# Inkjet Printing of High Index Zirconia Nanocomposite Materials

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## ABSTRACT

Nanocrystal-polymer nanocomposites, when inkjet-printed, are useful to many display components and aid the development of next generation displays. High refractive index (RI) nanocomposites have properties which surpass traditional polymers while maintaining manufacturability. This paper demonstrates inkjet printing capabilities using high RI, highly transparent PixClear® $ZrO_2$ nanocrystal dispersions and inks for OLED Display and OLED Lighting applications. To support formulation requirements for inkjet applications, Hansen solubility parameters have been measured. By controlling the surface capping agents, PixClear dispersions can be tailored to be broadly formulatable for optimized performance.

***Keywords***: inkjet, refractive index, light extraction, display, zirconia

## 1 INTRODUCTION

High RI materials have been successfully used in a variety of applications to provide increased optical performance. For example, PixClear $ZrO_2$ nanocrystal dispersions and nanocomposites have been employed to significantly increase light extraction (>100%) in OLED lighting devices [1]. PixClear materials dramatically increase the refractive index (RI) of monomers and polymers with $ZrO_2$ content as high as 90 wt% while maintaining high transparency over the visible light spectrum [2]. Furthermore these materials allow processing using ordinary solution phase techniques.

As one example of a highly transparent, high RI nanocomposite, when 1.0 micron films are produced by adding 90 wt% PixClear $ZrO_2$ nanocrystals to an acrylate monomer with RI (450 nm) of 1.55, transmission values $\geq$ 95% with RI (450 nm) values close to 1.78 can be achieved. These optical films exhibit high clarity and percent absorption values $\leq$ 3% at 450 nm. Vacuum aging in an oven at 250 C for 1 hour demonstrates that these nanocomposites are compatible with high temperature process, as the transmission values remain $\geq$ 95%.

To integrate these nanocomposites for OLED Lighting applications, nanocomposites are further formulated with larger scattering particles. To intgrate these nanocomposites for OLED Display applications, a variety of approaches are possible, including formation of high refractive index lenses to increase light extraction. In either case, integration into manufacturing requires scaling of these materials. Over the past five years, Pixelligent has invested significantly in designing and building its advanced product development and manufacturing platform, the PixClearProcess™. The full deployment of this proprietary PixClearProcess has enabled Pixelligent to scale from a manufacturing capacity of grams-per-year to multi-ton mass production volumes. Pixelligent has done this while maintaining the high quality, mono-dispersed nature of our materials, with excellent repeatability during scaling and extremely low optical densities.

Current OLED displays and OLED lighting are made using vacuum deposition processes that are cumbersome, have low throughputs in production and have a high material cost. In order to reduce the cost of OLED manufacturing and to be able to use a variety of materials, such as high RI highly transparent PixClear $ZrO_2$ nanocrystal dispersions and nanocomposites as light extraction materials, manufacturers are moving towards inkjet printing methods as an approach for overall device construction. There are several benefits of using inkjet printing methods to build OLED displays and OLED lighting panels such as effective material utilization, lower cost solution coating processes, and the ability to print unique patterns and 3-D structures [3] that provide a certain functionality and benefit to the OLED device and/or fixture.

In this paper we discuss results on PixClear technology as inkjet-printed light extraction structures for both OLED displays and OLED lighting. We demonstrate the ability of Pixelligent's zirconia nanocomposites to be inkjet-printed, emphasizing a new way in which high-refractive index materials are being incorporated into devices. When applying polymer thin films on glass substrates for display and lighting applications, there are a number of common coating techniques like spin-coating, slot-die coating and inkjet printing. Each method offers discrete benefits and challenges within laboratory and manufacturing environments and all are compatible with PixClear. With an efficient use of coating materials and the ability to place droplets on the micron-scale, inkjet printing can be used towards the creation of display components such as light extraction films/coatings, lenses, back lighting diffusers, barrier films, anti-reflective coatings, and index matching films [4][5][6].

# 2 METHODS

## 2.1 Ink Preparation

Pixelligent PixClear $ZrO_2$ nanocrystals are used for printing a transparent high refractive index formulation and a similar formulation containing additional scattering particles. Each formulation consists of zirconia nanocrystals with a UV-curable, acrylic binder and solvent. A second ink was created by adding larger scattering particles. The inks were prepared in the laboratory with appropriate dilution with propylene glycol methyl ether acetate (PGMEA) and/or dipropylene glycol methyl ether (DPGME) solvents to achieve viscosities for inkjet printing (1 – 20 cP). PGMEA and DPGME have boiling points of 146 and 190°C, respectively. Further formulation was carried out to improve inkjet printing and final film characteristics.

## 2.2 Substrate Cleaning, Film Drying and Curing

Glass substrates were subjected to the same cleaning procedure involving washing with a solution of detergent and water and isopropyl alcohol rinse followed by drying at room temperature.

After inkjet printing on glass substrates the films were dried at 50°C for 5 to 10 minutes followed by an additional 5 minutes at 100°C to remove the majority of solvent from the films. The dried films were UV-cured with an “H” - type Hg lamp at a total exposure of 6 J/cm$^2$.

## 2.3 Instrumentation

The inks were printed on a Dimatix DMP 2800 inkjet printer using 1 and 10 picoliter (pL) cartridges. The nominal nozzle diameter for the 1 and 10 pL cartridges are 9 and 20 microns. Film thicknesses and film quality were affected by key inkjet parameters, such as applied voltage for each nozzle, the slew rate (how fast the voltage is applied), the drop spacing on the substrate and applied heat of the printing surface/substrate.

Film thicknesses, non-uniformity and other film dimensions were measured with a Tencor Instruments P-2 Long Scan Profiler. Film non-uniformity was calculated with the following equation.

$$\%NU = \frac{L_{max}-L_{min}}{2*L_{avg}} * 100\% \quad (1)$$

$L_{max}$, $L_{min}$ and $L_{avg}$ are the maximum, minimum and average film thicknesses. Micrographs were taken with an AmScope binocular compound microscope and Canon PowerShot S100 digital camera. Pictures of inkjet-printed scatterer-containing films were taken with an Epson Perfection V600 photo scanner.

# 3 RESULTS AND DISCUSSION

Inkjet printing of PixClear light extraction coatings and structures has been successfully acheived. For example, Figure 1 shows a 254-micron drop array with diameters of ~120 microns. Drop spacing is a crucial parameter for inkjet printing and can affect overall film thickness (for blanket films) and film uniformity. By adjusting the drop spacing between 5 and 60 microns (Figure 2), a wide range of film thicknesses between 70 nm and 7 microns resulted for PixClear inks. High drop spacings can affect the film quality and give rise to visible non-uniformities in the form of lines in the film. Conversely, when the drop spacing is low (5 – 10 microns), it gives rise to high wet film thicknesses with high solvent content. Film quality tends to be poor when films require long drying times. The majority of uniform films (with calculated non-uniformity between 10 – 20%) were printed with drop spacings of 15 – 25 microns.

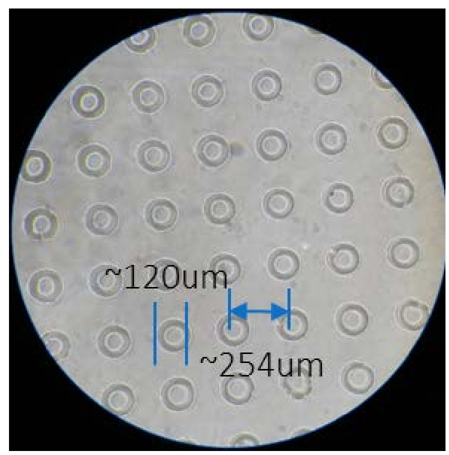


Figure 1: Optical micrograph of transparent high refractive index ink drop arrays on glass at 40x magnification.

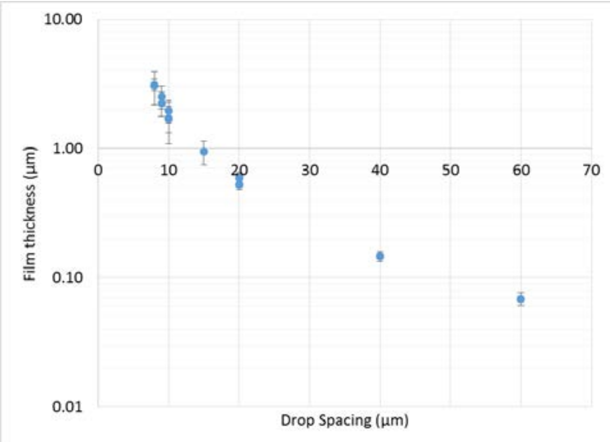


Figure 2: Film thickness dependence on drop spacing for the same formulation.

Another important property of formulations that are printable via inkjet is latency. Latency refers to the ability of an ink to be printed, then idled for a period, and subsequently printed later without any adverse issues with the nozzles of the inkjet cartridge. In order to demonstrate latency for our PixClear ink, an experiment was initiated by printing at four different time intervals over a 5-hour time period. Thin films of 0.55 microns were printed initially at t = 0, 15, 60 and 300 minutes, by using the ink in a single cartridge. Figure 3 demonstrates the consistency of producing film thicknesses between 0.5 and 0.6 microns with film non-uniformities of less than 12%.

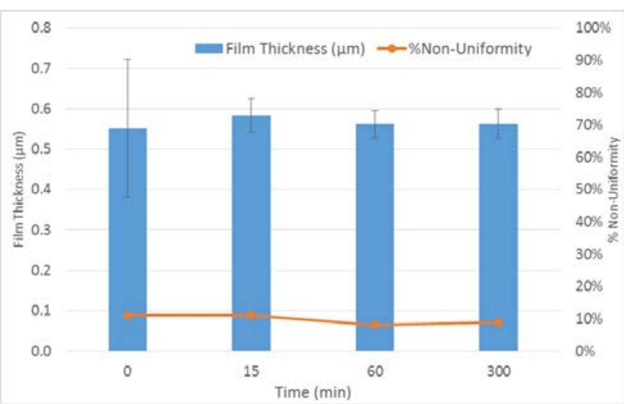


Figure 3: Graph of latency experiment for transparent high refractive index ink.

We have shown that PixClear inks with scattering particles can also be inkjet-printed as films and/or structures for the purpose of improved light extraction in devices for OLED displays and OLED lighting. For consistent firing of the inkjet nozzles in the cartridges the use of a high boiling point solvent such as DPGME as the main solvent has proven to be most beneficial. Figure 4 shows an IJ printed pattern of the scattering particle containing ink material at thicknesses of approximately 2 – 3 microns.

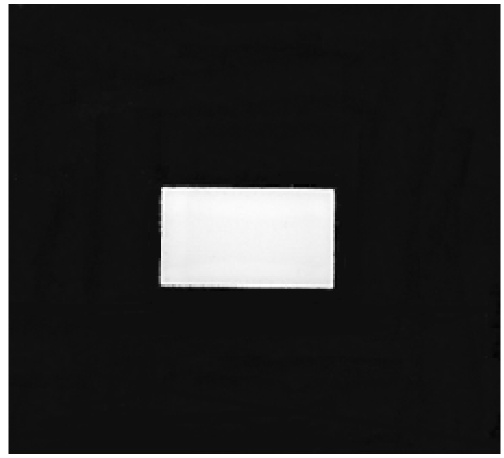

Figure 4: Example of a rectangular pattern printed with high refractive index scatterer-containing formulation.

Print quality was examined by surface profilometry and through further processing by ITO deposition and subsequent OLED Lighting device builds. Through careful modification of the ink formulations, improved pattern edge resolution and 'edge bump' profiles were achieved, and continuous, smooth ITO films were successfully deposited on these strucutres. Device testing is on-going.

The dispersibility of Pixelligent's nanocrystals in solvents, monomers, and polymers is controlled by the capping agents at the surface. Hansen solubility parameters (HSP) build upon the general concept of like dissolves/disperses like, by quantifying the interfacial interactions between component molecules in a mixture or formulation [7]. HSP values can accelerate the formulation process by guiding the choice of compatible components for a given PixClear dispersion. For Pixelligent's nanocrystals, the HSPs will change depending upon the capping agents at the surface. Favorable interactions between these capping agents and the matrix into which they are to be dispersed allow for aggregate-free clear dispersions and nanocomposites. PixClear dispersions show wide compatibility under HSP testing, which allows broad formulation opportunities to optimize inkjet performance. This compatibility is demonstrated in this paper by the excellent latency and print quality of nanocomposites made with PixClear dispersions.

## 4 CONCLUSIONS

Inkjet-printed, optically clear films containing Pixelligent's PixClear zirconia nanocrystals show excellent uniformity and are achievable with transparent high refractive index inks that can be printed with remarkable consistency (latency) for OLED Display applications. Films containing scattering particles in addition to the PixClear

$ZrO_2$ nanocrystals can be printed into various simple and complex patterns for OLED Lighting applications. Information from this paper gives strong support that these materials can be extremely useful as light extraction layers in a wide variety of display and lighting applications.

## 5 REFERENCES


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**Prior Publications**

A summary of Pixelligent’s inkjet-printing work is also available on www.pixelligent.com