Microemulsion Based Ink-jet Ink: Properties and Performance

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Oil-in-water microemulsions which contain a hydrophobic colorant were evaluated as water based ink jet inks.These microemulsion based ink jet inks are thermodynamically stable, have the features of dye based inks prior to printing, and the features of pigment based inks after printing. The microemulsion was prepared and printed, as described recently by Magdassi et al.[1,2] using the gemini-type surfactant, didodecyldiphenylether disulfonate, toluene, 1-propanol, water as the continuous phase and Nile Red or Sudan IV as the hydrophobic dye. Microemulsion average droplet size was measured by dynamic light scattering and found to be ~8 nm. We found by AFM imaging that the printed 20 – 60 μm droplets are composed of nanoparticles with average size of 130 nm. The printing process was evaluated by a fluorescence microscope, while images of the droplets were viewed as a function of time after impact with the substrate. It was found that the microemulsion droplets formed distorted spheres on ink jet paper, more perfectly shaped spheres on Forbo paper substrate and perfect round spheres on vinyl slides. When printed on glass, a 'bagel like' shape was obtained. The droplet size varied, depending on the surface energy of the substrate, being at least 20 μm for low energy surfaces and growing larger for higher energy substrates. It was noticed that the time scales for spreading on paper was less than tens of milliseconds accompanied and followed by fixation and drying of the droplets in less than 3 – 5 seconds.

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Introduction

Microemulsions are clear, thermodynamically stable, isotropic mixtures of oil, water and surfactant, usually in combination with a cosurfactant. Microemulsions are made of two immiscible liquid phases with the internal phase having a globule diameter less than 100 nm. They appear clear or translucent and do not cream. Microemulsion systems are interesting for water based coating applications because of the simplicity of making them, their excellent stability while in storage and their good potential to form a fast drying ink which is characterized by high water fastness and non-bleeding of the printed material.

The impact and spreading of liquid droplets on various surfaces is of interest for a wide range of applications, particularly the ink jet printing process. Resolution in the ink jet printing process is directly related to the degree of spreading, bleeding and drying of the ink after deposition.

There are only limited reports on the use of microemulsions as coating materials for applications requiring high loading of the printed material.[3,4] Most of these reports use a reversed microemulsion as the medium for solubilization. The preparation of inorganic nanoparticles, as bulk materials, by reverse microemulsions (water-in-oil) is well known, such as the formation of silver bromide nanoparticles with AOT/n-heptane/water microemulsions.[5] However, there is a relatively limited number of reports on formation of organic nanoparticles in microemulsion. Examples are the preparation of cholesterol nanoparticles from reverse microemulsion,[6] preparation of solid-lipid nanoparticles by dilution of oil-in-water microemulsion in water,[7] and preparation of latex nanoparticles via microemulsion polymerization.[8]

The use of microemulsions in ink jet printing for the graphic arts was previously described, aimed at overcoming problems related to ink stability and image quality such as feathering, bleeding and wicking. The reported microemulsions were utilized due to their inherent stability and, in some cases, due to their phase transition from liquid into liquid crystalline phases, at specific temperatures.[9–20] These patents are mostly applicable to thermal ink jet printing. However, the formation of patterns of organic nanoparticles using microemulsion-based ink jet inks has not been described.

This article describes the application of ink jet ink based on a microemulsion, applied to various substrates. The concept,[2] as illustrated in Fig. 1, is based on formation of a thermodynamically stable oil-in-water microemulsion in which volatile "oil" droplets contain the dissolved, water insoluble colorant. The microemulsion droplets are converted into organic nanoparticles upon impact with the substrate surface due to evaporation of the droplets volatile solvent, which takes place prior to evaporation of the aqueous continu-

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Color Plate 7 isprinted in the color plate section of this issue, pp. 371–376.

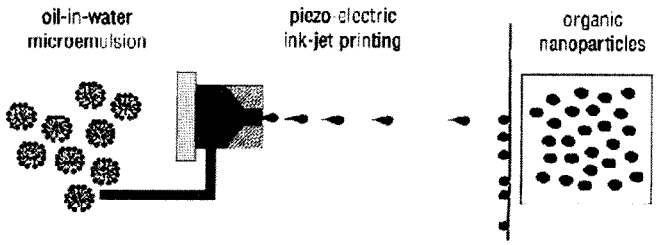

Figure 1. Schematic illustration of microemulsion conversion into nanoparticles by ink jet printing.

ous phase. Thus, each microemulsion droplet becomes a solid nanoparticle. The ink actually behaves as a dye based ink, as long as in the ink cartridge or container, but soon after printing, it behaves like a pigment-based ink. Thus, all problems associated with pigments clogging in the print head are prevented, and many benefits associated with pigments, such as non-bleeding, light and water fastness are achieved in the printed patterns.

In this research the concept is demonstrated for the system containing didodecyldiphenylether disulfonate (C12-DADS) microemulsion with 15% oil content (with 10% wt surfactant, 37.6% wt 1-Propanol and the rest water) with solubilized hydrophobic dye (Nile Red or Sudan IV).[2] In this work, we focus on the basic properties of the ink system as well as spreading and wetting behavior on various surfaces.

Experimental

Microemulsions were prepared as described elsewhere by Magdassi et al.[1] Sudan IV (Sigma) and Nile red (Fluka) were standard grade. These dyes are highly fluorescent. Muscovite mica films were obtained from Pelco International and freshly cleaved prior to spin coating. Ink jet paper IrisPRO semi matte ink jet media, was supplied by Creo Scitex, Forbo PVC coated mechanical paper was supplied by Forbo-CP (UK), vinyl slides were supplied from Verbatim, and glass slides from Marienfeld Laboratory Glassware (Germany).

The microemulsion studied throughout this report, is composed of 15% wt toluene, 10% wt surfactant, 37.6% wt 1-Propanol, 0.5% wt hydrophobic dye and 36.9% wt water. The microemulsion ink was prepared by dissolving the surfactant in water and cosolvent. The mixture was then stirred by vortex, followed by ultrasonic bath for 10 min. Then the hydrophobic dye was dissolved in oil, which was added to the surfactant solution to form a stable oil-in-water microemulsion. All mixing was performed at room temperature (22°C +/–1°C).

The average particle size of the samples was measured at 25°C by dynamic light scattering using 'Zetasizer-3000', Malvern Instruments, UK (70 mW Ar-laser, wavelength 488 nm, detector angle 90°, dispersant viscosity 0.89 cP, dispersant refractive index 1.33, sample refractive index 1.50). The particle size, according to the particle number distribution, was taken as a mean value of three measurements. Samples were filtered prior to measurements through a 0.2 μm filter.

Surface tension measurements were carried out for the microemulsion by the Wilhelmy plate method (plate with 4 cm circumference) using a Lauda mgw tensiometer. The surface tension was continuously recorded while the plate was immersed in solution, at 22°C, until the standard deviation of the mean of 10 measurements did not exceed 0.2 mN/m. The indicated surface tension is the mean of three consequent measurements in which the standard deviation of the mean did not exceed 1.5 mN/m.

The kinematic viscosity was determined using a reverse flow type viscometer for opaque liquids (N100) with a calibration constant of 0.01462 cSt/s at 40°C (Canon Instrument Co, USA). The sample was filtered through an 0.2 μm syringe filter before being transferred into the viscometer.

Tapping Mode Atomic Force Microscopy was carried out using a Solver P47 (NT-MDT, Moscow, Russia) scanning probe microscope. Two different tips of 90 μm and 110 μm length 'Ultrasharp' silicon tips with a radius of curvature of less than 35 nm (SC-12 series, NT-MDT), were used. These tips have a typical resonance frequency of 105 and 155 kHz, and typical spring constant of 0.95 and 1.75 N/m, respectively. Height mode images were collected along with either an amplitude or phase image. A scan rate of 2 – 2.5 Hz was typically sufficient to maintain good signal-to-noise ratio. Imaging was repeated using the different tips. Only features that were reproducible from tip-to-tip are reported. Multiple scans were imaged in each case, with a variety of areas examined for consistent sample morphology.

The microemulsion ink was injected from a distance of 2 mm onto the substrate by means of a glass pipette tip, which was vibrated at an ultrasonic frequency. The tips were hot-pulled to obtain an inner diameter of 30 ± 3 μm. The ultrasonic generator, 30 W "Pro Scale", was used at a frequency of 20 KHz. This injection produces drops with an average volume of about 25 pL, injected with a velocity of 8 – 15 m/s. The method proved to be a good lab simulation of industrial ink jet printing.[21]

The microemulsion injection was performed under a microscope thus enabling investigation of the drop evolution from the moment the ink approaches the substrate. The imaging system is based on the Olympus PROVIS microscope in the fluorescence mode of operation. The fluorescence images are read by a CCD camera and stored in a computer via ATI board as a pixel-to-pixel map of light intensity. Typically the images were stored at the maximum frequency of 30 frames per second. This frequency was found to be fast enough for changes taking place during the drying of the ink drops. The fluoresce excitation wavelength was 510 – 550 nm using a mercury lamp. The images represent all the emission above 600 nm, characteristic of the organic dyes incorporated in the microemulsion ink.

Results and Discussion

As shown previously[1] in the ternary phase diagram and by electrical conductivity measurements, the continuous phase in the microemulsion ink composition is water with conductivity values of about 10 mS. The maximum dye loading capacity in the microemulsion was about 5 times higher than the maximum dye content in the toluene fraction itself. The resulting ink has low viscosity of approximately 10 cP and the surface tension was 26 mN/m.

In order to evaluate the droplet size in the microemulsion containing the hydrophobic dye, we performed dynamic light scattering measurements of this composition. Figure 2 presents the average hydrodynamic diameter of the oil phase of a microemulsion of the said composition containing 0.5% wt of Nile Red. The measurements were performed before and after addition of the hydrophobic dye to the microemulsion and there was

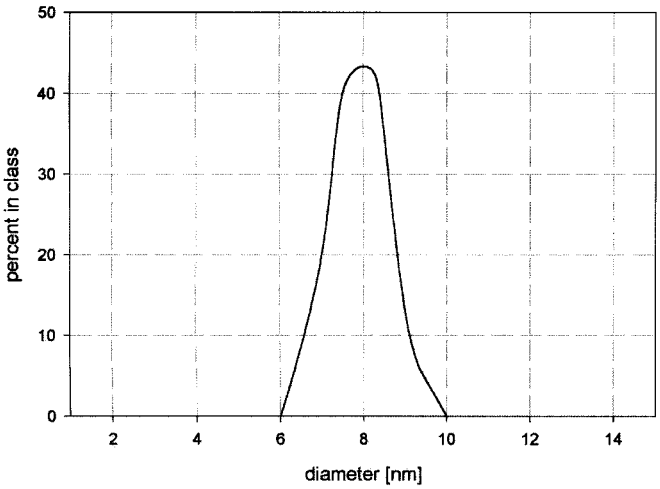

Figure 2. Average size of microemulsion droplets as measured by Dynamic Light Scattering.

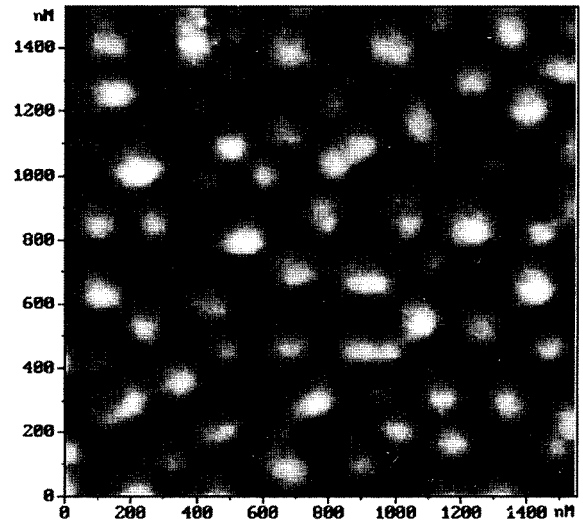

Figure 3. AFM images of organic nanoparticles which form after deposition of microemulsion based ink on muscovite mica, using a spin coating technique. Image size is 1.5 μm × 1.5 μm.

no significant change in the microemulsion average droplet size. In both cases the average diameter was found to be 8 nm, which is much smaller than particle size in conventional pigment based ink jet inks.

In order to evaluate the drying time and water fastness of the printed ink, we used a roll, with 24 μm grooves, to spread the ink on ink jet paper. Drying times of less than 3 seconds were observed; thereafter the dried ink could not be washed away from the ink jet paper under continuous water flow. These features of the microemulsion based composition, makes it attractive for ink jet applications, in which rapid fixation of the ink droplet is required, as described in our recent report on printing of microemulsions by a commercial ink jet printer.[2]

Color Plate 7, p. 376 shows the time evolution of the ink drops on various substrates: ink jet-paper, Forbo, vinyl slide and glass. The pictures represent the fluorescence intensity, which corresponds to the amount of dye at each point. A clear dependence of the drop evolution on the substrate properties is evident from the **Color Plate**. Using 'MatLab' based image-processing software we evaluated the drops formed on each substrate, averaging over 100 drops for each substrate. Here we concentrate on one of the most important parameters for high quality printing, the drop roundness.[9] A typical measure of roundness would be the minimum annulus (region between two concentric circumferences) containing the drop boundary. Numerically, we define roundness as the ratio of inner to outer radii of the annulus: the roundness is therefore equal to unity for a circle and zero for a straight line. This parameter should be of major practical importance, since tone reproduction in printing is calculated based on round shaped dots.

For both ink jet paper and Forbo, irregular shapes are formed corresponding to uneven spreading of the drop on the substrate. The roundness calculated in these cases is 0.65 and 0.83 respectively. The roundness of the drops printed on the vinyl slide is 0.97. In this case, analysis of the dye dispersion in each drop shows the development of perfect spheres. This behavior is typical of wetting problems as is evident from the movement of one of the droplets over 110 μm across the substrate, as indicated by the arrows in **Color Plate 7**. Finally, printing on glass resulted in relatively round dots (roundness = 0.71), which evolved into a "bagel" shape. The shift to the bagel shape takes place during the first 100 ms of ink–glass interaction.

The general trend for all four substrates is that the drops reach their final shape and size in less than a second, which corresponds to the fast drying process mentioned above. We note that the absence of further morphological changes in the drop does not necessarily indicate full drying but rather the achievement of high viscosity in the drop. However it is an important characteristic with respect to printing quality.

After examining the basic microemulsion based ink properties and the ejection, spreading and drying process, we investigated the coated ink after drying. Figure 3 presents a two-dimensional AFM image of the microemulsion-based ink after spin coating on a muscovite mica slide. This image reveals the formation of organic nanoparticles, upon application on the mica slide, with average diameter of 130 nm, which is about one-third to one-half the size of conventional pigments in ink jet inks. These nanoparticles are composed of the hydrophobic dye and the surfactant, which remain on the mica after the fast solvent and water evaporation. We have shown in our previous report that the drying rate and the oil content are key parameters controlling the size of the nanoparticles on the printed substrate.

Conclusions

In conclusion, oil-in-water microemulsions, which contain hydrophobic dyes, were evaluated as water based ink jet inks. Microemulsion average droplet size is ~8 nm, far below the size of pigments in conventional ink jet printing. We found by AFM imaging that the printed 20 – 60 μm droplets are composed of nanoparticles with average size of 130 nm. We think that by exploiting the microemulsion based ink concept, with an appropriate hydrophobic colorant or other water insoluble functional material, a large variety of water insoluble materials may be used in ink jet applications, without the need for their prior preparation in the form of sub-micron pigments.

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