

# Interactions between UV curing, hybrid-UV and sheetfed offset inks and coated paper – commercial print trials

Dr Sanna Rousu<sup>1</sup>, Jan Gustafsson<sup>2</sup>, Dr Janet Preston<sup>3</sup>, Dr Peter Heard<sup>4</sup>

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## Abstract

UV cured offset is a fast growing area of printing which has many diverse applications in printing both paper and other very different substrates such as plastics. However, there is very little published literature which reports the influence of paper properties on the printability and print quality obtained. This study consisted of full scale printing trials and laboratory analysis comparing the printability of UV, hybrid-UV and conventional sheetfed offset ink systems on a variety of coated papers.

Four pilot coated papers were prepared using a range of minerals (PCC, GCC, Kaolin and a GCC/Clay blend) and were calendered to the same gloss level. These papers were printed on a commercial sheetfed press using conventional oil-based, UV and hybrid-UV inks. Differences in the print quality, topography and gloss were assessed along with ink rub-off and ink set-off measurements immediately after printing. Imaging reflectometry was used to study differences in the surface topography of the dried ink films and FIB (focused ion beam) depth profiling was used for analysing the depth of penetration of the ink into the coatings.

This study has shown that optimisation of coating structure is required for good printability of coated paper surfaces in a similar manner to conventional inks. There is no set-off with UV curable inks, but differences in coating structure do influence ink rub, print gloss, ink hold-out and penetration.

## Introduction

Ultra Violet (UV) curing of offset printed substrates is an expanding area of printing technology /1-3/ with an estimated growth rate of UV inks 12 % compared to the average 4 % growth in all inks /4/. Even higher growth is expected especially in flexo 21 % and offset areas 14 %. This printing technology is diverse and the application areas numerous, including the field of packaging, direct mail, safety and security, the production of smart cards, CD/DVD and in printed circuit boards /5/.

The main difference with UV offset printing, in comparison with standard web or sheetfed offset, is the mode of ink drying. Ultra violet ink systems contain photo-initiators which when activated with the correct wavelength radiation, will undergo a rapid free radical reaction causing the ink to set rapidly forming a dry, tough resin film. Claimed benefits of UV curing are rapid drying with no ink set-off or smearing and an abrasion resistant surface, as well as a high gloss. There is also less problem of sample blocking, where undried ink films cause the sheets to stick together /6/. Some known draw-backs of UV printing include less stable press runnability, requirement of special consumables like blankets, washes etc. and in practice a dedicated press.

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1 Stora Enso UK, Stora Enso House, New Mill Road, Orpington, Kent BR53TW, UK

2 Stora Enso, Falun Research Centre, SE-79140 Falun, Sweden

3 Imerys Minerals, Par Moor Centre, Par, Cornwall, PL24 2SQ, UK

4 University of Bristol Interface Analysis Centre Oldbury House 121 St Michael's Hill

In an effort to overcome some of these draw-backs the ink manufacturers introduced hybrid-UV inks a few years ago. According to ink manufacturers /7/, hybrid-UV inks combine the best properties of both conventional inks and UV inks as they have a solvent phase added to the UV chemistry. A basic comparison of the different ink chemistries is summarised in table 1. With hybrid-UV inks, as with UV inks, the UV coating can be applied inline achieving similar or better gloss as with pure UV, and also giving a possibility to create special matt, gloss or textured varnish effects. The main benefit compared to pure UV is claimed to be the possibility to switch between hybrid-UV inks and conventional inks in one press more easily. Printers can therefore use the best process for each particular job. Despite these claimed advantages, UV tolerant consumables are still needed for hybrid-UV inks and naturally UV curing units are needed, preferably as inter-deck units. Also the cost of hybrid-UV inks can be up to a third higher than those of UV inks, which in themselves are already more expensive compared to conventional inks /8,9/.

Table 1. Different ink chemistries.

	<b>Conventional ink</b>	<b>UV ink</b>	<b>Hybrid-UV ink</b>
<i>Color</i>	<i>Pigment</i>	<i>Pigment</i>	<i>Pigment</i>
<i>Binder</i>	<i>Alkyd</i> <i>Hard resin</i>	<i>Prepolymer</i> <i>Monomer</i>	<i>Prepolymer</i> <i>Monomer</i>
<i>Solvent</i>	<i>Mineral oil</i> <i>Monoesters</i> <i>Drying oil</i>		<i>"Solvent"</i>
<i>Additives</i>	<i>Oxidants</i> <i>Antioxidants</i> <i>Wax</i>	<i>Photoinitiators</i>  <i>Wax</i>	<i>Photoinitiators</i>  <i>Wax</i>

A search of the literature has revealed little detailed research work in the area of UV printing or hybrid-UV printing, particularly with reference to substrate requirements. It is considered that, as these inks dry by cross-linking of the constituents, absorption characteristics of the substrate should be less important than for conventional inks. However, the fact that differences exist in the curing rate and final optical properties of prints on differing substrates, suggests that absorption and topographical properties of the paper may play some part. Very porous substrates may cause the ink to sink into the surface thus decreasing the print gloss /10/.

The topography and surface energy of the substrate have also been cited as important for properties for ink wettability and adhesion. This is especially the case for non-porous and smooth substrates such as plastic films or to some extent highly calendered and coated papers. These substrates may need to be treated using the Corona process to raise the surface energy to above 40 mJ/m<sup>2</sup> /10,11/.

Part 1 of our study on UV printability of coated papers looked at the influence of paper coating structure on UV printability in a laboratory study /12/. This work showed that there were significant differences in the ink penetration, print gloss and density between different coated papers. However in the lab work, it was not possible to cure the ink film until approximately 8-10 s after printing, and it was considered that these time-scales were far too long to relate to commercial practice.

In this work a number of different coating structures were reproduced on a pilot scale and then combined with selected commercial samples in a full scale print trial. This trial included 3 different ink types; conventional sheetfed, hybrid-UV and UV curing inks. The printed papers were also finished using UV and/or water based varnishes. The main questions set for this study were:

- 1 do UV and hybrid-UV ink components penetrate into the coating surface similarly as conventional ink components, or are the substrate properties less or totally insignificant?
- 2 if there is interaction between these inks and the paper surface, what are the mechanisms and more importantly what are the implications on print quality?
- 3 what are the differences between UV and hybrid-UV inks on interaction with coated paper?

## Experimental setup and materials

Four pilot coated papers were prepared using a range of minerals (PCC, GCC, kaolin and a 80%-20% GCC-Clay blend) and were calendered to the same gloss level. Although having similar TAPPI gloss levels (61-64 %), the different mineral particles which make up the coatings, produced paper surfaces with very different porosities and pore sizes, see table 2. It can be seen that the PCC coating has significantly more porosity and this results in the lower refractive index (RI). The clay coating has the highest RI, as would be expected from a closed and calendered coating surface. The gloss, micro and macro-roughness values are very similar for all four pilot coated papers. Thus, the pilot papers all have a similar topography and the air content is more a function of the pore size and volume in the surface layers. In addition to the pilot coated papers three commercial coated papers including gloss, silk and matt finishes were included in the printing trials but the results on these will not be thoroughly discussed.

Table 2. Properties of pilot coated papers.

	PCC	Clay	GCC	GCC/clay
TAPPI gloss 75°	63.5	61.1	64.2	62.1
CIE-Whiteness D65 (+UV)	103.1	87.1	100.3	98
CIE-Whiteness D65 (-UV)	88.2	77.9	85	84.7
Fluorescence	14.9	9.2	15.3	13.3
Brightness D65	90.5	84	88	87.7
PPS 1000 kPa ( m)	0.78	0.74	0.86	0.93
Refractive index	1.22	1.4	1.38	1.36
Macroroughness FWHM (°)	2.9	2.9	2.8	2.9
Microroughness (nm)	80	100	80	90
Hg Pore Size (nm)	58	41	36	32
Hg Pore Volume (cm <sup>3</sup> /kg)	59	54	41	45
Surface energy total mJ/m <sup>2</sup>	52	49	46	46

The printing trial was carried out at Lindgren&Söner in Gothenburg, Sweden, using a KBA Rapida 105 press with 6 units and 2 varnish units. The press had inter-deck UV lamps after unit 6 and an end-dryer after varnishing.

The inks used were commercial inks from Sun Chemicals: Ecolith (conventional sheetfed), HyBrite (hybrid) and Unicure CL Jet (UV). These inks were used regularly by the printer. The inks were analysed for emulsification and tack properties at TestPrint BV /13/. SunFount 460 which is specially designed for UV printing was used as the fount additive.

The print layout included technical printing areas for measuring ink setting, gloss, rub-resistance, density and dot gain, as well as whiteness both from varnished and unvarnished surfaces (figure 1). The method description used to evaluate ink setting, rub-resistance, ink penetration and surface properties with reflectometry /14/ are described in detail in the Appendix. Ink-paper surface interaction was additionally studied in lab scale using the ISIT device (Segan Ltd) /15/. Target ink densities were black 1.65, cyan 1.25, magenta 1.25 and yellow 1.2.

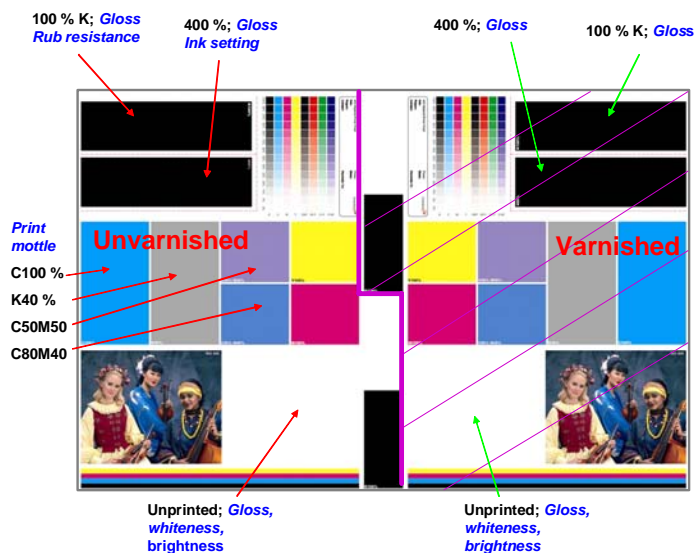


Figure 1. Print layout.

## Results and discussion

### Ink penetration into coatings – FIB and GPC

In order to investigate the ink penetration with the FIB analysis, the two extreme pilot coatings 100 % PCC with a very open surface and the 100 % kaolin with a closed coating surface were selected. Prints made with the UV ink and the conventional quickset inks were studied. In every case the 400 % black print areas were selected for this analysis to ensure that the coatings were completely covered with a layer of ink. The FIB images are shown in figures 2-5, and the following points can be made:

- A significant amount of UV ink components were found to penetrate into the surface pores of the PCC coating structure in a similar manner as seen in the initial lab study /12/. This is despite the fast curing of the UV ink which occurred on the commercial press. In concurrence with previous results it was shown that superior ink hold-out occurred for the kaolin coatings but even there some penetration is observable.
- The samples printed with the commercial ink also showed similar differences in ink penetration. Once again the PCC coating had imbibed far more ink vehicle than the kaolin coatings. It has been shown previously that the hard resins, extenders and ink pigments are too large to penetrate into the pore structure of calendered gloss coatings. It is likely therefore that the ink penetration observed is from the low molecular weight oil phase and possibly the fluid alkyd resins /16/.

These images clearly show the importance of coating structure design for good ink hold-out properties, even for ink systems which are cured immediately, such as UV inks.

In order to analyse which components absorb from the UV inks a set-off test combined with GPC analysis was done in the laboratory. At very short times after printing, the uncured prints were contacted with a 'chemically clean' filter paper, and the amount of set-off ink was measured optically and gravimetrically, and analysed using GPC. The analysis showed penetration of the low molecular weight monomers and photo-initiators.

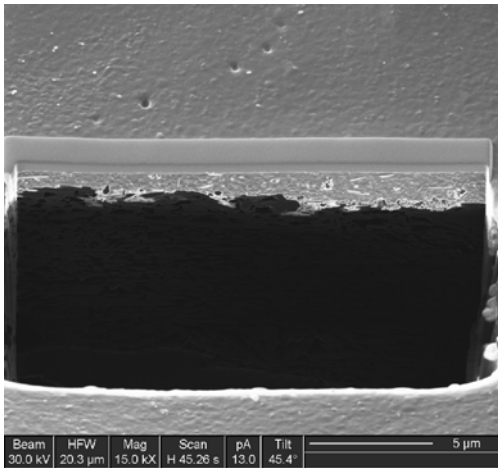


Fig. 2 *Kaolin-UV ink.*

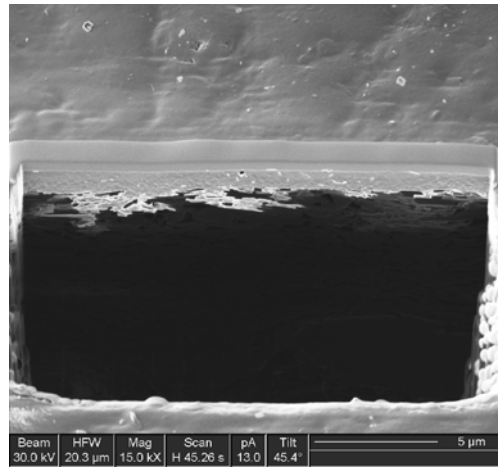


Fig. 3 *Kaolin-conventional ink.*

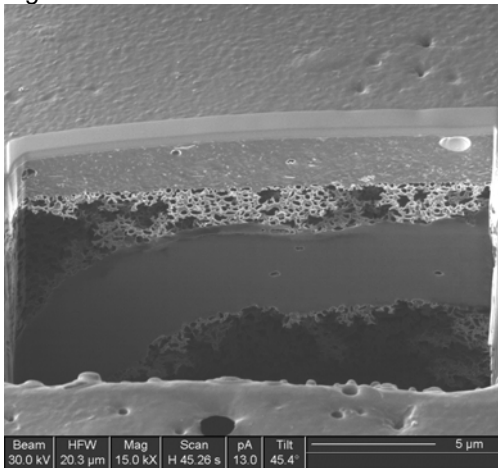


Fig. 4 *PCC-UV ink.*

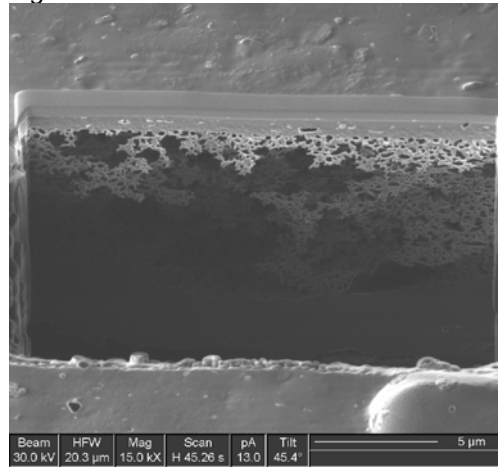


Fig. 5 *PCC-conventional ink.*

In summary, even with rapid curing of the UV ink in commercial scale printing, there is significant ink penetration into the surface layers of the coated papers. This can be visualised using the FIB sectioning technique. As the ink pigment has a particle size of approximately 1 μm, it is not likely to have penetrated the pores of the coated paper, however the polymer phase has intruded significantly.

### Print gloss

Final print gloss was measured from 100 % black and 400 % printed areas. As seen in figure 6, there are significant differences in print gloss depending on the paper used with all three different inks.

Conventional ink produces the highest print gloss in the range of 76-87 %, and between 13 and 26 % units increase from the original paper gloss (snap) on the solid black area. Both UV and hybrid-UV inks produced similar low print gloss on all papers between 55 and 64 %, the final printed gloss being below the original paper gloss with the exception of the clay coating. Exactly same behaviour was seen on the 400 % print surface but the print gloss levels were overall lower.

Print gloss differences between the papers are visible with all different ink types; on the conventional ink up to 10 % difference, with hybrid-UV up to 5 % difference and with UV up to 8 % difference between the highest print gloss clay paper and the lowest print gloss PCC paper were seen. Gloss dependence on substrate is thus smaller with the UV and hybrid-UV inks than conventional ink, nevertheless the differences are significant. The papers rank in

the same order with each ink, from highest to lowest print gloss: clay, GCC=GCC/clay and PCC. This order does not follow the order of the slight paper gloss differences and can therefore be attributed to the pore structure and chemistry differences in the coatings and inks. As expected the fast setting PCC coating creates the lowest ink gloss level due to less time for ink filament levelling combined with most penetration of the ink components into the substrate. The lower amount of binder that remained with pigments and extenders on the surface of the printed paper may explain the reduced print gloss. In the case of the kaolin coated paper, the ink has been largely held on the surface of the coating layer, and little penetration of the solvent or other low molecular weight components is seen.

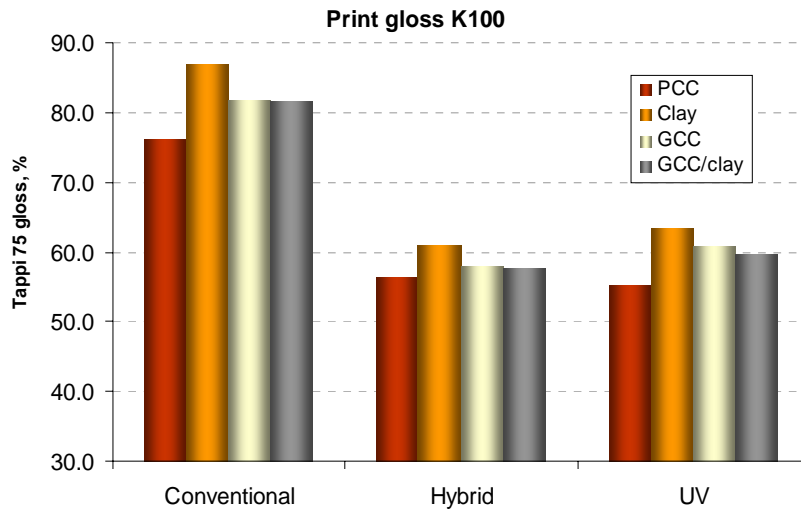
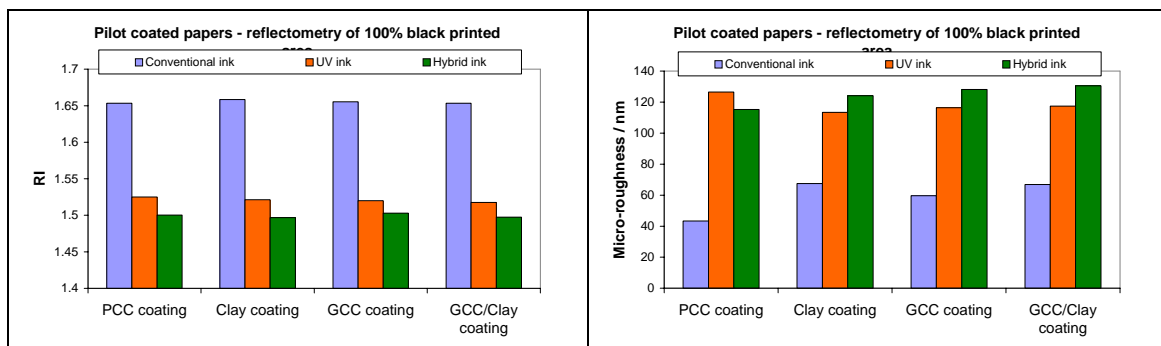


Fig. 6 Print gloss on 100% black with different ink and paper combinations.

The printed surfaces were also characterised using reflectometry, see figures 7 a-d. It can be concluded that the higher gloss with the conventional ink results from higher micro-roughness (macro- roughness is similar for all) and that the conventional ink forms a closed surface with high refractive index. UV and hybrid-UV inks have a low refractive index. This is probably dominated by the cured UV resin at the surface of the print. Another possible explanation for the print gloss and micro-roughness differences maybe that there is less time for UV curable ink filaments to level in between the nip split and “freezing” in the UV drying unit.



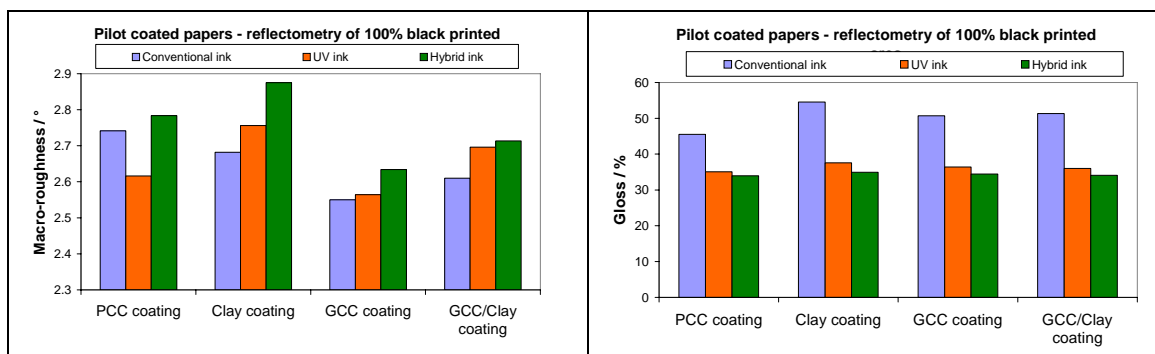


Fig. 7a-d Printed surface a) refractive index, b) micro-roughness, c) macro-roughness and d) gloss measured with Surfoptic reflectometry.

### Varnish surface gloss

In practice UV or hybrid-UV prints are nearly always UV-varnished, as on-line varnishing is possible with these ink systems. In this investigation UV and hybrid-UV prints were UV-varnished, and the conventional ink printed job was varnished on-line (water-based varnish) and additionally UV varnished after 8 hours.

Results on the gloss levels on different printed and unprinted varnished areas are summarised in figure 8. In this figure the conventional sheetfed offset ink was on-line varnished with a water-based varnish (WV), and it can be seen it did not produce as high gloss levels as with the UV-varnish. However, the printed UV-varnished surfaces showed similar high gloss levels on all three ink systems. The claimed gloss advantage for UV and hybrid-UV systems compared to conventional ink was thus not seen in these results when comparing the equal UV-varnished surfaces. The results also showed that no “primer” (in this case a water based varnish was used as primer) was needed for the conventional ink in order to achieve the high gloss on UV-varnishing. Nevertheless, it has to be kept in mind that the conventional ink had to be UV-varnished off-line whereas the UV and hybrid-UV can be varnished on-line.

On the unprinted areas it was seen that the UV-varnish produced nearly as high gloss as on the printed areas in most cases and thus nearly zero gloss difference between the picture and the background. However, a significant difference was seen for the porous PCC coating as well as the matt coated commercial paper in that unprinted UV-varnished surfaces appeared very matt and had significant gloss mottle (see figure 8). This gloss mottle was due to significant penetration of the varnish into some areas of the porous coatings, as was observed with the FIB sections through the surfaces of the varnished papers (Figure 9).

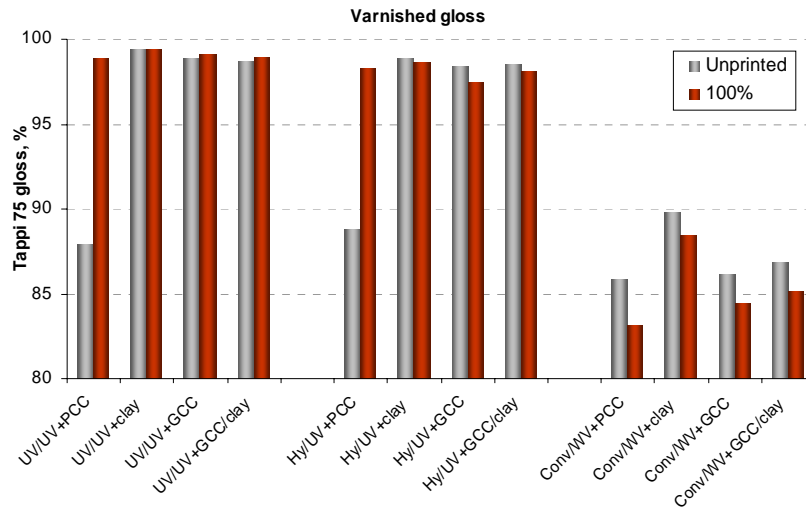
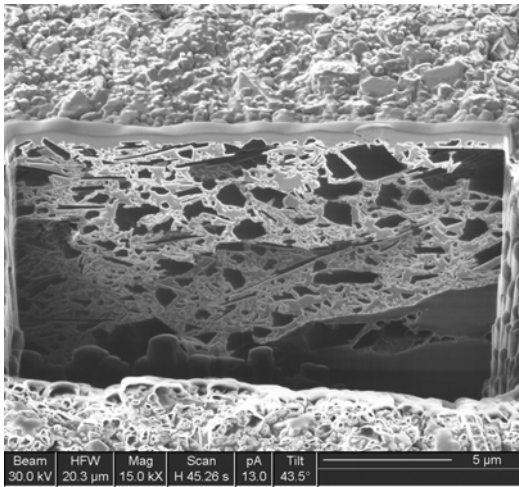
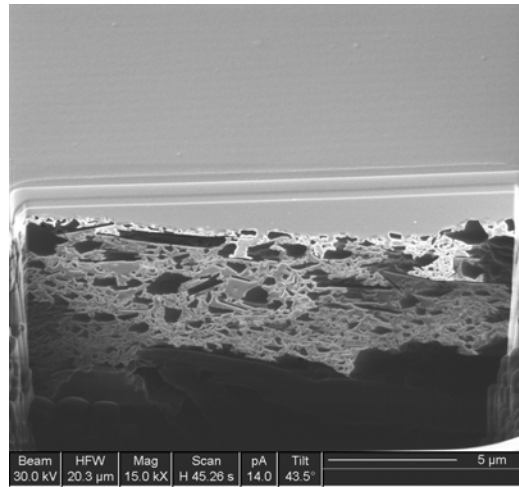


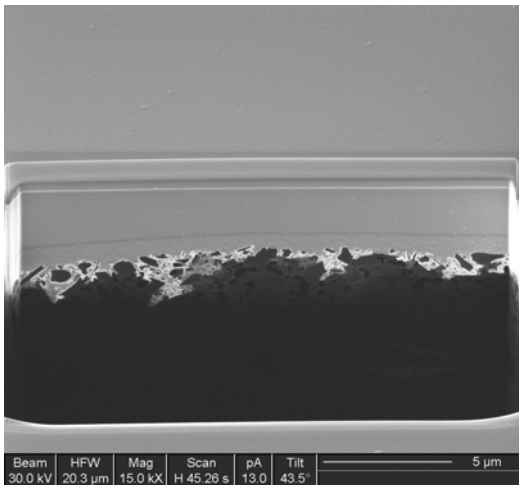
Fig. 8 Print gloss on 100% black with different ink and paper combinations.



a) Porous coatings absorb the UV varnish in certain areas giving rough low gloss patches



b) In other areas of the coating, good hold-out gives high gloss patches. Overall the porous coatings had a mottled finish.



c) UV varnish on top of water-based primer gives a high gloss finish.

Fig. 9 a-c) FIB images of varnished areas.



## Ink setting

Ink set-off measured directly after printing showed instant setting for both UV and hybrid-UV ink on all papers and thus no set-off could be measured from either unvarnished or varnished prints. Only conventional ink showed significant differences due to differences in surface porosity and absorption character: PCC 1.5 min, GCC/clay 2 min, GCC 2.5 min and clay 4 min.

Ink setting and tackification was also analysed in the laboratory using the ISIT device. UV and hybrid-UV inks did not show any tack response, whereas conventional ink behaved very similarly as measured in the set-off test from the commercial print (figure 10).

This result verifies the assumption of UV and hybrid-UV inks being a “homogenous” or a near one-phase system where the low molecular weight monomer does not pronouncedly separate from the polymer system to allow ink tackification. Thus, despite significant differences in ink oil penetration for the conventional ink depending on the coating structure and measured penetration of UV ink components into these coatings, no effect was seen on ink setting or tackification in the case of UV or hybrid-UV inks.

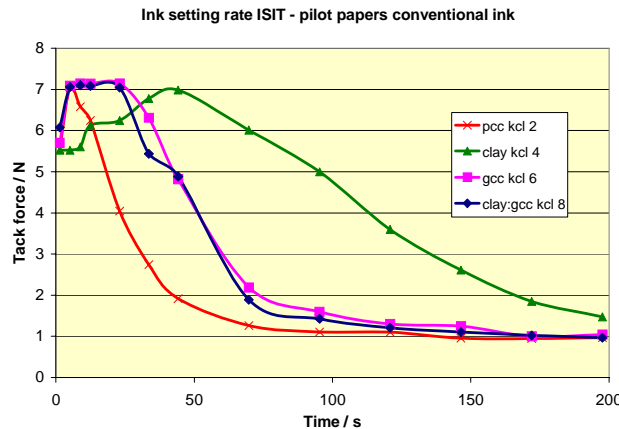


Fig. 10 ISIT setting of conventional sheetfed offset ink on the pilot papers.

## Rub-resistance

Rub resistance results show differences between the ink-paper combinations, fig 11. Generally, conventional offset ink was most prone to rub whereas UV and hybrid-UV inks showed less rub tendency. Nevertheless, also UV and hybrid-UV inks showed significant rub-off. UV and hybrid-UV ink show practically identical behaviour on one paper.

There were significant differences in rub-off between the papers with all inks, and the papers ranked in same order. The ranking from least to worst rub was clay, GCC/clay=GCC and PCC. In the case of UV the result is at least partially explainable by the penetration of the polymer phase into the porous PCC coating and therefore reducing the rub resistance compared to the low absorption clay coating holding out the polymers on the surface to give better rub.

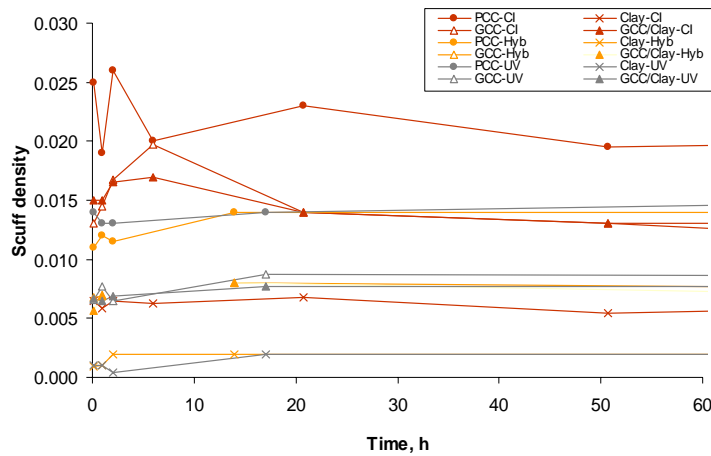


Fig. 11 Rub-off differences between inks and papers.

### Dot gain

In general, UV ink gave a higher dot gain than hybrid-UV or conventional ink (with the exception of yellow hybrid-UV ink having equally high dot gain as the UV ink). This may at least partially be explained by the fact that UV inks do not “set” and have less penetration and are thus more prone to spreading on the substrate surface than the other two ink types. The different process colours showed big differences in dot gain with the yellow spreading significantly more than the other inks as shown in figure 12.

Dot gain is lower for the PCC coating for the UV and hybrid-UV inks. There is less variation between coatings for the conventional ink and thus the coating structure appears to be more critical for the energy curable inks than for the conventional sheetfed ink in respect to dot gain. Surface energy differences between the papers do not explain the dot gain differences as these were very similar for all coatings (see table 1). Also the target density levels were reached, and the densities varied only within a small marginal.

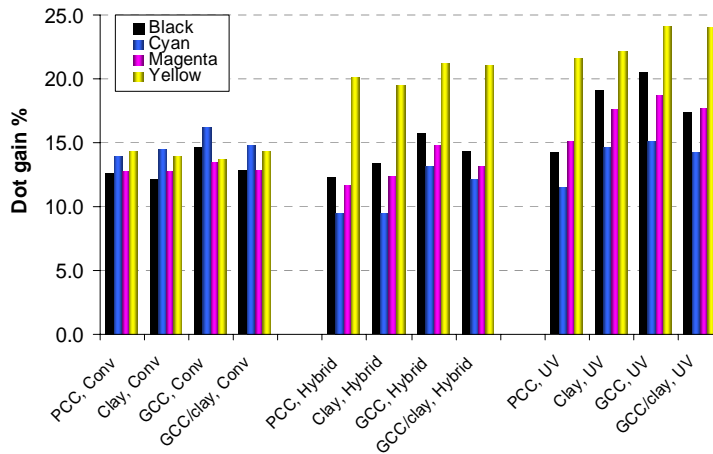


Fig. 12 Dot gain at 40% screen for different paper-ink combinations.

### Whiteness decrease with UV light

Reduction of paper whiteness under UV exposure is mentioned as one of the drawbacks of UV printing. In this trial it was found that the whiteness decreased more due to the UV-varnish (8-11 units on commercial coated papers) than the UV light exposure (4-5 units). Slightly smaller whiteness drop in whiteness on UV exposure was found with the pilot coated papers as the OBA levels were lower than with the commercial papers. Measuring the

whiteness with and without UV filters on the unvarnished area clearly indicated that the whiteness drop was on the UV fluorescence part of the whiteness and thus due to OBA destruction.

As seen in figure 13 the whiteness drop with the water-based varnish (orange poles) is much less than the whiteness reduction on UV varnishing. The drop of whiteness on varnishing was seen on the non-fluorescent part and may occur for two reasons; firstly the varnish itself may be slightly yellow and secondly the varnish may have been slightly absorbed into the surface layers of the coating and prevented light scattering in this region of the sheet. A decrease in light scattering would be seen as a drop in whiteness. As the whiteness reduction is similar on both the PCC and clay coatings, it is probable that the yellowness of the varnish itself is causing more yellowing than absorption.

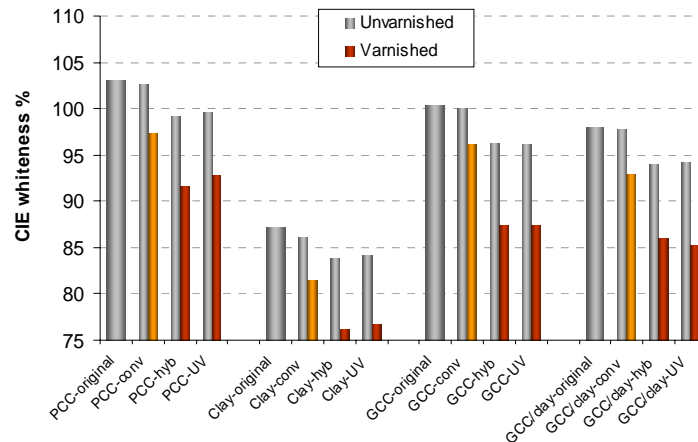


Fig. 13 Whiteness reduction of paper on varnishing and UV light exposure. The result here shown for the conventional ink is as using the water-based varnish.

### Tack and emulsification properties of the inks

UV inks are generally considered higher tack, less press stable and thus more difficult to run compared to conventional inks. In this study the inks were tested for emulsification (Hydro-scope™ /13/) including both tack and viscosity response as well as misting and using both distilled water and a fount designed for UV inks (Sun Fount 460). Also tack was measured (Tack-O-Scope™/13/). The results can be summarised as follows (see also figure 14):

- UV and hybrid-UV inks were tackier than conventional offset inks both as dry and as emulsified. The ink viscosities were similar in dry state, but when emulsified the UV ink viscosity dropped significantly. The Hydro-scope measurement measures both tack and viscosity response on emulsification.
- Conventional inks could take up more water than UV or hybrid-UV inks before becoming unstable.
- UV and hybrid-UV inks performed similarly on tack and viscosity properties, only on emulsification the hybrid-UV ink showed a more stable performance in respect to viscosity drop and consequently less misting.
- Misting was worst in the order UV, hybrid-UV and conventional. UV and hybrid-UV inks were thus much less stable on emulsification and had a narrower operating window than conventional inks. Degree of misting was evaluated visually from the amount of ink sprayed on a paper placed under the rolling nip.
- The stability and emulsification can be significantly improved by using the UV-designed fountain solution chemistry.

Also in practice the printer reduced the fountain solution feed for the UV and hybrid-UV inks. It can be stated that especially UV, but also hybrid-UV inks, can be more sensitive to the

fountain water feed and quality and may thus be more prone to fount associated printing problems like mottle, piling or dot gain if not controlled properly.

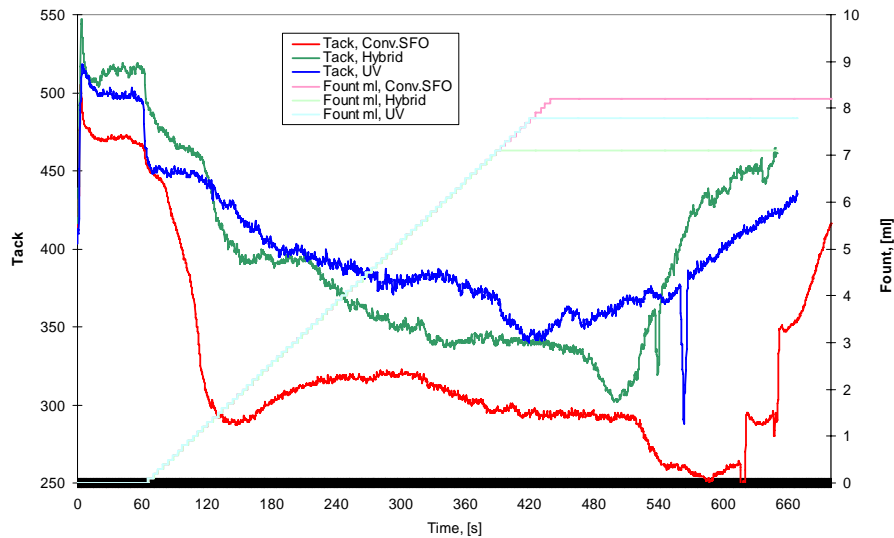


Fig. 14 Hybrid-UV, UV and conventional Ink emulsification using Hydro-scope.

## Conclusions

This paper has indicated that coating pore structure may have a significant influence on the distribution of ink components for UV and hybrid-UV printed offset papers, as is the case with the conventional ink. The main results can be summarised as follows:

- UV and hybrid-UV ink components (probably mainly monomers and photo-initiators, and the low molecular weight solvent in case of hybrid-UV ink) may penetrate into paper coating to varying degrees depending on the coating structure. This differential penetration has an impact on print gloss, rub-resistance and dot gain.
- The differences in print gloss and rub-resistance depending on the paper structure followed the same order as with the conventional inks but the mechanisms may be slightly different.
- Dot gain control is more challenging with UV ink than hybrid-UV or conventional ink, and the substrate properties have a greater impact than with conventional ink.
- The ink-water balance is more critical and challenging to control with the energy curable inks than with conventional ink.
- UV exposure does reduce paper whiteness, but a UV-varnish may cause more whiteness reduction than the UV exposure.
- Hybrid-UV and UV inks perform very similarly in nearly all properties.

Overall this study has shown that optimisation of coating structure is required for good printability of coated paper surfaces in a similar manner to conventional inks. There is no set-off problem, but differences in coating structure influence ink rub-off, print gloss, ink surface spread and penetration. An understanding of the pigment and formulation requirements for optimum printability is required for papers to be printed with energy curable inks.

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## Appendix – experimental methods

### Set-off

The ink setting time was determined using the Colormeter instrument. The soft rubber disk of the Colormeter is pressed at a fixed load first against a 400 % inked area and immediately thereafter against an unprinted part of the sheet. The test was performed every minute after printing and the time at which no contamination on the unprinted area can be seen was taken as the setting time. No instrumental evaluation was made.

### Ink rub-off

Ink rub-off at short times was monitored using the GRT rub-off test instrument. This was placed quite close to the press in order to make the short timescale measurements. Ink scuffing was determined after 10 minutes, 1, 2 and 6 hours after printing. A portion of the unprinted paper was contacted against the 100 % printed area of the same paper and rubbed with a single sweep, across the print at a low pressure. The procedure was repeated after one week to obtain the dry rub value. The rub-off value was determined as the density of the rub-off smear, calculated from reflectance measurements, following the SCAN-P8:93 procedure for the determination of Y-value, using an L&W Elrepho 3000 instrument with a 34 mm aperture.

### **The Surfoptic Imaging Reflectometer**

In this work the reflectometer was used to study changes in the gloss, micro- and macro-roughness and surface refractive index (RI) of the printed surface after printing. The reflectometer uses polarised light at two wavelengths to determine other surface properties, principally refractive index (a sensitive measure of surface composition) and optical roughness (roughness features  $\leq$  wavelength of light). Thus the Imaging Reflectometer /12/ provides most of the functionality of a 2-axis polarized light optical goniophotometer, albeit in a reduced angular range, but with the advantage of no moving parts, giving significant benefit in ease and speed of operation. Absolute reflectance, refractive index and optical roughness measurements are all referred to a calibration standard. Instrument repeatability for refractive index is typically  $\pm 0.001$ . The gloss quoted will differ from the Tappi gloss due to differences in the internal optical design of the instrument, the wavelength of the light and the acceptance angle of the detector aperture.

### **Focused ion beam, FIB**

An FEI FIB201 gallium focused ion beam instrument at the University of Bristol was used for sectioning and high-resolution imaging. The instrument is capable of producing a 30 keV gallium ion beam of between 7 nm and 300 nm in diameter using beam currents of 1 pA and 12 nA respectively. A platinum organometallic gas injector allows ion beam assisted deposition of platinum over selected areas of the sample. This facility was used prior to the sectioning in order to protect the top surface of the sample during ion milling. For sample sectioning, a large ion current was used initially to remove a staircase-shaped trench. A finer beam of lower current was then used to 'polish' the larger vertical face of the trench. This was done by scanning with the beam in a series of parallel tracks from the bottom to the top of the trench. The sample was then tilted to 45° and the polished face imaged using the same ion beam, generally at a much lower beam current to achieve high resolution. Typically 3 sections were made for each sample and then various magnification images were collected from each section.

### **Ink component penetration using GPC**

Chemical analysis on which ink components penetrated into the coatings was conducted at Stora Enso's Falun Research Centre. In this test, the laboratory printed uncured ink film is contacted with a clean filter paper under controlled pressure. The amount of set-off ink is analysed using a spectrophotometer. The clean filter paper is then extracted into toluene and the ink components analysed using GPC.