Development of Bistable Electronic Inks for Reflective Color Media

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Abstract

Electronic inks have been developed for each primary color to serve as the imaging fluids for novel electro-kinetic display (EKD) technology, which uses in-plane optical effects and out of plane switching fields to switch between color and clear states, allowing a stacked color layer approach. The need for compaction into small volumes to achieve a clear state and repeated cycles of spreading and compaction creates challenges for the stabilization and charging of colorant particles. Surfactants play a critical role in determining system behaviors. This paper reports on the latest findings of surfactant influence on optical switching and bistability characteristics of display performance for some proprietary surfactant formulations.

HP's combination of novel device architecture, proprietary inks, and R2R manufacturing platform enables the required attributes for electronic media such as flexibility, robustness, low power, transparency, print-quality color, and scalability at low cost. The innovations described in this paper are applicable to either segmented or pixilated electronic media, and are currently being developed for both digital signage and electronic paper markets.

Keywords: *Reflective display, Print-like color, Electrokinetic technology, Electronic inks, Roll-to-Roll manufacturing.*

Introduction

Reflective displays have seen tremendous growth recently with their application to eBook readers, enabled by the widespread adoption of E Ink Corporation's micro-encapsulated black and white electrophoretic (EP) display film [1]. This growth continues to drive technology development in related frontplane and backplane technologies, and especially in their integration required to provide compelling color solutions [2]. Conventional displays typically use a combination of side-by-side color elements to generate additive color (e.g., RGB or RGBW color filters), and this approach has been shown by others with black and white reflective electro-optic layers. Since reflective images rely solely on ambient light, the image will be bright and colorful only if the incident light is reflected efficiently. Side-by-side color approaches devote portions of each pixel to only certain colors, so they inherently absorb the majority of the incident light, and thus are inefficient (<50% efficiency), resulting in limited color gamut volume [2].

At Hewlett-Packard (HP), we are approaching the challenge of generating bright, high-quality reflective color images from the perspective of printing by layering subtractive colorants (CMYK) to allow every available color at every addressable pixel location. Layered colorants in electronic media can be enabled by stacking electro-optic layers that are modulated between colored and transparent optical states. In order to provide a transparent state with fast switching using circuits fabricated on a plastic substrate by a flexible roll-to-roll (R2R) manufacturing platform, HP has developed a novel electrokinetic display (EKD) frontplane architecture with electrically addressable inks. We have previously reported the application of HP's EKD technology to thin, flexible, segmented, and reflective "electronic skins" (eSkins) [3,4].

Capability to integrate this novel reflective color media with active matrix backplanes is the key to enabling pixelated reflective displays beyond eSkins. In order to provide full color with stacked architecture of layered colorants, each colorant layer needs to be addressed with electrical interconnect, either by providing vias from a common electronics layer, or by integration of a suitably transparent matrix of driving electronics. HP is developing a suitable active matrix backplane technology based on transparent oxide TFTs that are compatible with existing glass (AMLCD) fabs as well as eventual migration to a R2R manufacturing process [5,6].

In this paper, we report further details on our novel flexible reflective color media based on this EKD technology platform and on the latest findings of surfactant influence on optical switching and bistability characteristics of display performance for some proprietary surfactant formulations. We also demonstrate further advancements in the technology by integrating the frontplane with a transparent metal oxide TFT backplane to demonstrate a pixelated active matrix reflective display.

Novel EKD Technology Platform

Conventional EP architectures (e.g., E Ink's Pearl Imaging Film) are based on out-of-plane switching with out-of-plane optical effects, where the colorant particles are primarily moved perpendicular to the plane of the film by applying electric fields primarily perpendicular to the plane of the film[1]. These conventional architectures do not enable transparency or print-like full color. Alternative in-plane EP architectures based on in-plane switching with in-plane optical effects have been shown by IBM, Philips, and others [6,7], where the colorant particles are primarily moved parallel to the plane of the film by applying electric fields primarily parallel to the plane of the film. While in-plane EP architectures provide a transparent state which enables stacked layers for full color displays, they are generally limited by tradeoffs between clear aperture and switching speed, and also require electrical cross-overs of in-plane electrodes, which increase the manufacturing complexity.

To address these issues, we have developed EKD technology platform, which adopts out-of-plane switching fields with in-plane optical effects. This EKD technology allows transparency in the clear state, which in-turn allows stacked architecture for full color display. Response times have been improved by one order of magnitude compared to in-plane EP devices by reducing the distance the particles have to travel and increasing the driving force applied to the particles. Improved clear aperture with misalignment tolerant architecture is achieved by introducing a uniform distribution of dot arrays to minimize the areas where colorant particles are compacted.

Figure 1 shows schematic and microscopic images of unique colored and transparent states enabled by this architecture. Without an applied voltage, the colorant particles are spread uniformly, and the display element is in the dark state. Under a bias condition that provides compaction of colorant particles into dot-patterned cavities, the display element produces a transparent state. This transparent state can be maintained with a low-power holding voltage (<1 μ W/cm² at ~5 V typical). We have demonstrated relatively fast switching (< 300ms) and reflectance larger than 60% (brightness L* >80) having contrast ratio of 30:1 for black and white electronic media using our proprietary black inks and white reflector background (L* ~96). Inherent advantages resulting from the control of nanoscale colorants in an out-of-plane electrode geometry are wide viewing angle (180 degrees), continuous levels of gray, and high spatial resolution (>500PPI with single dot).

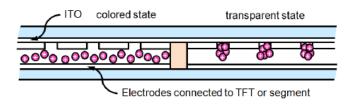


Figure 1a. Schematics of novel device architecture: Clear and dark state.

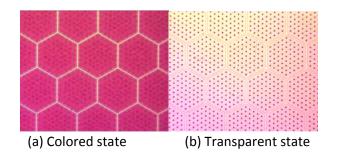


Figure 1b. Microscopic images of electrokinetic architecture.

Design and Development of Electronic Inks

A high performance electronic ink should exhibit good optical density, high mobility for fast switching speed, high cycle switching endurance, environmental stability, and low toxicity. Stable, charged colorant particle suspensions require at least the following four components: (1) colorant particle, (2) carrier fluid, (3) dispersant, and (4) charge director. The colorant particle provides the color and can participate in charging. Key considerations are the particle size, surface functional groups, dispersbility, hue, chroma, and lightfastness. The carrier fluid acts as a vehicle for dispersing the pigment as well as a low dielectric constant medium. When choosing the carrier fluid, its polarity, viscosity, resistivity, specific gravity, chemical stability, and toxicity must all be considered. The dispersant provides steric stabilization of the colorant particles to prevent particle aggregation. The charge director enables charging of the particles and carries counter charges. It should be colorless and dispersible or dissolvable in the carrier fluid. The charging mechanism is based on either preferred adsorption of charged reverse micelles or acid-base interaction between the particle surface and neutral reverse micelles [10, 11]. The counter-ions are stabilized by reverse micelles composed of the charge director.

In order to study structure property relationship of surfactants and their impact on device performance, a series of five polyisobutylene (PIB) succinimide surfactants were synthesized with systematic variations in the polar polyamine head and purified to separate di-substituted tails from the product (**Figure 2**). Also considered were commercially available PIB succinimide polyamine surfactant (OLOA 11000) and PIB succinic acid anhydride (OLOA 15500) from Chevron Oronite. The exact structures for the commercial products are not known. Surfactant samples were prepared to 3 wt% in isoparaffinic fluid (ExxonMobil) and sonicated for 20 minutes.

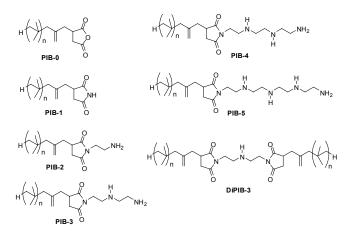


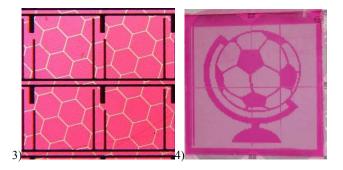
Figure 2. Surfactants studied

To study the structure property relationship of these new surfactants, we have used three techniques to measure the micelle sizes: small-angle light scattering (SAXS), dynamic light scattering (DLS), and transient current measurements. SAXS gives the micelle core plus an underestimated shell, while DLS and transient current measurements provide the micelle hydrodynamic radius. The results from SAXS agreed with DLS and showed that increasing polyamines in the surfactant head increased the micelle size. The hydrodynamic radius was also calculated based on transient current measurements, and agreed well with the DLS results.

The transient current technique further determined that increasing polyamines increased the charge stabilization capability of the micelles. Commercial OLOA 11000 behaves like PIB-3 suggesting it contains a triamine polar head, but likely with disubstituted by-products or a lower concentration of charge generating ions, since there are charge stabilization differences. Extending the surfactant variations to electronic ink performance showed that the triamine polar head was sufficient for acceptable device performance while the absence of amine made a poor dispersion. It is concluded that correlations between the charge concentrations of surfactant-only solutions with electronic ink performance need take into account surfactant chemistry differences. The presence of an anhydride, imide, or amine in the polar head group affects electronic ink performance differently, as well as even smaller chemistry differences, such as just the number of amines present. Through this systematic study, we have discovered a novel surfactant - HP-DEPBT, which shows greatly improved ink performance attributes such as extended lifetime and bistability of switching devices.

Integration and Driving

The out-of-plane electrode geometry used in our frontplane architecture provides compatibility with active matrix backplane. The flexible frontplane media has been integrated with electrically addressable ink onto a backplane array of transparent multicomponent oxide (MCO) TFTs. The plastic frontplane film is laminated onto the TFT backplane as shown from the transmission optical micrograph in Figure 3. To modulate the optical state of each pixel, the pixel plate electrodes are selectively activated through the TFT backplane array, while the top electrode is maintained at a fixed reference bias. Pixels are approximately 500 μ m square (limited here by the dimensions of the active matrix backplane; the effective resolution of the frontplane can exceed 100 ppi). There are 16834 pixels (128 rows x 128 columns) on the proto backplane design to demonstrate the feasibility of integration and active-matrix pixelation.



Figures 3. Transmission optical micrograph of integrated transparent TFT pixels with frontplane cells. 4) Integrated flexible frontplane with transparent oxide TFT backplane showing pixilation (16384 pixels).

Figure 4 shows an integrated active-matrix EKD prototype in operation. Optimization of the TFT backplane is still underway to improve voltage drive capability and provide even better optical and switching performance.

Improved Ink Performance by HP's Proprietary Surfactants

The inks based on HP's new surfactant (HP-DEPBT) showed much better initial contrast and retention of the initial contrast than the control and other commercial surfactants. Furthermore, the EKD devices based this new surfactant also showed bistability, which is the first bistable EP color device that gives transparent state [12]. **Figure 5** shows grey scale images of a bi-stable magenta ink, in an active matrix device, which shows image stability overnight for about 15 hours. Systematic investigation of solvents and additives yielded a bi-stable black ink. Shown in **Figure 6** are a bi-stable magenta on active matrix backplane and a bi-stable magenta device and a bi-stable black segmented devices.

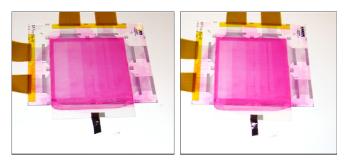


Photo at 0 hours Photo at 15 hours Figure 5. Integrated EKD device showing bistable grey scale overnight



Figure 6. Bi-stable Segmented Magenta and Black Devices

Integrated Print-Like Color Reflective Display

We have successfully developed primary colorant inks and applied these novel electronic inks to segmented stacked systems. **Fig. 7a** shows each colorant layer in a segmented design, **Fig 7b, c** & d shows a three layer reflective stack of primary colorants in three different states. Stacked layer design allows transflective operation enabling the use of our technology during the day with bright reflective mode or at night with front or back lighting unit. 3-layer stacked devices measured with gain reflectors, which also help suppress total internal reflection loss, have 33% reflectivity or L*=65. 3-layer stacked devices with Lambertian white reflector

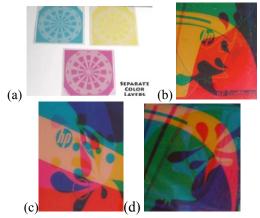


Figure 7. (a) Individual colorant layer, (b, c, d) Color demo from segmented three layer stack with $L^*=23$ in the fully dark state and $L^*=64$ in the clear state with a Lambertian white reflector.

have been measured at L*=64. Our modeling indicates white reflectance will provide L*~80 (meeting SNAP), if interface losses are minimized and the top surface is anti-reflection coated. Fig. 8 shows the images of electronic ink based pixilated stacked color reflective display using a three layer Cyan/Magenta/Yellow stack, each layer integrated with prototype TFT backplanes.



Figure 8 HP's prototype reflective display technology with print-like color (128 x 128 pixels).

Conclusion

A novel hybrid architecture adopting out-of-plane switching with in-plane optical effects (EKD) has been demonstrated that provides a transparent state with fast switching. Grayscale capability, pixilation, and transparency of EKD technology allow us to achieve full color reflective display. Based on optical modeling, the HP technology presented here is predicted to approach the SNAP printing standard using a system of layered colorants, enabling a level of image quality which is critical to extend the broad acceptance of full color reflective display technology. Integration of HP's R2R compatible frontplane and backplane technologies, demonstrates a scalable platform for low power, transparent, print-like media that opens up a path towards eco-friendly, bright, full color, flexible e-paper and digital signage applications. We have systematically studied structure property relationship of surfactants and their impact on performance of EKD devices based on these new surfactants. Through this systematic study, we have discovered a novel surfactant - HP-DEPBT, which shows greatly improved ink performances such as extended lifetime and bistability of switching devices. We have also demonstrated 3-layer stacked segmented reflective display

prototypes, as well as pixilated stacked color reflective display prototypes.

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Author Biography

Zhang-Lin Zhou received his B. S. in Polymer Chemistry from Zhejiang University in 1987, his M.S. And PhD in Organic Chemistry both from Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences in 1992. He has over 25 years of experiences on a wide variety of different chemistry fields including organic/polymer synthesis, drug discovery, Near-IR dyes, fluorescent probes, OLED materials, electrophoretic display and pigment dispersions. Since 2000, He has worked at Hewlett-Packard Labs in Palo Alto, California, USA, working on the project of "E-Print" program, which aims to develop portable, personal interactive electronic papers. He is a member of the IS&T, the American Chemical Society and Materials Research Society.