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INTERACTION BETWEEN OFFSET INK AND COATED PAPER – A REVIEW OF THE PRESENT UNDERSTANDING

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ABSTRACT

The printing speed of offset presses has increased significantly during the last decade and this puts increasing demands on the interaction between the paper and ink. Poor interaction may result in runnability problems and low quality of the printed product. The research in this area has been intensive during many years and the knowledge of important phenomena has been significantly improved, although a full understanding is still missing.

This review concentrate on offset printing of coated paper with special focus on sheet-fed offset. Properties of coatings and composition of offset inks are briefly discussed. Some data on ink film thickness and its lateral distribution is presented. Ink setting is reviewed in some detail and the effect of important coating properties (e.g. porosity, pore size, latex properties) and ink properties (ink oil viscosity and surface tension) are discussed. The interaction between latex binder and ink oil is given special attention.

The impact of coating structure and ink setting on print quality is covered in some details. The importance of ink filament formation and levelling as well as coating topography and ink film thickness on print gloss is well established. Recent findings on relations between mottle tendency and non-uniformity of coating structure and ink setting are included.

INTRODUCTION

The primary issue for a printer is to get the paper through the printing press. This is not a trivial task considering that the speed of a sheet-fed offset press range up to 18000 sheets per hour and that of a web-fed press can be as high as 15 m/s and in special cases even higher. This is an area that we normally refer to as *runnability*.

Printability is a common expression encompassing the ink drying behaviour of the newly printed paper and the quality of the print. The *printability of a particular paper* is the ability of the paper to be printed. It thus refers to how well the ink transfers, sets and dries on that paper without giving problems in the print shop or bookbindery, as well as the print quality obtained e.g. print density, print gloss, sharpness, evenness in print.

The most common phenomenon related to ink-paper interaction is ink setting, i.e. the quite fast separation of ink solvent from the fresh ink film which leads to a touch-proof but not completely dry ink layer. The separation of ink solvent can either take place through absorption by the paper surface layer, by evaporation or by both phenomena taking place simultaneously.

The interaction between ink and paper may influence both runnability and printability. A few examples are given below:

- *Ink piling* or *carryover piling* is a build-up of a deposit on the offset rubber blanket which causes production to stop in order to clean the blankets. The deposits can either originate from the ink or be a mixture of ink and paper components. A common cause of ink piling is a too fast ink setting rate.
- *Picking* is normally seen as a slight imperfection in the solid areas of the print. Small particles of the paper surface have been removed and the ink is thus not covering the paper surface completely, so that light areas are seen in the print. This is caused by low surface strength of the paper as well as a high tack force in the ink film, which may be due to ink setting being too fast.
- *Blocking* may occur in the delivery section of the printing press. The problem means that papers stick to each other due to poor ink setting and an ink that acts as an adhesive.
- Smearing of ink may be due to ink setting being too low.
- *Ink scuffing* and *carboning* may occur in the bookbindery if the ink film is not sufficient dry for the operations taking place in the bookbindery.
- *Low print* gloss may occur if ink setting is too fast. The ink will immobilise too early and reduce the levelling of ink filament ruptures.
- *Back trap mottling* is often explained as a consequence of uneven ink setting.

Sheet-fed offset printing is widely used for the production of high quality products with illustrations like art books, annual reports, brochures, exclusive magazines, commercial leaflets, etc. The paper is normally a coated fine paper, but both uncoated fine paper and board are printed in sheet-fed offset. *Heatset web offset* is used in production of magazines, catalogues, direct mail, etc. The papers used range from fully coated fine paper through various light weight coated papers (LWC) to supercalendered (SC) papers. *Coldset web offset* is mainly used for production of newspaper using newsprint and improved newsprint. See for instance Kipphan [1] for details on the offset printing technique.

PAPER AND INK

Paper

Coated fine papers, also sometimes referred to as graphic papers, normally have a base of wood-free pulp mainly hardwood, filled with calcium carbonate, quite often precipitated calcium carbonate (PCC). Important properties of the base paper are bulk, opacity, whiteness, formation and surface smoothness. The paper is coated with up to three coating layers. The first layer is often applied on-line and many matt-coated fine papers only have this coating layer. In order to improve smoothness, the paper can be coated off-line with a second and a third layer. Silk- and gloss-coated papers normally have two coating layers but three layers are not uncommon. The coat weights range from 12–15 to 35–40 g/m² per side. The ash content of a fully coated fine paper may be as high as 45 %. Silk-coated fine papers are calendered in a soft nip while gloss-coated are often calendered with hard nips.

The coating colour consists of pigment, latex binder, thickener and various additives like dispersion agents and optical brighteners. The most commonly used pigment in Europe is ground natural calcium carbonate due to its high brightness and low price. Kaolin clay is also used in fairly large amounts, while calcium sulphate (gypsum), talcum, satin white and plastic pigments occur but to a much lower extent. A standard coating colour formulation for graphic papers is 70–100 parts calcium carbonate, up to 30 parts clay, 10–12 parts latex binder, 0.5–1 part thickener such as carboxymethyl cellulose and small amounts of other additives.

Figure 1 shows a SEM picture of a double-coated fine paper. The coating thickness is high and shows local variations. A normal composition of a coating layer in volume -% is 60 vol.-% pigment, 15 vol.-% latex and 25 vol.-% voids.

The coating void structure is characterized by its pore volume, pore size,



Figure 1 SEM cross-section image of a double coated graphic paper.

pore shape and tortuosity. It is quite well known that the pore size increases with pigment particle size and pore volume increases with decreasing the latex content and when the pigment particle size distribution becomes narrower [2].

Figure 2 shows the coating porosity and pore size with increasing amount of latex binder for uncalendered laboratory coated sheets.

The main effects of calendering on the structure of the coating are increased smoothness [4, 5], closure of surface pores [6, 7], lower average pore radius and slightly lower pore volume [8]. The responses on optical properties are higher paper gloss, lower brightness and lower opacity [4].

Results of a pilot coating trial published by Karathanasis et al. [8] using different pigments (PCC, GCC and clay) showed that the average pore radius before calendering was between 40 nm and 100 nm but was reduced with roughly 20–30 % upon calendering in a nip of a polymer roll and a metal cylinder heated to 160 °C. The porosity was more or less the same for all coatings, 24 ± 3 % before calendering and 20 ± 2 % after calendering.

Ink

The principal components of a sheet-fed offset ink are colorant, binder, ink oil (polymeriseable and non-polymerisable), catalytic driers, antioxidants, wax particles, gelling agents and other additives like foaming agent and plasticizers [9].



Figure 2 Effect of SB-latex content on porosity and pore radius of laboratory coated papers containing a GCC (90%<2 μm) [3].

The colorant is normally an organic pigment. According to Kurtz [10] organic pigments can be classified with respect to their chromophore group into azo (monoazo and diazo), isoindolines, phthalocyanines, triphenylmethane and polycyclic carbonyls (quinacridone, dioxazine and anthraquinone).

Azo pigments contain one or two azo groups (-N = N-). They are most often yellow, orange or red. Disazo pigments are built up by dimers of azo molecules and have higher light fastness compared to azo pigments. Diarylide AAMX may serve as a representative for pigment in yellow ink. Red 202 Quinacridone magenta B is a high quality and also expensive pigment for magenta ink. This pigment belongs to the group of polycyclic carbonyls. Copper phthalocyanine is commonly used in cyan inks. Carbon black is used as pigment in black ink. Pigment particle size is in the order of 0.01–0.5 µm.

The ink binder is build up by a mixture of resins and drying oils. The term "resin" normally refers to a non-crystalline liquid or solid material with relatively high molar mass, while a drying oil is a liquid which can turn into a solid through an oxygen induced polymerisation at room temperature. A high number of resins are available and they are classified into natural resins and

synthetic resins. The natural resins are most often chemically modified. One example is rosin esters. They are manufactured by reacting rosin acids or polymerised rosin acids with a polyhydric alcohol such as glycerol or pentaerythritol. Two important synthetic resins are rosin modified phenolic resin and alkyd resin. Both may be classified as esters. The former is manufactured from pure phenolic resin, rosin acids and a polyhydric alcohol, while the latter is based on a polyhydric alcohol and a mixture of dibasic acids (e.g. phthalic acid) and unsaturated acid (e.g. oleic acid, linolic acid, linoleic acid). The solid resins are also referred to as hard resins.

Ink oils are classified as mineral oils and vegetable oils. Mineral oils are a mixture of hydrocarbons, actually the higher boiling fraction that are obtained from the distillation of petroleum. Vegetable oils are most often esters, for instance mono-esters and glycerol esters. The latter are esters of glycerol and a mixture of various unsaturated fatty acids. Common acids are oleic (one double bond), linolic (two double bonds) and linoleic (three double bonds). Glycerol esters are also referred to as triglycerides and examples are linseed oil, soya oil, tung oil and castor oil. They may be classified as drying, semidrying and non-drying oils depending on their ability to undergo polymerisation when exposed to oxygen. The reactivity is determined by the degree of unsaturation of the fatty acid and thus the fatty acid composition of the oil. A film of a drying oil undergoes polymerisation at normal room temperature, while a film of a semidrying oil requires heat for the reaction to take place. A non-drying oil does not polymerise due to inadequate content of double bonds. Alkyd resin may also be classified as drying, semidrying or non-drying depending on the amount and type of triglyceride used during manufacturing.

The ink vehicle is a solution of ink oils and binders. In practise the "ink vehicle" is a mixture of standard varnishes to which extra ink oil has been added. Most resins do not completely dissolve but solvate and form agglomerates, the size of which depends on the solvent. See papers by Szalkowski [11] and Sarnecki and Szabo [12] for further information on solubility and compatibility characteristics of resins. In order to improve ink rheology, the resin is thickened by adding small amounts of a gellant or by modify the ink resin to obtain self-gelling [13].

Common *catalytic driers* are soaps of cobalt or manganese. They speed up the decomposition of the hydroperoxide to free radicals, which is an important reaction during the oxygen induced polymerisation (oxidative drying) of the ink film. *Antioxidants* are used to prevent the polymerisation of drying oils on the press during longer stops. They stabilize the free radical until they are consumed. Examples of antioxidants are butylated hydroxy toluene (BHT), methyl ethyl ketoxime, cyclohexanone oxime and hydroquinone.

A typical sheet fed offset ink formulation is given in Table 1.

Ink constituent	Physical state	Content (%)		
Pigment and filler	Dispersed particles	15–22		
Hard resin (binder)	Dissolved polymer	20-30		
Alkyd resin (binder)	Liquid polymer	8-12		
Triglyceride ¹ (drying and semidrying oil)	High viscosity oil	10–25		
Mineral and/or vegetable oils (non-drving oils)	Low viscosity oil	15–25		
Additives e.g. wax, driers, antioxidants		3–5		

 Table 1
 A typical ink formulation

¹ Triglycerides are classified as vegetable oils

The formulations on inks published in textbooks [9, 14] are generic. However, analytical data of a mineral-oil and a vegetable-oil based sheet-fed offset ink was published a few years ago [15] and are given in Table 2.

Table 2	Analytical	data of a	vegetable of	oil and	mineral	oil in	wt%	[15]	
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Ink constituent	Vegetable-oil ink (%)	Mineral-oil ink (%)	
Dispersed solids (e.g. pigment, filler, wax particles)	21	21	
Triglyceride (TG)	28	18	
Mineral oil (MO)	2	24	
Vegetable oil (M-E) (mono-ester)	16	0	
Others, i.e. binder and additive	33	37	

The content of mineral oil and mono-ester was determined by gas chromatography, that of triglyceride was determined by gel permeation chromatography (GPC) and that of dispersed solids was determined gravimetrically. Figure 3 shows GP chromatograms of the two inks.



Figure 3 GP chromatogram of the vegetable-oil ink (left) and the mineral-oil ink (right) [15].

THICKNESS OF INK FILMS

The amount of ink transferred to the paper is low. It is generally believed that the ink required for one full tone layer is around 1 g/m^2 which should correspond to a thickness of roughly 1 µm for a wet ink film before ink oil absorption. The density setting for black ink is typically 1.9 for a smooth paper (gloss and silk grades) and 1.7 for a rougher paper (matt grade). Figure 4 displays data from a full-scale sheet-fed offset print trial where the ink amount had been determined by chemical analysis [16]. The data shows that these densities are reached at an ink amount of 0.9–1.1 g/m², which is in good agreement with the statement above. Cyan and magenta show values in the same region for a print density around 1.5, which is a typical setting for these colours [17].

The wet ink film is thin and the dry film after oil absorption is, of course, thinner. Figure 5a and b show cross-section SEM pictures of coated paper printed in full scale with four full tone layer on top of each other [18]. The thickness is just above 1 μ m.

The thickness distribution is shown in Figure 6 for three coated papers. The silk- and gloss-coated papers have more narrow thickness distribution compared to the matt-coated paper. This is also evident from Figure 5b. The average thickness of a dry 400% print is around 1.3–1.4 μ m [18]. These values are somewhat lower than expected (2 μ m), if one considers half of the ink layer to be absorbed by the coating and the ink density to be 1000 kg/m³.



Figure 4 Relation between print density and ink amount after full-scale sheet-fed offset printing for various commercial graphic papers [16].



Figure 5a SEM cross-section micrograph of a printed silk-coated paper. The ink film is seen between the coating and the white line, which is the reflection of a gold-palladium cover of the printed surface [18].



Figure 5b SEM cross-section micrographs of prints on matt- and silk-coated papers [18].



Figure 6 Thickness distribution of ink films on matt-, silk- and gloss-coated graphic papers obtained by image analysis of SEM cross-sections of 400% surfaces [18].

INK-PAPER INTERACTION: INK SETTING AND INK DRYING

The term ink-paper interaction is widely used but seldom defined. We may consider ink-paper interaction as:

- The wetting process when ink and paper meet.
- The absorption process taking place after initial contact, which is referred to as ink setting. This is a selective process where part of the ink (oil, diluent, low molar mass binder) is absorbed by the coating and the rest (pigment, binder) forms a film on top of the paper.
- The retention of colorant (e.g. dye in inkjet ink) to internal and external surface of the paper.
- Transfer of ink from a print to an adjacent paper, e.g. smearing, ink scuffing.

Of the ink-paper interaction phenomena listed above, ink setting is the most widely studied.

General understanding of ink setting and drying

Ink dries through depletion of ink oil from the ink film and (for inks containing drying oils) oxygen induced polymerisation of drying oils (alkyd resins and glycerol esters). The depletion of ink oil is normally referred to as physical drying and takes place through absorption by the coating and/or in the case of the heatset web offset process, by evaporation. Ink setting is the initial stage of the physical drying. The polymerisation of drying oils is referred to as chemical drying or oxidative drying. The chemical drying rate is strongly enhanced by increasing temperature [19]. At room temperature, it normally starts long after the physical drying is completed.

The ink film is:

- *Touch-dry* after ink setting. This is more or less the criterion for assessing if the ink film has set.
- *Semi-dry* when physical drying is completed.
- *Completely dry* when the chemical drying is completed.

The absorption of ink oil by the coating takes place by capillary absorption and absorption by the latex film. Extensive research has been conducted in this area during the last two decades and the knowledge is fairly good but a comprehensive theory is still missing. Through a number of model experiments and observations it is clear that the following factors have a strong impact on ink setting.

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- *Coating porosity, pore size and pore density* [8, 20–23]. Ink setting rate is increased by increasing porosity and increasing pore density. It is also increased by decreasing the pore size if porosity is constant. Coating porosity is controlled by the properties of the coating pigment or pigments and by the latex binder level and chemistry. A pigment having a steep particle size distribution gives a higher porosity than one with a broad range of sizes. The pore size can be controlled by pigment particle size and steepness. There may also be an influence from calendering.
- *Ink oil viscosity and surface tension*. Ink setting rate is strongly increased by the ratio surface tension to viscosity. This has clearly been demonstrated by Rousu [23].
- *Latex properties* such as gel content and polarity. More details are given below.

Ink setting can be studied with a number of different instruments. The Ink Surface Interaction Tester (ISIT) [24] and the Paper and Ink (P&I) Test [25, 26] are commonly used. The Deltack [27] is a newly developed pice of equipment. All these techniques basically determine the ink film splitting forces as the ink splits between the printed paper and a recipient surface. Measurements are taken at different times after ink transfer and a curve of ink splitting force (tack force) vs. time is constructed. Also the ink tack variation at



Figure 7 Ink tack curves measured by ISIT using a vegetable-oil ink and laboratory coated papers containing a 90 GCC and various amounts (parts) SB-latex binder (same paper as in Figure 2 [3]).



Figure 8 Ink setting vs. latex content from the data in Fig. 7, expressed as ink setting slope, time to max tack force and time to 3 N [3].

the millimetre scale can be determined using equipment described by Xiang et al. [28].

Figure 7 shows typical tack force-time curves obtained with the ISIT [3]. The curves contain information on the setting rate. Common values used for quantification of ink setting rate are: initial slope of tack rise, time to maximum tack force and time to when the tack force has declined to a certain value, for instance 3 N. Figure 8 shows examples were the different ink setting values have been plotted against the latex content of the coating. Both the porosity and the pore size decreases by increasing the latex content as already shown in Figure 2. All curves show a decrease in ink setting rate with increasing latex content.

An example on the effect of coating porosity on ink setting is found in Figure 9. This work was done by Preston et al. [22] using a large number of pilot coated papers containing a wide range of different coating pigments, both clays and carbonates.

An example on the effect of pore size on ink setting is given in Figure 10.

A study of the effect of ink oil surface tension to viscosity ratio on ink setting was conducted by Rousu et al. [29] using a series of model inks and laboratory coatings. Some results are given in Figure 11. The figure clearly shows the strong effect of surface tension to viscosity ratio, but it also shows the effect of pore structure and type of latex. The pore structure was quite different in 3 coatings due to different types of pigment (unfilled symbols) and this explains the difference in setting rate. Three coatings contained the same pigment but different latexes, which had a minor effect on porosity and



Figure 9 Ink setting given as time to max tack from ISIT curves [22].



Pore Diameter, nm

Figure 10 Ink setting, characterized by the P&I test, vs. mean pore size for pilot coated and uncalendered fine paper with a top coat consisting of mixtures of various calcium carbonates (GCC and PCC) and clay of similar porosities (24±3%) [8].



Figure 11 Influence of ink oil properties on setting rate for model inks on laboratory coated papers containing different pigments and latexes. The ink oils were rapeseed oil, linseed oil, aromatic mineral oil, tall oil ester and low-aromatic mineral oil and their surface tension to viscosity ratios were 0.54, 0.75, 1.94, 3.93 and 4.73 m/s respectively Rousu et al. [29].

pore diameter as characterized by mercury porosimetry. The difference in setting rate for these coatings is most likely due to the oil-latex interaction. The coatings with slowest setting rate contained styrene acrylate latex which has a low interaction with the ink oils

Observations on changes in ink film composition during oil depletion

Data on the change in ink film composition during physical drying have been reported [15] Figure 12a and b show the amount of remaining ink oil in the ink layer at different times after printing. The inks are the same as those described in Table 2 and Figure 3.

The data in Figure 12a shows a very fast absorption during the 2 first minutes and a slower absorption thereafter. This suggests that different ratedetermining processes take place in the different phases. The break point is close to the ink set time. It is probable that before the break point, the ratedetermining process is the capillary flow i.e. capillary pressure balanced with the viscous drag. But after the break point a significant gel layer of ink binder and ink pigment has been established in the lower part of the ink film and the



Figure 12a The amount of ink oils remaining in the ink film at different times after printing. M-E refers to mono-ester and TG refers to triglycerides [15].



Figure 12b Ink film composition in terms of pigment, binder, ink oil and other components. The content of ink oil was analysed at different times after printing. The original content of pigment (solids) was analysed. The calculations are based on data from Figure 12a and the assumption that only ink oil is absorbed by the coating, which also was concluded from the work [15].

time-dependent step is now diffusion of oil molecules through the gel phase to the ink-coating interface. Schoelkopf et al. [30] found a break point after about 100 s. Their experimental set up had no limitations in ink amount or coating thickness. This supports the suggestion that the imbibition rate in the slower regime not is controlled by normal capillary absorption but by a different mechanism such as the diffusion of ink oil molecules through a gel phase of solvated binders.

It is quite well established that a separation process takes place during ink setting and physical drying. Figure 12b shows this in terms of ink oil, binder, dispersed solids (pigment, filler, wax particles) and the other additives. The ink oil is absorbed by the coating and the ink film on top of the coating consists of pigment, binder and small amounts of ink oil. At ink set time (2 minutes) the amount of ink oil has been depleted by roughly 50 %. The depletion of ink oil from the ink film will continue during the course of the physical drying as is clearly seen from Figure 12b. The absorbing liquid is not the ink vehicle but a mixture of ink oils into which some low molar mass binder resin may be dissolved. Rousu [23, 31] gives more information on the differential absorption of offset ink constituents on coated papers.

Studies of adsorption of alkyd resin from solution onto various substrates relevant for ink-paper interaction has been reported by Johansson et al. [32, 33] and Wickman et al. [34, 35]. Johansson used cellulose [32] and clay [33] as substrates while Wickman used carbon black [34] and calcium carbonate [35] General findings were that adsorption was strong on all substrates and increased with decreased solubility of the alkyd resin as expected.

The depth profile of ink pigment in a dry ink layer has been studied by SIMS while the ink layer was etched away continuously [36, 37] The work showed clearly that ink pigment stayed on top of the coating and did not penetrate into the coating layer. Rough coatings showed a thin boundary with both ink and coating pigments. The analysis also showed a depletion of ink pigment at the outermost surface of the ink film, suggesting that the ink top layer is richer in ink binder than the rest of the ink layer.

The depth profile of ink vehicle constituents in newsprint after cold set printing has been chemically analysed by Mattila et al. [38]. They showed that the separation process continued for several days. The mineral oil showed deeper penetration and a more efficient separation from the resin than the alkyl ester or linseed oil. According to Gregersen et al. [39] the pigment penetration is negligible.

Heard et al. [40] used focussed ion beam imaging and focussed ion beam sectioning in combination with transmission electron microscopy to visualise the penetration of toluene-based rotogravure ink into clay coated publication paper. They showed that the ink penetration into a blocky clay coating was

significant and higher than that of a platey clay coating. Similar approach has also been used in the study of penetration of intaglio and screen printed papers [41] and offset printed papers [42].

Absorption of ink oil by latex and its effect on ink setting

Over 30 years ago, Kelly et al. [43] showed that ink setting was highly influenced by the interaction between the latex binder and the ink solvent. An increased solvent absorption by the latex resulted in faster ink setting. The many studies that have followed since then have led to the following conclusions, which are still the subject of debate:

- An increased latex content in the coating results in slower setting rate [44]. This is mainly due to a decreased porosity of the coating. Thus it is believed that ink oil absorption by the coating through the pore structure is more important than oil absorption through latex swelling. One indication of this is found in a paper by Xiang and Bousfield [45]. A controlled structure was obtained by preparing model coatings containing plastic pigments of different sizes. Both interactive and non-interactive latex binders were used. For normal levels of latex the ink setting rate was determined by the pore size and not by type of latex. The effect of latex became important at high latex levels where the pore volume was drastically reduced.
- For a given latex level in the coating a strong oil-latex interaction results in a faster ink setting. The relation between latex properties and ink setting is summarized in Table 3

Increasing value	Ink setting rate	References			
Butadiene content in SB latex	Increases	Triantafillopoulos, Lee [46]; Rousu [23]			
Polymer cross-linking (gel content)	Decreases	Triantafillopoulos, Lee [46]; Rousu [23]			
Latex particle size	Increases	Triantafillopoulos, Lee [46]			
Degree of surface polarity	Decreases	Van Gilder, Purfeerst [47]; Fouchet et al. [49]; Kan, Van Gilder [48]			
Content of polar co- polymer	Decreases	Van Gilder, Smith [50]; Kan, Van Gilder [48]			

 Table 3
 Conclusions regarding the relation between latex properties and ink setting rate.

Although several studies [20, 23, 43, 46, 47, 49] have shown that ink setting rate increases with increasing latex swelling. Xiang et al. [52] have shown the opposite. They explain their contradictory results with closure of surface pores due to latex swelling, which reduces the coating porosity and capillary absorption. It could be mentioned that the latex content of their coatings was fairly high at 14 parts as opposed to the 10–12 parts which is more normal for fine paper coatings.

The uptake of oil by the latex binder depends both on latex properties and the type of oil (see Table 4). Comprehensive studies of this have been published [23, 49] Fouchet et al. [49] claim that the uptake of oils by thin films of latex follows Fick's law of diffusion. It is interesting to note that the diffusion is highly temperature dependent. Not only mineral oils and glycerol esters diffuse into the latex, but also alkyd resins show a significant diffusion. Extrapolation of the data to micro-thick films, which is what we expect to be the case for real paper coatings, suggests that significant oil diffusion takes

Table 4 Gravimetric equilibrium uptake of oil by model (1–9) and commercial latexes. The oil uptake is given as wt.–% of the mass of the latex film. Latex 4, 9 and BASF S360D contained an addition of acrylonitrile. Abbreviations: SB=styrene-butadiene, SA=styrene-acrylate, Tg=glass transition temperature, Al M=aliphatic mineral oil, Ar M=aromatic mineral oil, TE=tall oil ester, Rap=rapeseed oil, Lin=linseed oil, δ =solubility parameter in MPa^{1/2} [23].

Latex and properties	Al M	Ar M	TE	Rap	Lin	δ
No 1, T _e =2 °C, gel content=78%	43	158	131	61	59	17.3
No 2, $T_{g}=6$ °C, gel content =59%	38	232	182	86	80	17.3
No 3, $T_{g}=1$ °C, gel content =54%	45	239	142	89	127	17.3
No 4, $T_{g}=12$ °C, gel content =70%	3	69	37	4	0	18.0
No 5, $T_{g}=15$ °C, gel content =78%	39	157	92	61	28	17.4
No 6, $T_{g}=23$ °C, gel content =77%	20	128	130	44	26	17.5
No 7, $T_{g}=7$ °C, gel content =65%	14	135	123	14	8	17.9
No 8, $T_{g}=24$ °C, gel content =59%	4	92	162	1	1	17.9
No 9, $T_{g}=6$ °C, gel content =79%	1	63	46	2	0	18.7
Dow 940,SB, T _g =22 °C	29	181	211	47	83	
Dow 920, SB, T _e =13 °C	31	111	99	31	47	
Dow 980, SB, T _e =-7 °C	26	112	89	38	53	
BASF S360D, SA, T _g =5 °C,	11	45	28	8	9	
Raisio SB370, SB, T =25 °C	30	121	159	42	57	
Eka Polymer L P5105, SB, T _g =-10 °C	58	186	149	92	97	
Eka Polymer L P7105, SB, T _g =17 °C	48	149	116	56	69	

place within a few seconds. It is surprising to note from the work of Fouchet et al. [49] that coatings with SA latex most often showed faster ink setting than coatings containing SB latex even though SA latex has a very low oil absorption capacity. This also demonstrates the difficulty to distinguish between latex effects and pore structure effects on ink setting.

Solubility parameters of latex and oils have been calculated by Rousu [23]. The result is presented in Table 4.

This work showed that SB latexes have a stronger interaction (here defined as a higher amount and faster uptake) with the oils compared to the SA latexes. This has also been shown by Fouchet et al. [49]. Coatings with SB latex also showed faster ink setting. Decreasing both T_g and gel content resulted in faster ink setting but no correlation with solubility parameter could be established. The solubility parameters of the latexes were calculated from the mass proportion of the monomers and their solubility values, and thus quite similar values are obtained. However, the author pointed out that this approach is not fully correct especially when comparing polymers having different gel contents. This might be one reason for the lack of correlation to solubility parameters.

Van Gilder and Purfeest [47] were more successful in their attempts to use solubility parameters to quantify ink oil-latex interaction and relate this to ink setting. They used a range of solvents with different solubility parameters (δ_s) and determined the amount of solvent that could be absorbed by films of various model latexes (linear, cross linked, high and low polarity). The solubility parameter of the latex (δ_p) was defined as the solubility parameter of the solvent which showed the highest absorption. This is a more experimental way to determine solubility parameters. The strength of the interaction was quantified as $\Delta\delta$ i.e. $|\delta_p - \delta_{io}|$, where δ_{io} is the solubility parameter of the ink oil. A low value of $\Delta\delta$ means a strong interaction. It was demonstrated that latex with strong interaction with ink oil also gave fast ink setting and showed piling when printed at full-scale on a six colour offset press.

They also showed that ink setting occurred on pure latex films. The setting rate was somewhat slower on the latex film compared to the coating containing the same latex. A slower setting on latex films compared to coatings were the same latex was used has also been shown by Rousu et al. [51].

Speculation on change in pore structure due to latex swelling during oil absorption

Consider an ink layer with a wet thickness of 2 μ m, with all ink components having densities of 1000 kg/m³ and 50 % of the ink is ink oil, half of which

(25 % of the total ink) is absorbed by the coating during ink setting. The coating pore volume is around 25 vol. % but not all is accessible to the ink oil [54]. A simple calculation shows that the ink oil will only fill up a small fraction of the available pore volume.

Since the latex forms a more or less continuous film in the pore system [55] ink oil will be transported further down into the coating through diffusion of oil molecules in the latex matrix. Thus we may have pore closure and pore opening during this process. The following paragraph illustrates this in more details.

The ink oil goes into the pores where the pore walls consist of latex. Once in the pores, oil molecules diffuses into the latex, which starts to swell and pores and/or pore necks may close. A pore that has been closed by latex swelling may open again when the swelling decreases due to a diffusion of oil molecules further down in the coating. Thus, both total oil uptake and rate of uptake may be important.

Transport mechanisms

Xiang et al. [57, 58] used Darcy's law for laminar flow through a filter cake to model ink setting. They assumed that a filter cake of ink pigments is formed when the coating absorbs the mobile phase of the ink. The driving force is the capillary pressure generated by the pore system of the coating. This pressure is reduced by the pressure drop across the filter cake and the pressure drop is dominated by the Darcy coefficient (filter cake permeability). The reduced pressure controls the flow of the mobile phase and the flow velocity is described by the Hagen-Poiseuille equation. The final equation of fluid uptake is the product of an ink/coating interaction function and square root of absorption time. The interaction function includes ink and coating parameters such as ink viscosity, ink surface tension, coating porosity, coating pore size, ink/coating contact angle as well as the Darcy coefficient. High filter cake permeability i.e. a high value of the Darcy coefficient means little or no influence of the filter cake and the equation is reduced to the Lucas-Washburn equation.

Evaluating the ink/coating interaction function for a significant filter cake resistance shows that the rate of absorption increases with decreasing pore size [58] which is the current understanding from experimental work [8, 20–23]. Moreover, for constant porosity the absorption rate becomes proportional to the 2/3 power of the pore radius, which also has been found experimentally [22]. Another interesting feature of this theory is that the ink/ coating interaction parameter is a function of porosity and pore size. At porosities that are relevant for paper coatings the interaction parameter

shows an optimum at a certain pore radius, which is in the relevant range for paper coatings.

One drawback of this theory is that it does not account for ink oil absorption by latex binder, although transport mechanisms of oil into latex was discussed [57]. Another drawback is that a filter cake of ink pigments is unlikely to form at the ink-coating boundary, since the ink solids (ink pigment, wax particles and fillers) to binder volume ratio is low, well below unity. Thus, during ink setting the pigments will form a dispersion where the dispersed media is a concentrated solution of binder, which becomes increasingly concentrated during oil absorption. This matrix made up by a concentrated binder solution and dispersed solids may be considered as a gel phase as suggested by Bristow and Bergenblad [59] and Schölkopf et al. [60]. The enrichment of ink binder at the coating surface can be concluded from work by Rousu et al. [51] using model inks and Ström et al. [15] using commercial inks. Diffusion of pigments in this highly viscous binder solution is negligible.

It is reasonable to believe that a concentration gradient of binder is formed with the highest concentration at the ink-coating boundary. The pores beneath this boundary will be filled with ink oil. Thus, an osmotic pressure gradient will arise since the ink oil in the pores contains basically no binder but the ink oil in the ink film above the boarder contains a high amount of binder. Capillary pressure will force the ink oil to penetrate into the pores but oil molecules have a lower chemical potential in the ink film which promotes a transport of oil molecules back to the ink film. The importance of osmotic pressure for ink oil absorption was suggested by Ström et al. [15] and has been further discussed by Voltair and Fogden [61]. Including the osmotic pressure in the ink-paper interaction process could explain a phenomenon often observed in the print shop, namely that the ink film during drying sometimes becomes more wet instead of more dry. This phenomenon is referred to as bleeding.

A number of publications [60, 62] stress the importance of inertia on ink oil absorption by the coating. Considering the coating void to consist of pores of different sizes connected by throats of different sizes the oil absorption will not proceed with a steady flow as is one of the constrains of the Lucas-Washburn equation. The absorption will instead proceed stepwise with acceleration and retardation. For such a case not only viscosity but also inertia will control absorption rate, and as a consequence a preferred pathway where small pores have advantage over large pores will show up. Thus, large pores will be by-passed and left partially unfilled.

INK-PAPER INTERACTION: PRINT QUALITY

Print gloss

Gloss is basically a function of the surface roughness and refractive index of the material. A straightforward equation of gloss (Tappi gloss) is given by:

$$Tappi_Gloss = 100 \frac{s(\theta, n)}{s(\theta, 1.567)} e^{-\left(\frac{4\pi \cdot rms \cdot \cos\theta}{\lambda}\right)^2},$$
(1)

where θ is the light incident angle, λ is the wavelength of light, rms is the root mean square value of the surface roughness, n is the apparent refractive index of the surface and $s(\theta,n)$ is the Fresnel factor for reflectance of unpolarized light.

Studies on how the human beings perceive print quality has shown that print gloss variation is more detrimental for the perceived print quality than a low average gloss value. Print gloss variation is believed to be strongly affected by variation in paper surface structure [63, 64].

Further readings on fundamentals of gloss and techniques to measure gloss are found in textbooks, for instance, Pauler [65] and articles by e.g. Hunter [66] and Gate et al. [67, 68].

It is well known that the rate of ink setting affects print gloss in particular that fast ink setting reduces print gloss [8, 69, 70]. This has been explained by poor (or ruptured) ink filament levelling. Fast ink setting results in a rapid increase in ink viscosity, which reduces the flow of excess ink resulting from filament rupture. This phenomenon has been widely studied by Bousfield and co-workers at the University of Maine.

Glatter and Bousfield [71] extended the "long-wave analysis" of Kheshgi and Scriven [72] to a system of ink filaments. The levelling driving force is local pressure created by the curvature of the rough ink surface, which is direct proportional to the surface tension of the ink. Ink viscosity is the resistant against levelling. The theory has been further developed by Desjumaux and Bousfield [73]. The theory predicts and experimental measurements confirm that the fine-scale (<0.1 mm) defects level rapidly but long scale (0.5 mm) features persist, which is detrimental for print gloss. Detailed structure characterizations of the printed surface revealed that the features from levelled filaments formed a ridge pattern that scaled with the ink film thickness. The same type of features was observed by Hayashi and Amari [74] Figure 13 shows a 1 s old Prüfbau print [3] The original image was taken with a CCD camera and mathematically processed to give a three-dimensional view of the filaments during ink levelling. Further reading on ink film splitting and filament properties are found in papers by Myers et al. [75] Tayler



Figure 13 Image of a 1 s old print showing filament craters that undergo levelling [3].

and Zettlemoyer [76], De Grâce et al. [77], MacPhee [78], Ercan and Bousfield [79, 80] and Nguyen et al. [81].

Many reports are available on gloss dynamics [82–85]. Most often they report gloss improvements with time after printing and attribute the findings to the levelling of ink filaments. Fast ink setting gives slow levelling and low gloss improvement. Preston et al. [84] report a maximum in print gloss after roughly 50 s and thereafter gloss decreases slightly. This is explained by an increased roughness in the ink film which could be due to protruding ink pigments as a result of surface resin depletion.

Figure 14 may serve as an example of data showing the gloss development due to ink filament levelling [84]. All coatings were calendered to the same paper gloss (74% at Tappi 75°) but showed different porosities and pore sizes, which resulted in the papers having different setting rates. The setting rated decreased in the order PCC = fine US kaolin > narrow PSD US kaolin > UK kaolin. The print gloss development increased in roughly the same order, i.e. PCC < fine US kaolin < narrow PSD US kaolin.



Figure 14 Print gloss development with time for coatings with different pore structure and setting rates but the same paper gloss [84].

Although ink levelling has an impact on print gloss in general, the strongest effect is found for glossy-coated papers with low macro roughness [21] since the roughness induced by interrupted ink filament levelling is in the macro or sub-macro range. For papers with a significant macro roughness (e.g. matt-coated) the roughening by poor levelling may be swamped by the coating macro roughness. The levelling theory [71] also predicts that the ink flows to low regions of the substrate, thus reducing the macro roughness. Figure 5b (matt-coated) also suggests that the ink film thickness is higher in the lower regions of the coating.

Arai and Nojima [86] showed for cast-coated paper that print gloss was strongly reduced by a fast ink setting during the first minute. They also found that a lower fraction of surface pores promoted print gloss.

Donigian et al. [69] reported a laboratory study of PCC-clay (50:50) coated and supercalendered papers with sheet gloss between 65 and 70 %. They clearly demonstrated the decrease in print gloss with increasing ink setting rate, characterized as the P&I slope. The results, shown in Figure 15 also show an increase in print gloss with ink amount, as expected. The decrease in print gloss due to fast ink setting has also been demonstrated after full scale printing [8] although one may expect the effect to be less pronounced in full scale printing where the ink is transferred in several nips, and thus the fila-



Figure 15 Heat set printed gloss vs. ink setting rate given as P&I slope for coatings containing 14–19 parts binder at different ink amounts [69].

ments are expected to be smaller since the filament length decreases with decreasing ink film thickness [77, 80] and the content of emulsified water [74].

Resent research in this area suggests that for a print on a coated paper/ board we may consider:

- The coating roughness and how well this is smoothed by the ink layer.
- The structure formed by the ink layer itself. Examples are micro cracks in the ink film, wax particles used to reduce smearing and pigment particles.
- The structure formed in the ink layer, but caused by the ink-paper interaction. Insufficient ink levelling due to fast ink setting as discussed above is probably the most important phenomena, but protrusion of solid ink constituents (wax particles, pigments, fillers) due to poor ink vehicle hold out is also a phenomena to consider [21].
- The refractive index of the ink layer [21].

The importance of ink layer smoothness for development of print gloss was discussed 40 years ago by Fetsko and Zettlemoyer [87]. They pointed out the importance of ink film thickness and the holdout of the vehicle. Oittinen [88] discussed print gloss in terms of micro and macro roughness. A recent report on the effect of coating topography [16] on print gloss after full scale printing suggests that the micro roughness but not the macro roughness is completely covered by ink at high ink amounts. The micro roughness of an unprinted



Figure 16 AFM image of a pilot coated paper (left) and a print (400% area) of the same paper (right). Image size is $5 \times 5 \ (\mu m)^2$, which means that micro scale topography is shown [16].

and printed coated fine paper can be visualized from the AFM micrographs shown in Figure 16. It is clear that the topography formed by the coating pigment (micro roughness) is completely covered by the ink. The surface of the print is, not, however, mirror-smooth, and a texture appears which may be regarded as the micro roughness of the ink film itself.

Since the coating micro roughness is completely covered by the ink at high inking levels it has little influence on print gloss. Instead the print gloss will be strongly influenced by the coating macro roughness. Figure 17 shows a plot of print gloss vs. PPS, which is a good measure of macro roughness. The printed surfaces all carried four full tone layers (i.e. 400%). A good correlation between print gloss and coating macro roughness is seen for these heavily inked surfaces. At low inking levels the micro roughness may not be completely covered and thus influence print gloss [16].

The effect of ink film thickness on print gloss has also been demonstrated by several research groups [87, 89] using laboratory printing equipment. Often an optimum in print gloss is found for a certain ink film thickness. The optimum is most likely a result of two competing phenomena: filling up the micro structure of the coating which dominates at low inking level and increasing the macro roughness caused by insufficient ink levelling which dominates at high ink level. The size of the filaments increases with ink film thickness [77, 80] and thus also their detrimental effect on print gloss.



Figure 17 Correlation between print gloss (400% area) and the PPS roughness of unprinted papers for pilot coated (B and C) and commercially made graphic papers (A) [16].

Print mottle

Xiang et al. [28] measured local variation in ink setting using a 1.1 mm probe and found a good correlation between the coefficient of variation in ink setting and back trap mottle. The papers used were pilot coated and soft calendered. The correlation was less good when a larger probe (2.2 mm) was used. Results are given in Figure 18.

Xiang and Bousfield [53] showed in laboratory coating that the coating pore volume was lower for coatings with high coat weight compared to low coat weight. The coating with high coat weight also showed slower ink setting, which is expected due to the lower porosity. The print density after one nip was the same for both papers showing that ink transfer was the same. When the two prints were subjected to a second nip without ink, the densities decreased due to back trapping. The reduction was much higher for the paper with high coat weight, which also showed slow ink setting due to low porosity. They also used commercial manufactured papers and observed variation in



Figure 18 A comparison between back trap mottle ranking and local variation (i.e. coefficient of variation) of ink setting, measured with a 1.1 mm probe and expressed as first tack force (solid) and ink tack slope (open) [28].

print density. Low print density areas were found on areas with high coat weight. The importance of coat weight variation for back trap mottle has also been indicated by Engström [90]. A strong evidence of the coat weight effect on print mottle is shown in Figure 19 which is unpublished data by Sävborg



Figure 19 Relation between coating thickness variation (from direct measurement of coating thickness in cross section of the coated paper) and halftone mottling [91].

and Wigge at Stora Enso in Falun, Sweden. The work was recently presented by Kolseth [91].

It is generally understood that print mottle is more severe for a glossycoated paper than for a matt coated and that calendering may evoke mottling tendency. Several authors [6, 7] have pointed out that calendering causes areas with low almost closed porosity. Chinga and Helle [92] recently developed an analytical procedure based on scanning electron microscopy (back scattering mode) and advanced image analysis to quantify the fraction of closed area in a rectangular area of 0.4×0.5 mm. By measuring 20 individual images for each paper the mean value of the closed area fraction as well as the standard deviation were calculated. A good correlation between mottling and closed area variation (standard deviation) was found when the area considered was large enough. Results are shown in Figure 20 for areas>8000 $(\mu m)^2$. The correlation decreased with decreasing area and was insignificant for areas<3000 (µm)². No correlation was found between mottling and the mean value of closed area fraction. Such a correlation was however found by Xiang et al. [56] for a set of pilot coated paper. Variation in closed area was not reported. The only difference between the papers was the drying conditions. Base stock, coating composition, coat weight and soft nip calendering were the same. PPS values and paper gloss (75°) were 1.20-1.35 μ m and 60–68%, respectively. These papers also showed local variation in ink setting rate as shown in Figure 18.

The effect of ink-paper interaction on back trap mottle is thus quite well established. The reason is local variation in setting rate which gives local variation in ink immobilisation and thus local variation in ink amount lifted



Figure 20 Left: Relation between variation in closed area and mottling. Closed area $<8000 \ (\mu m)^2$ are not considered. Right: Correlation coefficients for the linear relations between mottling and closed area variation for closed areas larger than a ertain area [92].

off from the print in subsequent printing nips. A common reason for the local variation in ink setting rate is local variation in coating structure, which in turn may be due to local variation in coat weight and/or induced by calendering. The effect of latex binder, local variation in binder content and binder migration is less well established although there are data in the literature indicating that a variation in latex distribution induces print mottle [90] Binder migration was probably more important in the past when starch frequently was used as binder in the top coat. In those days mottle was also a much more severe problem that today. In a pilot coating trial Engström et al. [93] used a mixture of latex and starch in combination with clay and showed the effect of drying conditions on binder migration and its impact on print mottle. The binder migration, most likely the low molar mass starch was characterized by ESCA

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REFERENCES

- 1. Kipphan, H. Handbook of print media Technologies and production methods ISBN 3–540–67326–1 Springer-Verlag Berlin Heidelberg New York, 2001.
- 2. Nutbeem, C., Husband, J., C. and Preston, J., S. The role of pigments in controlling coating structure. In proc. *PITA 2005 Coating Conference*, 2005.
- 3. Karathanasis, M. and Ström, G., R. To be published.
- Hiorns, A., G., Elton, N., J., Coggon, L. and Parsons, D., J. Analysis of differences in coating structure induced through variable calandering conditions. In proc. *Tappi 1998 Coating/papermakers Conference*. pp. 583–602, Atlanta, GA, Tappi Press, 1998.
- Elton, N., J. and Preston, J., S. Reflectometry and polarized light for studies of paper coating structure. In proc *Tappi 2005 Coating Conference*. Tappi Press, Atlanta, GA, 2005.
- Whalen-Shaw, M. and Eby, T. An investigation of factors related to back trap mottle in coated papers using electron probe micro analysis. In proc. *Tappi 1991 Coating Conference Proceedings*, pp. 401–409, Tappi Press, Atlanta, GA, 1991.
- 7. Allem, R. Characterization of paper coatings by scanning electron microscopy. *JPPS* **24**(10): 329, 1998.
- 8. Karathanasis, M., Carne, T., Dahlvik, P. Haugwitz, B. and Ström, G. Importance

of coating structure for sheet-fed offset print quality. *Wochenblatt für papierfabrikation* **7**:426–432, 2001.

- 9. Todd, R. E. Printing inks Formulation principles, manufacture and quality control testing procedures, Pira International, Leatherhead, Surrey, UK, ISBN 1 85802 027 1, 1994.
- Kurts, W. Organic pigments for printing inks. *American Ink Maker* 64:12, 20–42, 1986.
- 11. Szalkowski, N. The importance of understanding solubility and compatibility parameters of resins", *American Ink Maker*, October, 43–46, 1997.
- 12. Sarnecki, G. and Szarbo, B. Resin solubility in 3-D: Using cloud points and Hansen solubility parameters to better understand a litho resin's interaction with solvent. *American Ink Maker*, March, 36–41, 2001.
- Pavlin, M., S. And West, J., C. Highly elastic lithographic ink resins. *American Ink* Maker, March, 58–64, 1998.
- 14. Flink E., W. **Printing ink formulations**, ISBN 0-815-1014-4, Noyes Publications, Park Ridge, New Jersy, 1985.
- Ström, G., R., Sjölin, K. and Gustafsson, J. Separation of ink constituents during ink setting on coated substrates. In proc. *Tappi 2000 International Printing and Graphic Arts Conference*, pp. 89–100, Tappi Press, Atlanta, GA, 2000.
- Ström, G., Englund, A. and Karathanasis, M. Importance of coating structure on print gloss after sheet-fed offset printing. *Nord Pulp Pap Res J* 18: 108–115, 2003.
- MacPhee, J. and Lind, J. Measurements of ink film thickness printed by the litho process. In proc. *TAGA 1991 Printing and Graphic Arts Conference*, pp. 550–573, 1991.
- Granat, L. Method for determination of thickness distribution of the ink film for offset printed coated papers. Master of Science Thesis, KTH, Department of Pulp and Paper Chemistry and Technology, 2002 (in Swedish).
- Ström, G. and Gustafsson, J. Ink drying in sheet-fed offset printing-Effect of temperature. In proc. 2004 International Printing and Graphic Arts Conference, pp. 35–41, 2004.
- Lee, D. I. The critical pigment to volume concentration concept for paper coatings: I. Model coating systems using plastic pigments and latex binders for paper coating applications. In proc. *Tappi 1998 Coating/papermakers Conference*, pp. 311–335, Tappi Press, Atlanta, GA, 1998.
- 21. Preston, J., Nutbeem, C., Parsons, J. and Jones, A. The printability of coated papers with controlled microstructure. *Paper Technology* **42**(2):33–41, 2001.
- 22. Preston, J., S., Elton, N., J., Legrix, A. and Nutbeem, C., The role of pore density in the setting of offset printing ink on coated paper. In proc. *Tappi 2001 Advanced Coating Fundamentals Symposium*, pp. 21–48, San Diego, CA, USA, 2001.
- Rousu, S. Differential absorption of offset ink constituents on coated paper. Dissertation, Åbo Akademi University, Laboratory of Paper Chemistry, Faculty of Chemical Engineering, ISBN 952–12–0944–5, 2002.
- Gane, P. and Seyler, E. Tack development: an analysis of ink/paper interaction in offset printing. In proc. *Tappi 1994 Coating Conference*, pp 243, Tappi Press, Atlanta, GA, 1994.

- 25. Concannon, P., W. and Wilson, L., A. A method for measuring tack build of offset printing inks on coated paper. In proc. *TAGA 1992 Printing and Graphic Arts Conference*, pp.282–301, 1992.
- Plowman, N. Ink tack part 3: surface measurements. *Graphic Arts Monthly* 61(6):114, 1989 and Ink tack part 4: Blanket release forces. *Graphic Arts Monthly* 61(8):133, 1989.
- Smith, D., A., Desjumaux, D., Kessler, H., H., Nicholas, N., R., Sharman, S. and Wright, A. Operational principles and sensitivity of an instrument designed to measure and explore offset ink tack dynamics, substrate failure and ink transfer mechanisms. In proc. *Tappi 2004 International Printing and Graphic Arts Conference*, pp 103–115, Tappi Press, Atlanta, GA, 2004.
- Xiang, Y., Bousfield, D., W., Hassler, P., Coleman, P. and Osgood, A. Measurement of local variation of ink tack dynamics. *JPPS* 25(9):326–330, 1999.
- 29. Rousu, S., Gane, P. and Eklund, D. Distribution of offset ink constituents in paper coatings and implications for print quality. In proc. *Tappi 2003 Advanced Coating Fundamentals Symposium*, Chicago, II, USA, 2003.
- Schoelkopf, J., Gane, P., A., C., Ridgway, C., J., Spielmann, D., C. and Matthews, G. P. Rate of vehicle removal from offset inks: a gravimetric determination of the imbibition behaviour of pigmented coating structures. In proc. *Tappi 2001 Advanced Coating Fundamentals Symposium* pp. 1–18, San Diego, CA, USA, 2001.
- Rousu, S., M., Gane, P., A., C., Spielmann, D., C. and Eklund, D., E. Differential absorption of offset ink components on coated paper. In proc. *Tappi 2000 International Printing and Graphic Arts Conference*, pp. 55–70, Tappi Press, Atlanta, GA, 2000.
- Johansson, K., Ström, G. Stenius, P. Sorption of alkyd resin on cellulose. In proc. Tenth Cellulose Conference on Cellulose and Wood – Chemistry and Technology, pp. 1473–1496, Syracuse, USA, May–June, 1988.
- Johansson, K., Ström, G. and Stenius, P. The interaction between alkyd resin binders and kaolinite. *Colloids Surfaces* 56:313–338, 1991.
- Wickman M. Surface chemical behaviour of alkyd resins in offset printing inks. Dissertation, Department of Pulp and Paper Technology, KTH, Stockholm, 1998, TRITA-PMT 1998:7.
- Wickman, M., Beadle, A., Sebring, T., Gurrera, L. and Larsson, A. The effect of alkyd resin composition on the adsorption on calcium carbonate", *NPPRJ* 9(2):94–100, 1994.
- Preston, J., S, Elton, N., J., Husband, J., C., Heard, P., J. and Allen, G., C. SIMS analysis of printed paper surfaces to determine distribution of ink components after printing. In proc. *Tappi 2000 International Printing and Graphic Arts Conference*, pp. 101–120, Tappi Press, Atlanta, GA, 2000.
- Dalton, J. S., Preston, J., S., Heard, P., J., Allen, G., C., Elton, N., J. and Husband, J., C. Investigation into the distribution of ink components throughout printed coated paper. Part 2: Utilising XPS and SIMS. *Colloid and Surfaces A* 205:199– 213, 2002.
- 38. Mattila, U., Tahkola, K., Nieminen, S. and Kleen, M. Penetration and separation

of coldset ink resin and oils in uncoated paper studied by chromatographic methods. *NPPJ* **18**:4:413–420, 2003.

- 39. Gregersen, Ö., W., Johnsen, P.,O. And Helle, T. Small-scale topographic variations of newsprint surface and their effects on printing ink transfer distribution. *J. Pulp and Paper Sci.* 21(10):J331, 1995.
- 40. Heard, P., J., Preston, J., S., Parsons, D., J., Cox, J. and Allen, G., C. Visualization of distribution of ink components in printed coated paper using focused ion beam techniques. *Colloids and Surfaces A: Physicochem. Eng. Aspects* **244**:67–71, 2004.
- 41. Uchimura, H, Ozaki, Y., Maruyama, S. and Sawatari, A. Observation of printing ink transference to and penetration into the paper: Application of the cross-section preparation method using a focused ion beam. In proc. *11th International Printing and Graphic Arts Conference*, Bordeaux Lac, France, 2002.
- 42. Rousu, S., Gustafsson, J., Preston, J. and Heard, P. Interactions between UV curing, hybrid-UV and sheetfed offset inks and coated paper-commercial print trials. In proc. *TAGA 2005 Printing and Graphic Arts Conference*, p 107, Toronto, Canada, 2005.
- 43. Kelly, J., M., Russell, P., J. and Graham, H., F. Forestall ink-setting problems on coated papers. *Pulp and Paper Canada* 76(1):T8–T11, 1975.
- 44. Karathanasis, M. and Fogden, A. The concept of critical ink setting time and its relation to print gloss Influence of latex binder. *NPPJ* 19(2):145–149, 2003.
- 45. Xiang, Y. and Bousfield, D., W. Influence of coating structure on ink tack dynamics. *JPPS* 26(6):221–227, 2000.
- Triantafillopoulos, N. and Lee, D. Coated paper and offset ink interactions. In proc. *Tappi 1996 International Printing and Graphic Arts Conference*, pp. 97–110, Tappi Press, Atlanta, GA, 1997.
- 47. Van Gilder, R., L. and Purfeest, R. D. Latex binder modification to reduce coating pick on six-color offset presses. *Tappi J*, 77(5):230–239, 1994.
- 48. Kan, C., S. and Van Gilder, R., L. Measurement of latex surface energy and role in paper coating applications. In proc. *Tappi 2004 Coating Conference*, 2004.
- Fouchet, B., Noirot, P.-A., Desjumaux, D. and Van Gilder, R. L. Diffusion dynamics of offset ink components in very thin latex films of different structure and composition. In proc. *Tappi 2004 International Printing and Graphic Arts Conference*, pp. 43–58, Tappi Press, Atlanta, GA, 2004.
- Van Gilder, R., L. and Smith, D., A. Development of a high polarity latex polymer for waterless sheet fed offset paper coatings. *Paper Technology*, March 2001, p. 50–56, 2001.
- Rousu, S., Gane, P., Spielmann, D. and Eklund, D. Separation of off-set ink components during absorption into pigment coating structures. *NPPJ* 15:527– 535, 2000.
- 52. Xiang, Y., Bousfield, D., W., Haynes, P., C., Kettle, J. and Hultgren, L. Effect of latex swelling on ink tack build and ink gloss dynamics of coatings. *Tappi 2000 International Printing and Graphic Arts Conference*, pp.139–151, Tappi Press, Atlanta, GA, 2000.
- 53. Xiang, Y. and Bousfield, D., W. The influence of ink-coating interaction on final print density in multicolour offset printing. In proc. *Tappi 2000 International*

Printing and Graphic Arts Conference, pp. 299–309, Tappi Press, Atlanta, GA, 2000.

- Gane, P. A., C., Schoelkopf, J., Spielmann, D., C., Matthews, G., P. and Ridgway, C., J. Fluid transport into porous coating structures: Some novel findings. *Tappi J.* 83:(5):77–78, 2000.
- 55. Lundqvist, Å. And Ödberg, L. Surface energy characterization of pigment coatings by inverse gas chromatography. *JPPS* 23(6):J298, 1997.
- Xiang, Y., Bousfield, D., W., Coleman, P. and Osgood, A. The cause of back trap mottle: chemical or physical. In proc. *Tappi 2000 Coating Conference and Trade Fair*, pp. 45–58, Tappi Press, Atlanta, GA, 2000.
- 57. Xiang, Y. and Bousfield, D., W. The influence of coating structure on ink tack development. In proc. *TAPPI 1998 International Printing and Graphic Arts Conference*, pp. 93–101, Tappi Press, Atlanta, GA, 1998.
- 58. Xiang, Y., Bousfield, D., W., Haynes, P., C. and Kettle, J. A model to predict inksetting rates based on pore-size distribution. *JPPS* 30(5):117–120, 2004.
- Bristow, J., A. and Bergenblad, H. Paper structure and ink-setting: factors influencing the set-off test. In Advances in Printing Sci. and Techn. Vol 21 (Ed. W. H. Banks) Pentech Press Ltd, 1992.
- Schoelkopf, J. and Gane, P., A., C The moment ink contacts the surface: A fresh look at the absorption dynamic into coated papers. *Das Papier* 2004:T26–T32, 2004.
- 61. Voltair, J. and Fogden, A. Modelling setting and tack of a sheet-fed offset ink printed on a coated paper. In proc. *11th International Printing and Graphic Arts Conference,* Bordeaux Lac, France, 2002.
- 62. Schoelkopf, J., Gane, P. A. C., Ridgway, C., J. Matthews, G., P. Influence of inertia on liquid absorption into paper coating structures. *NPRJ* **15**:422–430, 2000.
- MacGregor, M., Johansson, P.-Å. and Béland, M.-C. Measurement of small-scale variation in printed paper. – Paper topography explains much of the variation. In proc. *Tappi 1994 International Printing and Graphic Arts Conference* pp. 33–43, Tappi Press, Atlanta, GA, 1994.
- Beland, M.-C., Lindberg, S. and Johansson, P.-Å. Optical measurement and perception of gloss quality of printed matte-coated papers. *Journal of Pulp and Paper Science* 26(3):120–123, 2000.
- 65. Pauler, N. Paper optics. AB Lorentzen & Wettre, Kista, Sweden ISBN: 91–971 765–6–7, 1993.
- 66. Hunter, R., S. Methods of determining gloss. *American society for testing and materials (ASTM) Proceedings*, 1936, 30, part II: 738–806, 1936.
- 67. Gate, L., F., Windle, W. and Hine, M. The relationship between gloss and micro-texture of coatings. *Tappi J.* 56:61–64, 1973.
- Gate, L., F. and Leaity, K. New aspects on the gloss of coated paper. In proc. *Tappi 1991 Coating Conference*. pp 473–481, Tappi Press, Atlanta, GA. 1991.
- 69. Donigian, D., W., Ishley, J., N. and Wise, K., J. Coating pore structure and offset printed gloss. *Tappi J* 80(5): 165–172, 1997.
- 70. Preston, J., Daun, M., Nutbeem, C. and Jones, A. Attaining print performance through pigment engineering. *Wochenblatt für Papierfabrikation* 5:252–265, 2000.

- Glatter, T. and Bousfield, D., W. Print gloss development on a model substrate. *Tappi J*, 80(7):125–132, 1997.
- 72. Kheshgi, H. S. and Scriven, L. E. Chem. Eng. Sci. 43(4):793, 1988.
- 73. Desjumaux, D., M. and Bousfield, D., M. Modeling of ink film levelling with mobile phase removal. In proc. *Tappi 1998 International Printing and Graphic Arts Conference*, pp. 103–109, Tappi Press, Atlanta, GA, 1998.
- 74. Hayashi, T. and Amari, T. Dynamics of transfer and splitting of emulsified ink. In proc. *Tappi 1992 International Printing and Graphic Arts Conference* p. 75, Tappi Press, Atlanta, GA, 1992.
- 75. Myres, R., R., Miller, J., C. and Zettlemoyer, A., C. The splitting of thin liquid films, kinematics. *J Colloid Sci.* 14:287, 1958.
- 76. Taylor, JR., J., H. and Zettlemoyer, A., C. Hypothesis on the mechanism of ink splitting during printing. *Tappi J* 41(12):749, 1958.
- 77. De Grâce, J., H., Dalphond, J., E. and Mangin, P. J. A mechanistic approach to ink transfer, part III: Properties of ink filaments in printing nips. *Advances in Printing Science and Technology*, **21**:312, 1992.
- MacPhee, J. A unified view of the film splitting process, part II. American Ink Maker, February, 51–56, 1997.
- Ercan, S. N and Bousfield, D., W. Influence of process parameters on filament size distribution. In proc. *Tappi 1998 International Printing and Graphic Arts Conference*, pp. 111–115, Tappi Press, Atlanta, GA, 1998.
- Ercan, S. N and Bousfield, D., W. Influence of fluid rheology on filament size. In proc. *Tappi 2000 International Printing and Graphic Arts Conference*, pp. 121–132, Tappi Press, Atlanta, GA, 2000.
- Nguyen, N., Jordan, B. And De Grâce, J. Measurement of ink filament splitting patterns by image analysis. In proc. *Tappi 1992 International Printing and Graphic Arts Conference* pp. 81–85, Tappi Press, Atlanta, GA, 1992.
- Desjumaux, D., M., Bousfield, D., W., Glatter, T., P. and Van Gilder, R., L. Dynamics of ink gloss influence of latex type over a range of pigment volume concentration. In proc. *Tappi 1998 Coating & Papermaking Conference*, pp. 875– 894, Tappi Press, Atlanta, GA, 1998.
- Xiang, Y, Desjumaux, D., Bousfield, D. and Forbes, M., F. The relationship between coating layer composition, ink setting rate, and offset print gloss. In proc. *Tappi 1998 International Printing and Graphic Arts Conference*, pp. 85–91, Tappi Press, Atlanta, GA, 1998.
- Preston, J., S., Parsons, D., J., Husband, J., C. and Nutbeem, C. Ink gloss development mechanisms at short time-scales after printing, Part 2 – The influence of substrate. In proc. *Tappi 2003 Advanced Coating Fundamentals Symposium*, Chicago, II, USA. 2003.
- Enomae, T., Teramoto, M., Onabe, F., Hayano, S., Naito, H., Takano, K. and Kamada, K. Mechanisms of print gloss development. In proc. *Tappi 2000 International Printing and Graphic Arts Conference*, pp. 1–8, Tappi Press, Atlanta, GA, 2000.
- Arai, Y. and Nojima, K. Coating structure for obtaining high print gloss. *Tappi J.* 81(5):213–221, 1998.

- Fetsko, J., M. And Zettlemoyer, A., C. Factors affecting print gloss and uniformity. *Tappi J.* 8:667–680, 1962.
- 88. Oittinen, P. The limits of gloss in print. Paperi ja Puu 11:718–724, 1983 or Adv. Print. Sci. and Technol. 15:344, 1980.
- Zang, Y., H. And Aspler, J., S. The influence of coating structure on ink receptivity and print gloss of model clay coatings. *Tappi J.* 78(1):147–154, 1995.
- Engström, G., Rigdahl, M., Kline, J and Ahlros, J. Binder distribution and mass distribution of the coating layer – cause and consequence. *Tappi J*, 74(5):171–179, 1991.
- 91. Kolseth, P. Coating structure and print quality. Paper presented at *New Concepts in Paper Surface Treatment*, Stockholm, October 19–20, 2004.
- 92. Chinga, G. and Helle, T. Relationship between the coating surface structural variation and print quality. *JPPS* 29(6):179–184, 2003.
- 93. Engström, G., Ström, G. And Nordahl, P. Studies of the drying process and its effect on binder migration and offset mottle. *Tappi J.* 70(12):45–49, 1987.

Transcription of Discussion

INTERACTION BETWEEN OFFSET INK AND COATED PAPER – A REVIEW OF THE PRESENT UNDERSTANDING

Göran Ström

STFI-Packforsk and Royal Institute of Technology (KTH), Stockholm, Sweden

Harshad Pande Domtar Inc

How important is the role of base-sheet properties like formation and porosity in this?

Göran Ström

The properties of the base sheet are very important since they influence the structure of the coating. For instance, a rough base with poor formation will give a coating layer with strong variations in coat weight and this also affects the structure of the coating layer. Also if you have rough paper and then calender it hard you will close up the pore structure which will have a big effect on the coating.

Bob Pelton McMaster University

Nice presentation. I do not work in this area and I was just sitting here and thinking of what I could do. So, what are the big unresolved issues? What are the big research opportunities?

Göran Ström

Although we have learnt quite a lot during the last 10 years there are still may

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unresolved issues. The mechanism for ink setting is still not known in detail, for instance, the role of capillarity compared to latex swelling. An important problem for the printing industry is ink scuffing which takes place in the bookbindery. It is a transfer of ink from a printed image to an unprinted area of an adjacent sheet of paper. Then we have print quality issues like ghosting and mottling.

Christian Schmid Hewlett-Packard

You had a chart that showed oil content in the ink film versus time. Could you explain how that was done?

Göran Ström

Yes, we printed the paper in a laboratory printing press and then scraped off the ink film at different times after printing. We then analysed, using gas chromatography and gel permeation chromatography, the content of oil in this scraped-off ink.

Christian Schmid

One comment on Bob's question about what research is left to be done. I think one area that would be really exciting from my point of view is applying some of the neat imaging techniques to actually looking at the ink coating itself. You know we saw a lot earlier today about imaging the paper structure. I think that would be an exciting area for somebody in the ink field.

Lars Wågberg KTH

Thank you for a very nice presentation and good survey. I share your interest in ink setting. If I understood one of your graphs correctly, you showed that ink setting is faster with smaller pores. How do you look upon that process? Is it dewatering, or more correctly, de-oiling of a gel, or something else?

Göran Ström

It is a complex capillary absorption, because the oil is sucked out from an ink film which contains many components. There are at least three different mechanisms or three different processes that play major roles here. The oil can go into the pores due to capillary suction, it can diffuse into the latex, but it can also dilute the ink binder.

Lars Wågberg

But if it was capillary absorption the larger pores would give faster ink setting.

Göran Ström

Considering the Lucas-Washburn equation this is what one would expect. But for this complex absorption process we find that smaller pores give faster ink setting. One possible explanation for this is that inertia is very important and the Lucas-Washburn equation does not account for this. Another is that ink oil is the solvent for the binder and thus has a lower chemical potential in the ink binder on top of the coating than in the pores where it is located as a more or less pure oil.

Wolfgang Bauer Graz University of Technology

I think you mentioned that the amount of oil is very small compared to the amount of coating we have on the paper. So now when we talk about the coating thickness distribution, can it really have an influence on mottling? I think it is more a question of surface porosity and surrounding air.

Göran Ström

Yes, for many paper grades the coating layer is quite thick and the oil will not go through the whole coating, but if there is variation in coating thickness there will be variation in coating structure and this is important, since variation in coating structure may induce print mottle.

Richard Bown IMERYS Minerals Ltd

My comment is rather related to that last question, and to Prof. Wågberg's question. There is a very small amount of ink and the oil is only going into the very top surface of the paper, in fact it may just fill the surface voids of the paper. The number of pores in the surface is just as important as the size of the pores which is something that Janet Preston came across in the work she was doing and reported in her PhD thesis.

Joseph Aspler PAPRICAN

Very nice review. I am surprised you never mentioned filter cake formation

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with the ink pigment. Do you feel that the filter cake would affect the drainage of the oil and the binder into the coating layer?

Göran Ström

I did not mention this because I do not believe that a filter cake will be formed. In order to form a filter cake the pigment particles must touch each other but the content of binder is high and prevents this. Instead a gel phase will be formed and this gel phase is filled with pigment. However, the penetration of ink oil through such a gel phase is mathematically very similar to the penetration of oil through a filter cake.