The chemistry and properties of the organic, synthetic insoluble polymer powder, cross-linked, swellable polyvinyl polymyrrlidone (PVPP) make it suitable for use with silica for efficacious ink jet coatings. The use of PVPP and silica improves the drying time of printed images. Other benefits of this product combination include low impact on gloss, ease of use, formulation compatibility and a boost to the water resistance of the printed image.

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The image quality of inkjet printing is now similar to that of silver halide photography and these advances have carried inkjet printing to the point where further advance now depends on the quality of the inkjet substrate. An inkjet printing paper is in many ways similar to a silver image on photographic paper, but it becomes difficult to distinguish between the two when the inkjet printing is done on high grade photo paper.

Three main types of glossy inkjet paper are commonly used: cast-coated, swelling and microporous. Cast-coated paper may be of limited image quality as its base paper absorbs ink. Swelling and microporous papers avoid this because they use a polyethylene (PE) coated base paper that makes the base impermeable to ink.

Quality depends on image-receiving layers

The PE coated bases do not absorb ink so the image quality of swelling and microporous papers depends chiefly on the mechanisms of the image-receiving layers. Swelling papers consist mainly of water soluble polymers (eg polyvinyl pyrrolidone (PVP)). These offer high optical density but, where formulations are not optimized, they may be slow drying or have low gloss, curl or low water resistance.

This initial study describes a combination of silica and fully cross-linked particles of PVP known as 'polyvinyl polymyrrlidone' (PVPP). It was hoped that such a combination would present a honeycomb of pores with which to receive the ink. It would avoid some disadvantages of swelling paper and should achieve high ink absorbing speed. It could be used in a 'microporous'-type layer beneath a photo-glossy layer.

Selecting the materials

Fumed silica from Sigma-Aldrich was chosen for this study and differs from precipitated or gel grades since it has little or no internal porosity. Other grades of silica are commonly engineered to have specific porosity characteristics which are key factors in differentiating products and determining their performance for printing. The fumed silica is a very fine particle size product with high levels of microporosity. The grade used had a Brunauer, Emmett & Teller (BET) determined surface area of 380 m²/g. The bulk density is very high. Particle size is in the range of 10 - 30µm and the particles stick together to form agglomerate particle chains.

The grade of fully cross-linked PVP powder used in this study is commercially available as "ViviPrint PS-10" and has been found to have an average particle size of 15 - 20µm and a BET surface area of 300 m²/g. PVPP is not micro-porous in nature but is water swellable. Hence it was anticipated that it would not give quite so good a print resolution as fumed silica but would offer advantages in terms of image permanence, dry time and processing.

Making up simple blends of PVPP and silica

Polymer enhances ink-jet image quality

In order to assess the benefits of PVPP as an additive to fumed silica in ink jet printable coatings, simple blends incorporating PVPP and silica in ratios of 30:70 and 50:50 by weight respectively were prepared. A blend with no PVPP was also included.

Components were minimised to ensure that printing receptivity and water resistance were observed without the influence of other factors. Commercially available polyvinyl alcohol (PVA) ("Alcotex 864" from Synthomer, 35% solids in water, medium hydrolysis) was used as a binder. The ratio of PVA to silica/PVPP was 1:2. The formulations were all 18% w/w solids (Table 1).

Blends of components used in this study are referred to as 'formulations' here to a siilica and fumed silica combination would present a honeycomb of pores with which to receive the ink. It would avoid some disadvantages of swelling paper and should achieve high ink absorbing speed. It could be used in a 'microporous'-type layer beneath a photo-glossy layer.

Assessing the coated paper

Evaluation of coated paper was assessed by printing on both thermal and piezoelectric print head systems:
- HP DeskJet "930C" - plain paper draft mode, print quality 300x600dpi
- Epson "Stylus Photo 890" - plain paper mode, automatic, microweave on, high speed on, 360dpi
A standard test pattern containing four colour sets each with black, cyan, magenta and yellow blocks was printed on both printers for each formulation and the uncoated base paper (as a reference for optical density measurements).

Printing assessments were made in the drying times and changes in optical density after water immersion.

Prints dried within a minute

Each print was allowed to dry for 1 minute after printing, and then each colour block was transfer tested (blotted) onto ASA 80gsm paper. The amount of ink transferred was visually interpreted and scored from 0 (total transfer) to 10 (no transfer). All formulations scored 10 with no ink transfer.

More detailed information on the dry time benefits of combinations of PVPP and silica are covered later in this paper.

Coating composition affects optical density

Optical density was determined using a GretagMacbeth "D196". Initial optical density was measured at 6 positions for each colour block in each of the four sets. The average optical density was determined and the distribution for each colour calculated to give the degree of mottle.

After water immersion (23°C for 10min) the optical density of one set of colour blocks was measured and compared to pre-immersion readings to determine the percentage optical density loss after water immersion.

The initial optical density values for each formulation and the uncoated base paper are shown for both the Epson and the HP printers (Figure 1 and 2 respectively). Vertical error bars indicate the variation in the optical density, ie the degree of mottle.

For the Epson inks the trend was for a slight decrease in initial optical density as the silica was replaced by PVPP. The highly microporous structure of the silica gave very...
good print definition and ink resolution. The PVPP is swellable and hence there is slight ink spread as the solvent is absorbed, giving some reduction in OD.

**Replacing silica with PVPP reduces mottle**

The degree of variation in optical density (mottle) however, decreased as the silica was replaced by PVPP (Figure 1). This is believed to be due to the PVPP benefitting the coating structure by providing a more even coating. PVPP is a known dispersant and is able to ensure a more even distribution of water insoluble particles (such as silica) in water.

The trend for a decrease in optical density as the silica is replaced by PVPP as seen with Epson (Figure 1) was very much less marked with the HP inks (Figure 2). The black HP pigmented ink showed no trend for a change in optical density with PVPP presence.

Results from the water immersion test are given (Figures 3 and 4). These are stated as percentage loss of optical density after 10 minutes immersion in water.

**Increasing PVPP boosts water resistance**

As the silica was replaced by increasing levels of PVPP the water resistance of the print increased significantly for both the Epson and the HP inks. The Epson inks gave up to 68% loss of optical density after water immersion with no PVPP present, up to 13% loss with 30% PVPP and only a maximum of 7% loss with 50% PVPP.

The boost in water resistance was more pronounced with the Epson inks than with the HP inks except for the black pigmented HP ink which gave less than 10% loss in optical density in all formulations. The coloured HP inks gave up to a 73% loss of optical density with 0% PVPP, a maximum of 52% loss with 30% PVPP and 31% loss with 50% PVPP.

This study has shown that PVPP is a suitable additive to fumed silica for an inkjet receptive coating layer. The highly microporous nature of fumed silica provides excellent print resolution and definition under the conditions used in this study. The addition of PVPP to the fumed silica significantly enhanced the water resistance of the print for both the Epson and the HP inks.

**PVPP benefits drying time**

A second study was initiated to look in detail at the beneficial effect of PVPP on dry time when combined with silica. For this study a silica gel with an average particle size of 8μm was chosen as an example of a typical silica gel for inkjet applications.

The water absorption capacity was examined (Figure 5). There is a synergistic improvement in water absorption capacity by combining the PVPP with the silica gel. In practical terms this means that a 50:50 combination of the two products is able to reduce the dry time of a printed substrate more than either material alone. This was demonstrated in another study summarised below.

**Evaluating coatings properties**

Coatings were applied to a white polyester film ("Melinex" from DuPont) at 9g/m². Evaluation of coated paper was again assessed by printing a standard test pattern on both thermal and piezoelectric print head systems:
- HP "990Cse" - photo quality settings
- Epson "Stylus Photo 785 EPX" - photo quality settings

Dry times were assessed by applying a 2kg roller with white copy paper over the printed image which has a calibrated time scale. The point of transfer of any colour to the white paper was recorded as the dry time (Table 2). Gloss was measured using a BYK Gardner "Gloss Meter" at 60°.

The PVP film of Formulation 1 gave a very glossy finish but had a slow dry time. The addition of microporous silica to PVP (Formulation 2) dramatically improves dry time but at the expense of gloss. The addition of the water-swellable PVPP to PVP improved dry time but not as well as with silica. However, it had less of an impact on gloss and resulted in a satin finish.

**Benefits of combining silica and PVPP**

The synergistic benefits in water absorbance from combining silica with PVPP (Figure 5) were confirmed with the dry times recorded for Formulation 4. Dry time for the water-based HP inks was reduced to only 10 seconds. With the Epson solvent-based inks dry time is slightly higher than with silica alone (5s) but still only 30s. However a further advantage of PVPP and silica blend was the reduced impact on gloss when half of the silica was replaced with an equal amount of PVPP compared to using silica alone.

Finally, an example formulation of a matte finish fast dry paper coating especially suitable for solvent-based inks is given (Table 3).

**Independent pre-dispersion is recommended**

It is recommended that the PVPP and silica gel are independently pre-dispersed in water. These should then be homogenised together. PVPP is a very powerful dispersant and ensures an even distribution of silica in water. This PVPP/silica dispersion can then be added to a solution of PVA and PVPP in water prior to adding the wetting agent.

The ability of PVPP to act as a dispersant allows settled coating dispersions (which may form a ‘cake’ of non-dispersed material in water when left standing) to be readily re-dispersed through simple mixing. The formulation above was applied to calendared cast coated 80gsm paper with a number 20 metering rod at a coat weight of 8g/m². Evaluation was on thermal ("HP 3820") and piezoelectric ("Epson B25") printers:

- The dry time of ink on the matte finish coating was 120s with HP and 90s with Epson printers. Gloss was measured as 4.9 with a very good quality matte finish.
- This demonstration formulation (Table 3) provides a low gloss fast dry paper. The use of equal quantities of PVPP and silica gel make it especially suitable for reducing dry times with solvent-based inks (90s). Levels of inorganic pigments and organic soluble PVP/PVPP can be modified should a higher level of gloss be desirable.

**Acknowledgements**

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**Results at a glance**

- Increasing levels of the polymer PVPP in the coating significantly increased the water resistance of inks from both Epson and HP.
- The Epson inks gave up to 68% loss of optical density after water immersion with no PVPP present, up to 13% loss with 30% PVPP and only a maximum of 7% loss with 50% PVPP.
- Coloured HP inks gave up to a 73% loss of optical density with 0% PVPP, a maximum of 52% loss with 30% PVPP and 31% loss with 50% PVPP.
- Colouring HP inks gave up to a 73% loss of optical density with 0% PVPP, a maximum of 52% loss with 30% PVPP and 31% loss with 50% "ViviPrint PS-10".
- A 50:50 combination of PVPP and silica is able to reduce the dry time of a printed substrate more than either material alone.
- The impact on gloss was reduced when half of the silica...
was replaced with an equal amount of PVPP compared to using silica alone.
- An added benefit of PVPP was the ability to disperse silica. This resulted in an easy-to-use formulation (no 'caking') and a more even coating giving less density variation.

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Figure 1: Initial Optical Densities using the Epson Printer.

Figure 2: Initial Optical Densities using the HP Printer.

Figure 3: Water Immersion Test: Percentage Loss of Optical Densities using the Epson Printer.
Figure 4: Water Immersion Test: Percentage Loss of Optical Densities using the HP Printer

Figure 5: Water Absorption Capacity per Gram of PVPP / Silica Gel Mixtures
### Table 1: Formulations A, B and C for Fumed Silica and PVPP Study

<table>
<thead>
<tr>
<th>Component</th>
<th>Formulation A0 % PVPP</th>
<th>Formulation B30 % PVPP</th>
<th>Formulation C50 % PVPP</th>
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<tbody>
<tr>
<td>PVA (35% solution)</td>
<td>100</td>
<td>100</td>
<td>100</td>
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<tr>
<td>Fumed Silica (15% dispersion)</td>
<td>470</td>
<td>329</td>
<td>235</td>
</tr>
<tr>
<td>PVPP (15% dispersion)</td>
<td>–</td>
<td>141</td>
<td>235</td>
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<tr>
<td>Water</td>
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Table 2: Summary of Study Combining Fumed Silica and PVPP

<table>
<thead>
<tr>
<th>Sample Formulations</th>
<th>Dry Time (seconds)</th>
<th>Gloss of Coated Film</th>
<th>Image Quality</th>
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<tr>
<td></td>
<td>HP</td>
<td>Epson</td>
<td></td>
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<tr>
<td>No 1. PVP K-90, water</td>
<td>120</td>
<td>Does not dry</td>
<td>95</td>
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<tr>
<td>(control)</td>
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<td></td>
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<tr>
<td>No 2. PVP K-90, Silica</td>
<td>30</td>
<td>5</td>
<td>4.2</td>
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<tr>
<td>No 3. PVP K-90, PVPP</td>
<td>70</td>
<td>180</td>
<td>18.5</td>
</tr>
<tr>
<td>No 4. PVP K-90, PVPP, Silica</td>
<td>10</td>
<td>30</td>
<td>17.5</td>
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Table 3: Matte Finish Paper Coating Formulation

<table>
<thead>
<tr>
<th>Chemical Ingredient</th>
<th>Trade Name</th>
<th>Supplier</th>
<th>% w/w</th>
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<tbody>
<tr>
<td>PVP/PVPP Composite</td>
<td>ViviPrint™ 540</td>
<td>ISP</td>
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<tr>
<td>PVPP (15µm)</td>
<td>ViviPrint™ PS-10</td>
<td>ISP</td>
<td>1.13</td>
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<tr>
<td>PVA (88% hydrolysed, 20% solution)</td>
<td>Aldrich</td>
<td></td>
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</tr>
<tr>
<td>Silica gel (6µm)</td>
<td>Silcron® G-100</td>
<td>Millennium Chemicals</td>
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<tr>
<td>$p$-isononylphenoxypoly (glycidol)</td>
<td>Surfactant 10G</td>
<td>Olin</td>
<td>0.14</td>
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<tr>
<td>Water</td>
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