Dyed polymeric microparticle colloid dispersions for full colour electrophoretic displays

Mark James, Louise Farrand, Ashley Smith, Nils Greinert, Henry Wilson, Claire Topping, Roger Kemp, Emily Markham, Mark Goulding and Johannes Canisius
Merck Chemicals Ltd., Advanced Technologies, Chilworth Technical Centre, University Parkway, Southampton, Hampshire, SO16 7QD, UK
Richard Vidal
Merck Chimie, Center Production ESTAPOR, Zone Industrielle,
Rue du Moulin de la Canne, 45 300 Pithiviers, France.

Abstract

Realizing bright and vivid full colour performance in electrophoretic displays presents a significant challenge to display architects and material designers. A range of dyed polymeric microparticles with tunable size, charge and colour have been developed. When formulated as colloidal dispersions in low dielectric constant media, the particles are electrophoretically active and are suitable for use in full colour or monochrome electrophoretic displays.

1. Introduction

The field of e-paper / flexible display / digital signage represents a significant growth opportunity for all parts of the display manufacturing value chain and electrophoretic displays are a viable candidate, due to their low power consumption, paper-like appearance and daylight readability. Current electrophoretic displays (EPDs) are based on e-ink Visplex®[1,2,3] or Sipix Microcup®[4,5,6,7] films. It is recognized that although their performance is suitable for monochrome application, some limitations may arise for bright and vivid full colour performance, due to the necessity of additive colour display architectures and the use of colour filter arrays, overlaid onto the electrophoretic film. One approach to increase the colour and brightness of a full colour EPD is to eliminate the use of colour filters and to utilize coloured particles in the pixel using the subtractive colour principle. Several groups are active in the field of materials and devices for full colour electrophoretic displays[8,9,10,11,12,13,14]. This paper describes a new class of dyed polymeric microparticles and their stable colloidal dispersions in low dielectric media, which exhibit electrophoretic activity. In a similar manner to the offering of "ready to use" liquid crystal mixtures; custom designed electrophoretic display fluids offer increased freedom in the design of advanced pixel architectures for colour-filter-free electrophoretic displays to potential manufacturers, with increased colour performance.

By use of a common approach to particle design, the colour, particle size, charge and surface functionality can be altered and optimized. By use of suitable dyes, it is possible to realize red, green and blue particles for additive colour pixel architectures or cyan, magenta, yellow and black particles for subtractive colour pixel architectures

The degree of optical scattering can be tuned by modification of the difference in refractive index between particle and fluid phase or by particle size modification. The colloidal stability can be tuned by density matching the particle relative to the fluid phase. Fluid parameter tunability can also be advantageous in the design of high performance pixel architectures.

This paper will describe colour data for a range of fluids and electro-optical switching data for both single and dual component fluids in both vertical and in-plane switching configurations.

2. Experimental

The generic polymeric microparticle structure is shown in Figure 1. Dye, charge (of either sign) and steric stabilizing surface modification can be built into the particle by controlling the synthetic conditions. It is also possible to vary the particle size from 100–2000nm for any given particle type, whilst retaining a narrow size distribution. Dynamic light scattering (DLS, non-invasive backscattering technique (NIBS), angle of measurement = 173°) and scanning electron microscopy were used to determine particle size and polydispersity. Electrophoretic mobility and zeta potential were determined using either a Malvern Zetasizer nano ZS™ instrument (diluted sample, angle of measurement = 13°**)** or by direct measurement in a suitable test cell. Colour of particles as formulated fluids was measured on an x-rite colour i5 spectrophotometer in 50□m gap cells, using double pass transmission with a white reflective backstop. Electro-optical data (EOC) for EPD fluids in simple test cells were measured using an Autronics DMS-301[15].

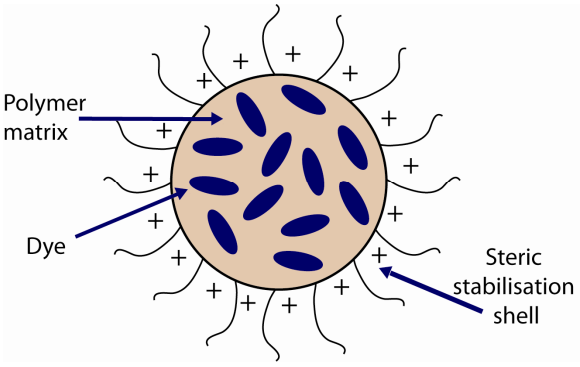


Figure 1. Generic dyed polymer microparticle structure

3. Results and Discussion

3.1 Particle Size & Polydispersity

Table 1 below shows size and polydispersity data for typical red, green, blue, cyan, magenta and yellow particles. A range of different sized particles is shown to demonstrate the versatility of the particle design approach.

Table 1. Polymer Microparticle Size and Polydispersity Data

Particle colour	Particle size / nm (DLS)	Polydispersity Index
Red	381	0.091
Green	826	0.437
Blue	311	0.070
Cyan	549	0.090
Magenta	259	0.095
Yellow	254	0.077

Figure 2 shows a scanning electron micrograph of typical particles, demonstrating their uniform size. It is believed that close control of polydispersity in the polymeric particles will be advantageous for EPD fluid electro-optics and ultimately, front-of-screen performance.

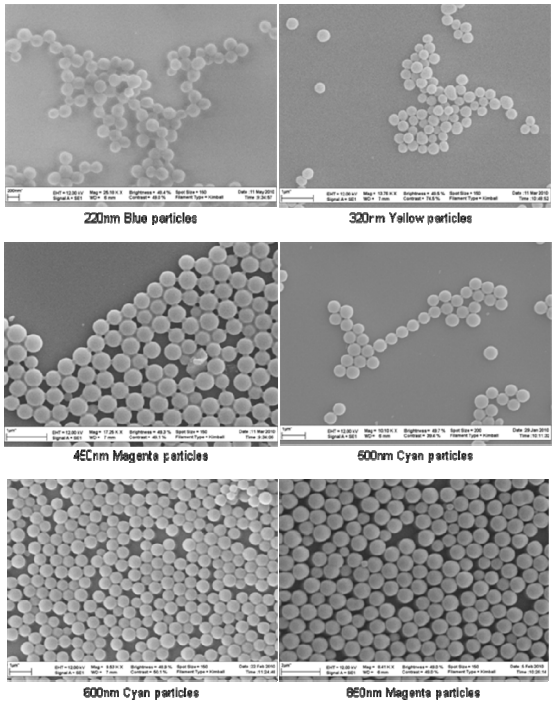


Figure 2. Scanning Electron Micrograph of Various Particles

3.2 Particle Zeta Potential and Electrophoretic Mobility

Table 2 shows zeta potential and electrophoretic mobility data for typical red, green, blue, cyan, magenta and yellow particles. Electrophoretic mobility, U_E, of the particles in low dielectric constant media is determined by the Henry equation (1)[16].

$$U_E = \frac{2\varepsilon\zeta}{3\eta}.F(ka) \quad (1)$$

Where ε is the dielectric constant of the dispersion medium, η is viscosity of the dispersion medium (Pa s), and ζ is the zeta potential. When using particles <1μm diameter in low dielectric media, the Huckel approximation is used[16], and F(ka) is assumed to be 1.

Table 2. Polymer Microparticle Zeta Potential and Electrophoretic Mobility Data

Particle colour	Zeta Potential mV	Electro-phoretic Mobility $m^2/Vs \times 10^{-10}$	Zeta Potential mV	Electro-phoretic Mobility $m^2/Vs \times 10^{-10}$
	-ve charge particles		+ve charge particles	
Red	-63.9	5.93	+49.3	4.57
Green	-87.6	8.13	+76.5	7.10
Blue	-24.8	2.31	+89.5	8.30
Cyan	-65.2	6.05	+68.3	6.34
Magenta	-73.2	6.79	+65.7	6.10
Yellow	-70.9	6.58	+51.6	4.79

From the data shown above, it can be seen that particles can be synthesized in all colours with either a positive or a negative charge. The polymer microparticles demonstrate high values of electrophoretic mobility. This is beneficial for electro-optical properties.

3.3 Particle Spectra and Colour

Figure 3 and Tables 3a & 3b show the colour gamut of particles in CIE L*a*b* colour space under D65 illumination and optical density data for typical red, green, blue, cyan, magenta and yellow particles, when suitably formulated into EPD fluids.

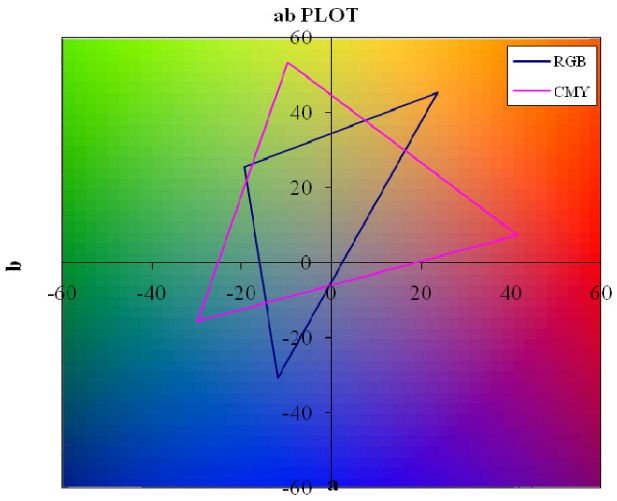


*Figure 3. CIE L*a*b* colour gamut of particles (D65 illumination.)*

It is possible to increase the colour intensity and optical density by increasing either particle volume fraction in the fluid or dye content in the particle. Tunability of colour in the fluid, through either a large number of lower dye content particles or a lower number of higher dye content particles could be advantageous in pixel design. This increases the degree of flexibility for display designers in both transmissive and reflective applications.

Table 3a. EPD Fluid colour data

Particle colour	Colour Data XYZ xy Measured under d65 illumination, 50 □m cells				
	X	Y	Z	x	y
Red	37.672	32.567	10.567	0.4662	0.4030
Green	37.957	46.696	29.233	0.3333	0.4100
Blue	23.377	27.577	55.847	0.2189	0.2582
Cyan	18.824	26.592	40.172	0.2199	0.3107
Magenta	24.672	17.176	22.313	0.3845	0.2677
Yellow	59.458	67.143	24.226	0.3942	0.4452

Table 3b. EPD Fluid optical density (OD) and L*a*b* colour data

Particle colour (volume fraction)	Colour Data L* a*b* d65, 50 □m cells			OD d65, 50 □m cells
	L*	a*	b*	
Red (0.1)	63.81	23.58	45.24	0.5193
Green (0.35)	73.99	-19.40	25.51	0.4294
Blue (0.1)	59.50	-11.92	-30.70	0.4701
Cyan (0.46)	58.59	-29.84	-15.53	0.5976
Magenta (0.1)	48.48	41.28	-7.31	0.5556
Yellow (0.1)	85.58	-9.85	53.35	0.2632

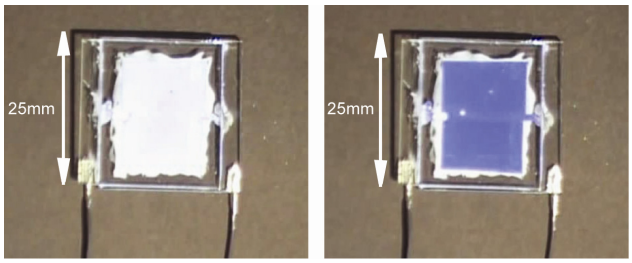
3.4 Electro-optical studies

The EPD fluids so far described comprise a single species of polymeric microparticles plus additives in a low dielelectric constant fluid, such as dodecane. Fluids of this type are suitable for in-plane or shutter mode EPD pixel architectures. This concept can be extended to blends of two different-coloured particles in a single fluid to achieve more complex in-plane electro-optical effects. It is also possible to blend coloured particles with white reflective particles (e.g. TiO_2 or polymer / inorganic hybrid particles) to achieve reflective EPD fluids and demonstrate vertical switching EPD pixel architectures.

3.41 Vertical EPD switching

In order to demonstrate vertical EPD switching of fluids containing dyed polymeric microparticles and white reflective particles, test cell was constructed from ITO coated glass and a PET cell spacer of 50 & 100□m. No microcellular division was used in the test cell.

Figures 4a and 4b show the two switched states of a simple vertical EPD test cell (+60VDC & -60VDC), containing a blue to white reflective EPD fluid, under D65 illumination. Contrast ratio for this cell was measured at 7.3:1 for the blue to white switching curve. The EOC as measured at 20ºC with an Autronics DMS-301 (type A illumination) is shown in Figure 5 for a comparable 50□m cell. Contrast ratio for this cell was measured at 3.2:1 for the blue to white switching curve. The unsymmetrical nature of the EOC in Figure 5 may be due to charge and density differences in the two particle types.



Figures 4a and 4b. Vertical EPD switching of Blue / Reflective White fluid (100□m cell gap; CR = 7.3:1).

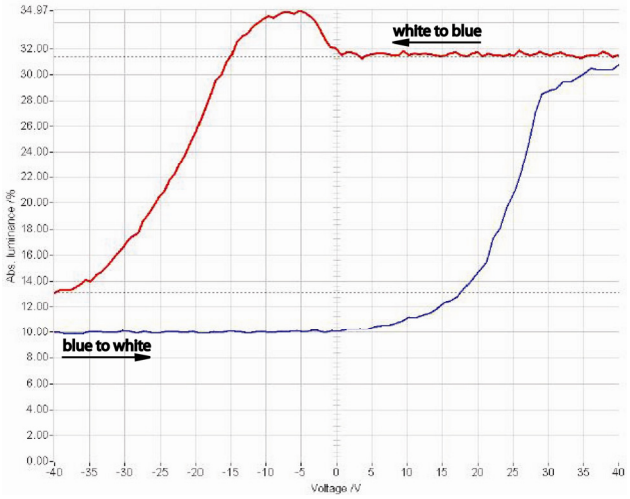
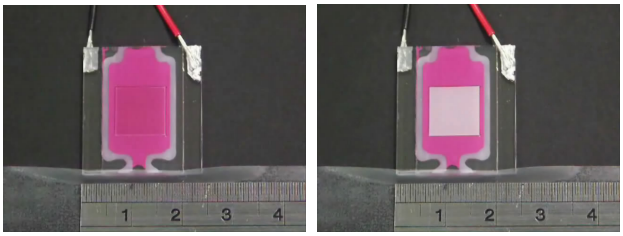


Figure 5. Electro-optical Curve for Blue / Reflective White EPD fluid (50□m cell gap; (CR = 3.2:1).

Figures 6a and 6b show the two switched states of a simple 50□m vertical EPD test cell (+30VDC and -30VDC) containing Magenta dyed polymeric particles and white reflective polymer / inorganic hybrid particles under D65 illumination. The EOC as measured at 20°C with an Autronics DMS-301 (type A illumination) is shown in figure 7. Contrast ratio for this cell was measured at 2.4:1 for the magenta to white switching curve.



Figures 6a and 6b. Vertical EPD switching of Magenta / Reflective White fluid (50□m cell gap; CR = 7.3:1).

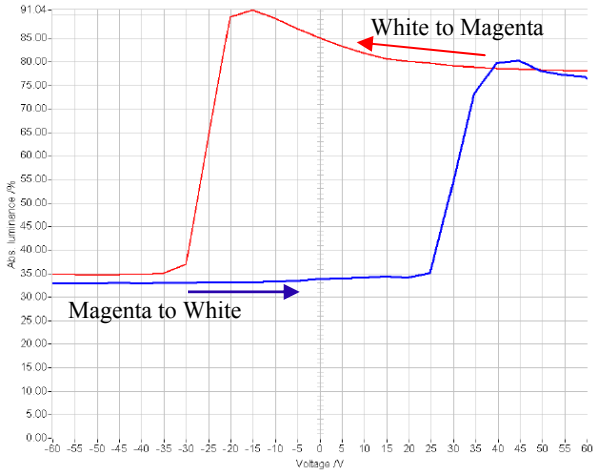
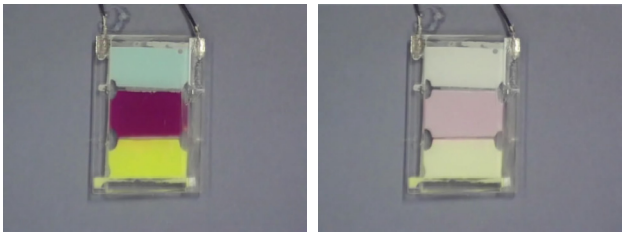


Figure 7. Electro-optical Curve for Magenta / Reflective White EPD fluid (50□m cell gap; (CR = 2.4:1).

Figures 8a and 8b show images of a prototype CMY cell. Each segment contains the dyed polymeric particle and a reflective white. The cell gap is 100□m.



Coloured state White state

Figures 8a and 8b. Vertical EPD switching of Cyan / reflective white fluid, Magenta / Reflective White fluid, and Yellow / Reflective white fluid.

3.42 In-Plane Electrophoretic Switching

In order to demonstrate in-plane electrophoretic switching, a simple test cell was constructed (see Figure 9). Interdigitated Indium-Tin oxide electrodes were created by photolithography and etching (10□m electrode width, 500□m interelectrode spacing, 80nm ITO thickness). A 13□m Mylar spacer was applied and the cell cavity was completed by use of a top glass substrate. The electrophoretic fluid was introduced into the cavity by capillary action and the cell edge was then sealed with a UV cured optical adhesive.

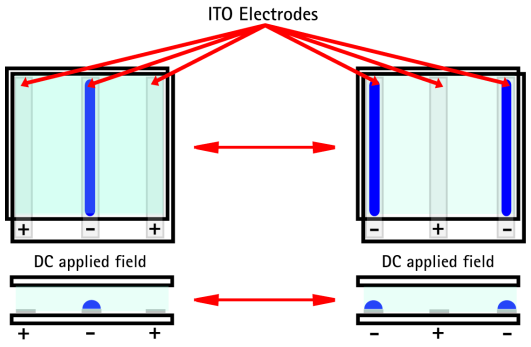
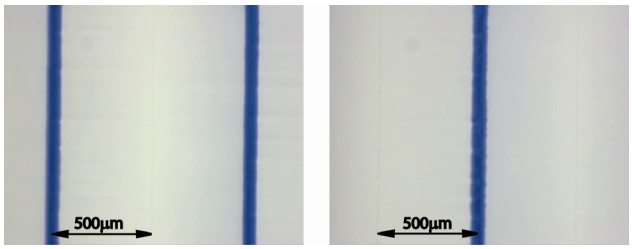


Figure 9. In-Plane Electrophoretic test cell diagram (Single Component fluid)



Figures 10a and 10b. In-Plane Electrophoretic switching Photomicrographs for Single Component fluid.

Figures 10a and 10b show photomicrographs of a single component EPD fluid comprising positively charged blue particles in a clear continuous phase. Figure 10a shows the fluid approximately 10 seconds after application of 30V DC to the electrodes. Figure 10b shows the fluid approximately 10 seconds after reversal of the field. Video sequences, which will be shown during the oral presentation, demonstrate smooth motion of particles between the electrodes. Quantitative electro-optical measurements were not performed on this cell/fluid architecture. The same test cell architecture can also be used to demonstrate in-plane electrophoretic switching for dual component EPD fluids, shown in Figure 11 and Figures 12a and 12b. Here, a two component fluid, comprising positively charged blue particles and negatively charged red particles demonstrates the independent switching characteristics of the two particle types.

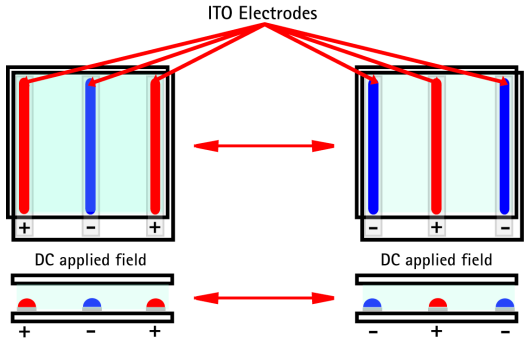
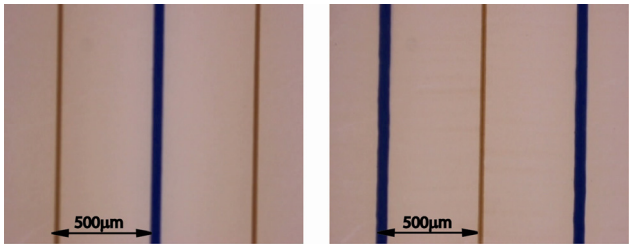


Figure 11. In-Plane Electrophoretic test cell diagram (Dual Component fluid)



Figures 12a and 12b. In-Plane Electrophoretic switching Photomicrographs for Dual Component fluid.

4. Conclusions

The particle concept described in this paper will enable the development of displays with improved colour and brightness properties when compared to colour-filter-based approaches. The development of "ready to use" coloured EPD fluids, based on dyed polymeric microparticles will offer an improved range of design opportunities to the displays industry.

References

[1] http://www.eink.com/technology/howitworks.html

[2] Bouchard, Alain. Electro-optic displays and colour filters: (E Ink Corporation, USA). PCT Int. Appl. (2009) WO2009117730 A1

[3] Whitesides, Thomas H.; Oleson, Andrew Y. Particles for use in electrophoretic displays: (E Ink Corporation, USA). PCT Int. Appl. (2008) WO 2008008945 A2

[4] http://www.sipix.com/technology/epaper.html

[5] Lin, Craig; Sprague, Robert A. Colour electrophoretic display devices: (Sipix Imaging, Inc., USA). PCT Int. Appl. (2009), WO 2009134889 A1

[6] Hwang, Jiunn Jye; Zang, Hongmei; Chen, Yajuan; Weng, Xin; Hou, Jack; Liang, Rong-Chang. Electrophoretic compositions: (Sipix Imaging, Inc., USA). U.S. (2007), US7277218 B2 20071002

[7] Yang, Jin; Feng, Kai-chia; Li, Ying-syi; Zang, Hong Mei; Wang, Hong; Chou, Chien-hung; Liang, Rong-chang. Fluorinated dyes or colourants and their uses for electrophoretic displays: (Sipix Imaging, Inc., USA). PCT Int. Appl. (2005), 56 pp. CODEN: PIXXD2 WO 2005017046 A2

[8] Baisch, Gabriele; Oehrlein, Reinhold; Simmendinger, Peter; De Keyzer, Gerardus; Fontana, Margherita; Mumbaikar, Vilas N. Coloured organic electrophoretic particles and their manufacture and use: (Ciba Specialty Chemicals Holding Inc., Switz.). PCT Int. Appl. (2008), WO 2008003604 A2

[9] Fontana, Margherita; De Keyzer, Gerardus; Bugnon, Philippe; Hahn, Marcel; Mistry, Kishor Kumar; Auschra, Clemens., Encapsulated dispersions comprising electrophoretically mobile organic colourants: Ciba Specialty Chemicals Holding Inc., Switz.). PCT Int. Appl. (2008), WO 2008003619 A2

[10] Tae Hee Kim, Yoon Soo Ko, and Yong Ku Kwon, Preparation and characterization of coloured electronic ink nanoparticles by high temperature-assisted dyeing for electrophoretic displays: Department of Polymer Science and Engineering, Inha University, J. nanosci. nanotechnol, 2006, Vol6, No. 11, pp3450-3454

[11] Yong Eui Lee, Young Tae Cho, Yong Gir Choi, Seoung Chul Park, Mung Hak Lee, Young Mi Park, Do Yun Kim, and Chul Hwan Kim, Low Voltage and Rapid Response Time Electrophoretic Display: Eurodisplay 2009, 19.4

[12] Meyoung Ju Joung, Chul Am Kim, Seong Deok Ahn, Yong Eui Lee, Seung Youl Kang, Kyung Soo Suh, and Chul Hwan Kim, Microencapsulation of Polymer Coated Colour Pigments for Multi-Colour Electrophoretic Display: Electronics and Telecommunications Research Institute, 161 Gajeong-Dong, Yuseong-Gu Daejeon, 305-350, KOREA, Mat. Res. Soc. Symp. Proc. Vol. 769, H6.20.1 – H6.20.6

[13] Lenssen, Kars-Michiel H.; Baesjou, Patrick J.; Van Delden, Martinus H. W. M.; Roosendaal, Sander J.; Stofmeel, Leon W. G.; Verschueren, Alwin R. M. Electrophoretic colour display panel using cyan, magenta and yellow: (Koninklijke Philips Electronics N.V., Neth.). PCT Int. Appl. (2008), WO 2008065605 A2 20080605.

[14] Goulding, Mark John; Smith, Ashley Nathan; Canisius, Johannes; Vidal, Richard; Khoukh, Sihame; Koch, Matthias. Fluid compositions containing coloured polymer nanoparticles for colour electrophoretic displays: (Merck Patent GmbH, Germany). PCT Int. Appl. (2009), WO 2009100803 A2

[15] http://autronic-melchers.com/index.php?product=4

[16] Huckel, E., Physik.Z., 25, 204 (1924)

Author Biography

Mark James received a BSc from Durham and a PhD from Newcastle-upon-Tyne, specializing in organic synthesis. After postdoctoral research at Southampton, he joined ICI and remained there for 18 years seeing the transformation through Zeneca to Avecia InkJet Limited. For 10 years he ran IJ projects ranging from colorant design to developing industrials processes to manufacture PCBs. In 2005 he moved to the Centre for Process Innovation to set up and manage their flexible electronics substrate research and manufacturing operation. Returning to IJ in 2006, Mark now leads Merck Chemicals (EMD Chemicals) functional material patterning activities in e-paper, OLED, OSC and PV technologies.