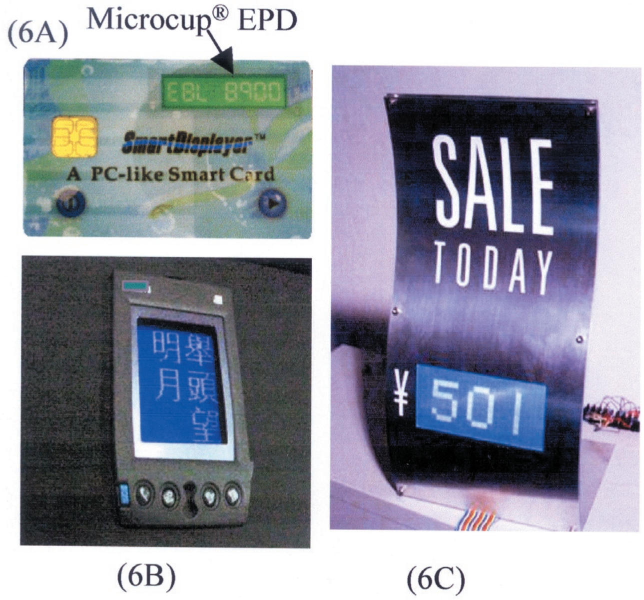

Figure 6. Some first generation Microcup® EPD products
(A) A smart-card with a segment Microcup® EPD
(B) An active matrix Microcup® PDA
(C) A passive matrix Microcup® price tag and sign

the defect area of a Microcup® panel may be cut off without any deterioration of performance in other areas.

Two types of Microcup® EPD films as thin as 0.15 mm and as light as 0.4 gm/in^2 have been manufactured by the SiPix roll-to-roll process: (1) pre-laminated PMEPD rolls sandwiched between row and column electrodes and (2) ready-to-laminate EPD rolls sandwiched between a release liner and a common electrode film for active matrix (AMEPDs) or direct drive EPDs. The PMEPD rolls may be cut to desired size and formats, followed by asymmetrical cutting and stripping processes to expose the row and column electrodes for connection to outside driver and circuitry. To prepare AMEPDs or direct drive EPDs, the top-sealed Microcup® on common electrode film may be cut and laminated onto a patterned electrode film or a TFT back plane after the release liner is removed. Figure 6 shows some first generation Microcup® EPD products: (6A) a paper-like Smart Card integrated with a segment Microcup® EPD, (6B) an active matrix Microcup® PDA on an a-Si backplane with a contrast ratio of ≥8, a frame rate of ≤0.4 sec, and an image bistability of ≥24 hours at ±10V, and (6C) a passive matrix Microcup® price tag and on-sale sign.

Passive Matrix Microcup® EPD

A PMEPD driven by traditional column and row electrodes has been generally considered a major technical challenge mainly because the threshold characteristics, which is necessary to suppress the undesirable cross-talking effects among adjacent pixels during multiplexing driving, does not exist in most electrophoretic systems. An electrophoretic fluid having inherent threshold characteristics has been reported,[14] however, with undesirable tradeoffs in response time, operation voltage, brightness, image uniformity, and display longevity.

In contrast, by optimizing the particle-particle, particle-sealing layer, and particle-Microcup® interactions, satisfactory threshold characteristics have been demonstrated without the tradeoffs. The unique Microcup® structure allows the compositions of the electrophoretic fluid, the Microcups®, and the top-sealing and adhesive layers to be optimized independently for optimum display performances. High performance Microcup® PMEPDs have been prepared at high throughput by the SiPix roll-to-roll process using inexpensive column and row patterned ITO/PET films. Figure 7A shows the typical electro-optical response curve of a Microcup® PMEPD as a function of driving voltage from 0~40 volts. Saturated optical signal could be reached at ≥30 volts with a t_{on} of about 60 msec, but no signal was detected at all at ≤10 volts. Figure 7B shows that the PMEPD exhibits a contrast ratio of about 10 at ≥25 volts and a threshold voltage of about 10 volts. Excellent image uniformity and shelf-life stability were also observed. By optimizing the compositions of the electrophoretic fluid, the Microcups®, and the sealing/adhesive layers, high performance passive matrix Microcup® EPDs having threshold voltages ranging from 10V to 50V have been demonstrated.[5,8]

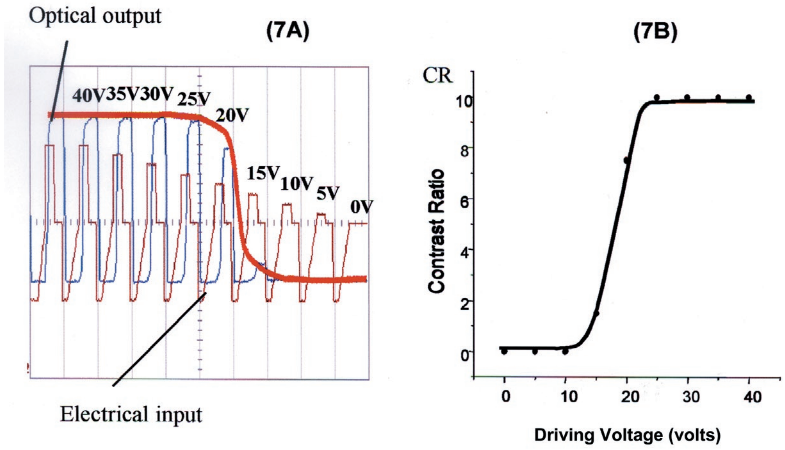

Figure 7. Electro-optical response (7A) and contrast ratio-voltage (7B) curves of the first generation Microcup® PMEPD.

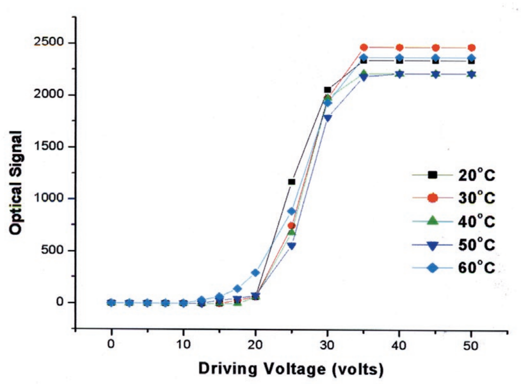

Figure 8. Electro-optical characteristic curve of a typical Microcup® PMEPD operated at 20-60 °C.

More importantly, the threshold voltage and the gamma of the electro-optical response curve remain essentially unchanged in a wide range (20-60 °C) of operation temperature (Figure 8).

Photostabilization of Color Microcup® EPDs

Besides the above-mentioned switching performances, a stable and reproducible color rendition is also of critical importance for any display or electronic paper. To stabilize the colorants against fading or discoloration due to thermo- and/or photo-oxidation, stabilizers such as antioxidants, singlet oxygen quenchers, hindered amines, and UV absorbers[15,16] may be incorporated in the EPD compositions or substrate layers. For any stabilizer to stabilize the colorant in the electrophoretic fluid, a good color stability should not be obtained at the expense of any critical display switching characteristics such as response rate, operation and threshold voltage, and image bistability.

A series of metal-containing quenchers/stabilizers (Figure 9), particularly Ni complexes, have been synthesized at SiPix and their effect on both the colorant stability and EPD performance were evaluated.[17] To be effective, the R and R^1 groups of the quenchers (Figure 9) must be optimized to assure a good solubility in the dielectric solvent. Highly fluorinated R and R^1 are particularly useful when a fluorinated dielectric solvent is used in the electrophoretic fluid. As it is evident from Table 1, the Q_1-1 quencher (wherein M is Ni, R and R^1 are alkyl and fluorinated alkyl, respectively) very effectively quenched the photodegradation of the fluorinated Cu phthalocyanine dye (Blue-1). The dye solution of the control (2A) showed an OD loss of 11% at 620 nm after two hours of exposure under a collimated 150W Xe-Arc lamp, while no loss of OD was observed in the stabilized dye solution (1A) containing 100 ppm of quencher Q_1-1. Compared with the control display sample (2A), negligible degradation of display contrast ratio or Dmin reflectivity was observed in the display samples (1A and 1B) containing 100 ppm of Q_1-1 in the EPD fluid even after 17 hours of high-intensity white light exposure at its Dmax state using a standard EKE bulb connected directly onto the sample surface by an optical fiber. In contrast, the control sample (2B) is no longer functional after the same white light exposure.

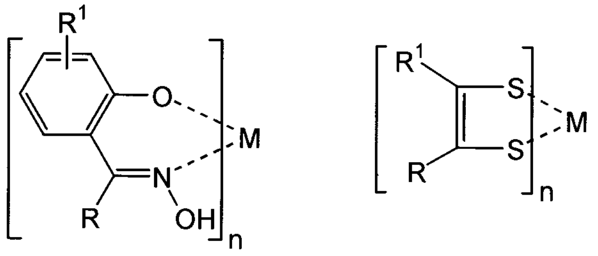

Figure 9. Metal-containing quenchers for the stabilization of electrophoretic fluid.

Conclusion

In summary, Microcup® EPDs with excellent performance and photochemical stability have been prepared by the SiPix roll-to-roll manufacturing process based on

Table 1. The effect of quencher Q_1-1 on the photostabilization of EPD containing a fluorinated Cu phthalocyanine dye (Blue-1) in a highly fluorinated dielectric solvent

	Concentration of Q_1-1 (ppm in EPD fluid)	OD_{620nm} loss after 2 hrs under a collimated 150W Xe-Arc lamp*	White light exposure (hrs)	Normalized % decrease in display reflectance at the D_{min} state @ 40V	Display contrast ratio at 40V, 0.2 Hz
1A	100	0%	0	6.9%	7.1
1B	100	-	17	2.3%	7.6
2A	0	11%	0	0.0%	7.4
2B	0	-	17	86.0%	1.1

* Optical density loss of the dye solution.

proprietary electrophoretic compositions and innovative top-sealing technologies. The world's first plastic PMEPDs prepared on inexpensive row/column ITO/PET films have shown threshold voltages ranging from 5 to 50V with a sharp gamma, fast response time, super image bistability, and wide operation temperature latitude. Low voltage driving Microcup® AMEPDs based on a-Si TFT backplane have also been demonstrated. Microcup® EPDs bring new perspectives into the display industry with its excellent flexibility, PM driving ability, format flexibility, grayscale bistability, low power consumption, and low cost structure.

In addition to the EPD mentioned above, format flexible Microcup® LCDs have also been prepared by the same roll-to-roll Microcup® and top-sealing technologies with Microcup® of much smaller dimensions.[18] This new type of LCD is essentially a mono-dispersed PDLC[19] (polymer dispersed liquid crystal) with a superior cost structure, physicomechanical properties, and switching characteristics including fast response rate, low orientation field, and negligible hysteresis.

Because of their outstanding performance, durability, flexibility and cost structure, the ultra-thin and ultra light-weight Microcup® electronic paper/displays may be used in a variety of applications. These include cell phones, PDAs, vehicle displays, clocks, electronic signage, electronic price tags, smart-cards, electronic news paper/books, electronic bulletins, electronic whiteboards, tablet PC, electronic security ID cards, displays for education appliances and kids toys, wearable displays, etc.

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About the Authors

Dr. HongMei Zang received her Ph.D. in photochemical sciences from Bowling Green State University under the direction of Dr. D. C. Neckers in 2000. She is currently the Senior Manager of the Polymer Technology group at SiPix Imaging where she has worked on the invention and development of the Microcup® electronic paper. Dr. Zang has coauthored four technical papers and more than 30 U.S. patents and applications since December 1999. Dr. Zang can be reached at hong-mei.zang@sipix.com.

Dr. R. C. Liang is currently the CTO and Vice Chairman of SiPix Group. He recieved his Ph.D. in Polymer Science Engineering at Polytechnic University in New York. He was an Asistant Professor at the Imaging Institute at Polytechnic University, a Research Fellow at Mead Imaging, and Research Fellow and Program Director at Polaroid. Dr. Liang also serves as an Adjunct Professor and Scientific Advisory Board member at the Center for Photochemcial Sciences at Bowling Green State University. The web address for SiPix is www.sipix.com. Dr. Liang's e-mail is rc.liang@sipix.com.

Marcus Continued from Page 7

Then I went to work at the National Research Council, and the main advisor there was E. W. R. Stacy, a world-renowned photochemist, and he was a stiffer individual but you felt you were really doing cutting edge science, which I hadn't felt at McGill, but part of that was the war effort, and so that was quite different. With Steacie, you really felt as through you were dealing with somebody who wanted to get it right, who wanted to do those experiments right. He had a big skepticism of theory. There was a certain amount of theory going on where one juggled the parameters in order to fit the activation energy of each reaction. But I felt there's somebody who was a real professional. I would say that O. K. Rice was the one who had the most lasting effect on me.

The Spectrum: What was your first experiment as child?

Marcus: Well, of course, I had a chemistry set. One of those things that had about 20 experiments where you made soap and God knows what. It was one of the standard sets, perhaps a Gilbert. You know, it brings us back to the 1930s. That was sort of standard cookbook thing. I don't know what effect that had on my career. Maybe more than that was the idea of construction.

As you know only too well, part of science is you build things, whether you're building ideas or theories or apparatus of what have you, you put parts together, you set them into what you hope will be kind of a logical ho-ho. I played incessantly with things like erector sets and Tinker Toys. But it was the Erector set with all of the construction that I spent a lot of time with. I suspect that those kinds of experiments, building things, perhaps had more to do with the idea of science than the chemistry set.

The Spectrum: And you continued building theories the rest of your life?

Marcus: Oh, yeah. That's right. I love to try—I'm sure many of us do—to try to get at the physical essence of the problem. You know, not just see a bunch of mathematics or a lot of equations of what have you. First of all, I'm interested in phenomena. And what is the physical essence of the phenomenon? Has somebody else captured it? Sometimes you get very excited about some work that somebody's done, some beautiful simple approach to things, like Raleigh's work in the late 1890s on the explosion of charged droplets which in later came into Fenn's electrospray which in turn found its way into the Nobel Prize.

You know there's a beauty of some relatively simple idea which captures the essence of a phenomenon. That's what I look for, so that when I see something which is a bit puzzling, one of which of course that electron transfer was a paradox in the Libby paper, then I get interested in trying to see how basic I could answer it. And can I get at the essence?

The most recent example of that is in the problem of unusual isotopes of oxygen in the ozone in the stratosphere and also in the laboratory. That problem remained a puzzle for about 20 years and then finally with the aid of two students, Yi Qin Gao and Bryan Hathorn, we came up with an explanation that certainly quite a few people have accepted. We published a number of papers on it in any event. That's the sort of thing I mean. How do you *explain* it? The fact that carries us through under those conditions if we have confidence in the experiments is that there has to be an explanation. Whether or not we will find it is something else again. But there has to be an explanation. So that sometimes carries us through on a problem.

End of perspective