# INFLUENCE OF LATEX – OIL INTERACTIONS ON OFFSET INK SETTING AND COMPONENT DISTRIBUTION ON COATED PAPER

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## SUMMARY

The objective in this work was to reveal the causes of the specific diffusional and wetting interactions between absorbing offset ink oils and the coating latex distributed within the porous network of mineral pigment on coated paper. The significance of these interactions on the ink setting dynamic, in combination with the pre-definable effects of porous media absorption, was studied.

It is mainly the bulk properties of latex and ink oil that contribute to the observable differences in the ink setting dynamics rather than surface chemical wetting differences or changes in porous structure related to the inclusion of latex. It can be generalised that low latex solubility parameter (butadiene < styrene = acrylate < acrylonitrile) leads to greater oil interaction. Furthermore, latices with low Tg and gel-% show increased interactivity with ink oils. High oil solubility parameter, resulting from reactive groups in vegetable oils and aromaticity in mineral oils, causes greater latex affinity.

The diffusional interaction between ink oil and coating latex may in some cases affect ink setting rate as strongly as the capillary-driven absorption within the coating pore structure. Additionally, oil viscosity influences the dynamics of diffusion within the polymer network. However, the relative importance of the diffusional effect depends on the time-frame set by the capillary forces. The dynamic nature of the latex-oil interaction is more important in practical ink-paper contact than the volume of equilibrium uptake of oil by a cured latex film.

Keywords: Coating – ink interactions, chromatography in porous structures, differential absorption, printing, offset ink tack, ink absorption, coating structure, fluid separation, offset inks, porous structure, coated paper.

## Introduction

With the increasing use of pigment coated paper, and with offset printing remaining the major printing practice, the fundamental understanding of the interactions between offset inks and coated paper is essential in order to maintain and to further improve the attractiveness of printed media. Support of high quality print, short and flexible delivery with minimal environmental impact and maximum profit are continual challenges for both the paper and ink suppliers to the graphic industry. Furthermore, variable data digital printing has brought new competition, and, more importantly, new opportunities for the development of conventional printing methods and its consumables. For example, combining different printing methods, like offset printing and digital personalisation, in one run has become a viable option for expanding the graphical industry end-use range. These opportunities further stress the importance for detailed comprehension of the chemical processes behind ink-paper interactive systems. Ink-coating interactions have significance right from the initial ink transfer from the printing plate onto the blanket, and from there offset onto the paper surface, during ink drying via penetration of ink components into paper as well as in the long term stability of the ink on the paper surface (adhesion). The main driving forces for these essentially thermodynamic interactions are the capillary forces and chemical diffusion gradients. During initial ink drying, capillary pressure is acknowledged to be the main driving force in offset ink oil transport in a typical paper coating porous structure /1,2/. With increased latex content, diffusion-driven transport of ink chemicals into the latex counterpart of the coating layer becomes important /3-5/. In addition to the presence of many time and concentration dependent phenomena, the interaction process is complicated by the complex nature of the dynamically changing multi-phase ink film /1,6/.

This work is part of a larger project aiming at clarifying mechanisms behind the phase separation of offset ink constituents in contact with coated paper /7/. Here we concentrate on the coating latex and ink oil interactions. The objective is to reveal the main causes and mechanisms for these interactions, from both the coating latex and ink perspectives, by using well-defined chemicals and investigative methods. The importance of the latex-oil affinity is then related to preferential absorption of particular ink oils into paper coatings containing certain latices in the realistic dimensions and time-frame of ink-coating contact.

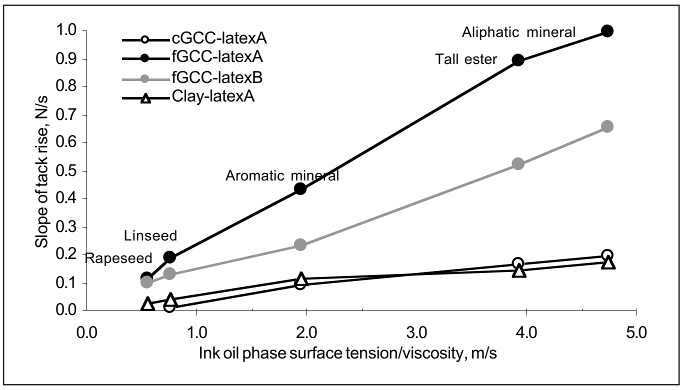
## Background

### *Chromatographic separation of ink constituents*

Optimally, ink pigment and resins are retained at the paper surface while the oil-based mobile phase is absorbed in a controlled way into the porous coating structure. Despite the many advances taken in understanding ink-coating interactions, and the absorption mechanisms during printing, the contribution of the ink properties has often been overlooked. Reference is typically made only to the absorption of low viscous mineral oils, even though modern inks are based on high proportions of vegetable oils /8/. Furthermore, the distribution character of the multi-component ink components has long been acknowledged to be important, but has only gained attention in fundamental studies during recent years /7,9,10/.

The pigments and resins have been verified, at least for the most part, to be size-excluded and/or chemically retained at the coating surface. From the ink perspective, the properties of the ink oil phase (surface tension/viscosity ratio) thus determine the rate of absorption and interaction with the coating layer (figure 1) /7/. Absorption kinetics in a given porous structure are primarily affected by oil viscosity, which may vary widely between 1 and 60 mPas for different mineral and vegetable oils. Enhanced chemical compatibility between the ink resins and oils may inhibit the rate at which the oil initially releases from the ink, but this effect is small in relation to the other gradients that force the ink oil to separate and penetrate into the paper coating layer.

Fig. 1 The rate of ink oil phase absorption (from ISIT , see experimental) into coated paper is determined by the surface tension/viscosity ratio of the ink oil-phase. 5 test inks are based on the oils as marked; 4 coatings based on coarse and fine ground calcium carbonate (cGCC, fGCC) and fine clay, each containing 10 pph of commercial styrene-butadiene latex A or B /7/.



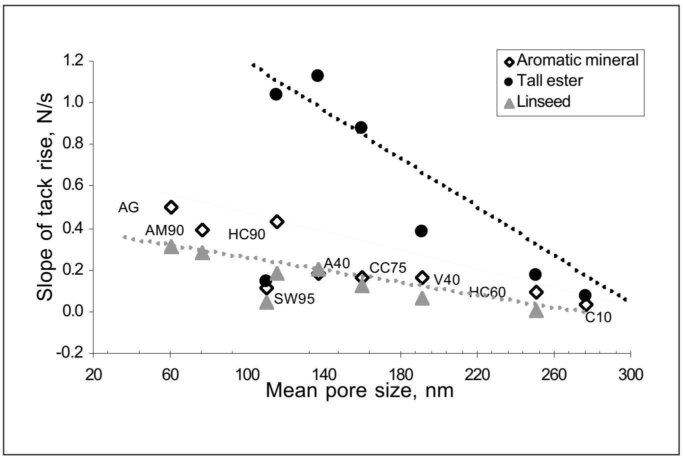
Inks often contain a mixture of practically non-polar mineral oils and slightly polar vegetable oils. Coating pigments have been shown to cause adsorption chromatographic separation of these chemically different oils during their absorption into the coating layer /11/. The hydrophilic dispersed coating pigment surface performs as a site for adsorption and thereby retardation of the polar components, i.e. vegetable oils and, on occasion, ink resins, allowing the non-polar mineral oil species to absorb further into the structure. In practical cases with fine coating structures, the oil separation from resins showed to be complete and the chromatographic separation of the individual oils did not observably influence the ink setting rate. However, the differential distribution of the ink oils in a coating was shown to influence the final print gloss and density /7/.

### *Capillary absorption in ink setting*

In coated paper grades, where coating coverage is good, the pressure conditions and inertial effects exerted on the offset blanket, ink and coating layers, as well as the fine pore size of the coated paper surface, prevent pressure-driven penetration of ink constituents within the printing nip /12,13/. Absorption is thus driven by thermodynamic interactions between ink and the coating layer and by capillary forces after the nip. Capillary-driven transport is considered to be the major driving force for ink setting and has been the main research focus over the years.

Pore size, total available pore volume, as well as, for example, tortuosity, are the major coating porous structure variables affecting ink setting. In all practical cases of ink – coated paper interaction, smaller pores are found to result in faster ink setting /9,10,14-16/, as shown in figure 2 /7/. Recent advances in the area include the adoption of the inertial flow mechanism to explain the rate dependency of the short time-scale absorption in small capillaries like those of the coating layer pores /2/. Also, the formation of a continually viscosifying sheet fed offset ink layer rather than a filtercake formation has been demonstrated /1/. These findings have enabled the understanding of the formation of "preferential pathways" in the coating, which means that the porous structure is not saturated by the liquid along the absorption line but the smaller capillaries are preferentially filled first. This has been shown to be the case particularly when the pore shape is of low aspect ratio /17/.

Fig. 2 Absorption rate of oil from an ink layer into a coating structure (ISIT tack rise rate, see experimental) is inversely proportional to coating pore size. Different pore sizes are accomplished with different types of clay and $CaCO_3$ pigments at 10 pph latex addition level /7/.



### *Latex-oil interaction*

Coating latex is acknowledged to contribute to offset ink setting rate and ink-paper adhesion, as well as to the final print quality, such as print gloss. Generally, increased latex interaction with ink solvents is seen to enhance rapid absorption and lead to faster ink setting. Differential performance of latex on chemical interaction with ink oils is primarily explained by polarity and solubility parameter variables. Also, changes in the coating structure, i.e. both physically (porosity, pore size, shape, connectivity) and surface chemistry are recognised as controlling factors. The level of latex addition in the coating is acknowledged to have major relevance for the dominance of diffusional versus coating structural or wettability factors /4/. However, there seems to be some confusion between the mechanisms themselves and the controlling factors as it has been difficult to discuss these individually when both the ink and paper systems are not clearly and separately defined.

Latex properties, such as the level of cross-linking (gel-%) and polymer chemistry, namely higher or lower surface energy/polarity, have been shown to generate different oil/ink-interactive coatings /3/. Lower cross-linking and higher surface energy/polarity were shown to be more interactive. Decreased butadiene level /18/ and addition of acrylonitrile into styrene-butadiene latex have been shown to decrease interactivity and hence the rate of absorption /19/. The parameters of the latex are thus to some extent discussed already in the published work, although precise definition of the polymers and absorbing liquids is lacking. The cause for the differences in interaction is also only dealt with in respect to equilibrium solubility parameter differences without detailed analysis or definition, especially within the context of the coating pore network.

Even though the absorbing ink oil-phase properties are equally important for the absorption and diffusion-driven affinity, the wide range of available offset ink oils has been generally by-passed in the published works. A difference of interaction between different aromaticity and boiling point mineral oils is commented on in the work of VanGilder /20/, but their differences were not further discussed. Desjumaux found greater interaction of latex with linseed oil compared to mineral oil /4/. The differences in interaction and absorption behaviour between tall oil ester, linseed and low-aromatic mineral oils with commercial grade latices were reported earlier by the current authors /5/.

### *Solvent and polymer cohesion – solubility parameter and diffusion*

As mentioned above, the solubility/cohesion parameter concept has been used to explain the differences in association between coating latices and ink solvents. The Hildebrand solubility/cohesion parameter, δ, is a fairly simple and practical measure for describing the chemical interaction character of a liquid or a polymer /21/. It is defined as the square root of the cohesive energy density required to convert a liquid into gas (Eqn. 1). In order to describe the interaction energies more specifically, the solubility parameter can be divided into dispersion, polar and hydrogen bonding energy contributions according to Hansen /22/.

$$\delta = \frac{(\Delta H_v\text{-}RT)^{0.5}}{V_m} = \frac{(\Delta E)^{0.5}}{V_m} \qquad \textbf{Eqn. 1}$$

where $V_m$ is the molar volume of liquid, $\Delta H_V$ is its enthalpy of vaporisation, $\Delta E$ energy of vaporisation, R is the molar gas constant (8.3144 $JK^{-1}mol^{-1}$) and T is absolute temperature. The solubility parameter has units of $MPa^{1/2}$, which is 2.0455 times larger than the value expressed in $(cal/cm^3)^{1/2}$ still often used.

The solubility parameter is thus a directly measurable property of a liquid. The solubility factor for a mixture of miscible liquids is directly proportional to the volume fraction of the individual solubility parameters of the components. For polymers, the solubility parameter may be determined using indirect methods. A common way is to test the swelling character of the polymer in a spectrum of liquids with a range of solubility parameters. Liquid and polymer species with similar solubility parameters have greater affinity towards each other. The solubility parameter for a co-polymer is more complex than for liquid mixtures but can be roughly estimated from the solubility parameters of the monomers and their volume or mass fraction in the co-polymer /23/.

A vast range of both mineral and vegetable oils are used as the solvent phase in offset inks. For mineral oils, Hildebrand solubility parameter values between 14 and 18 $MPa^{1/2}$ are reported, depending mainly on the aromaticity /24,25/. Increased aromaticity leads to increased solubility, and aliphatic grades have the lowest values. Reported Hildebrand solubility parameters for vegetable oils vary depending on the fatty acid composition /24/. For example, 14.9 $MPa^{1/2}$ is reported for linseed oil and 16.6 $MPa^{1/2}$ for pine oil (tall oil). For mineral oils, the whole solubility energy is of an apolar/dispersion type, whereas for vegetable oils approximately 1/3 of the solubility energy is of polar and hydrogen bonding type.

The parameter values for the monomers of typical coating grade latices differ from each other quite significantly; for example, poly-butadiene 17.0 $MPa^{1/2}$, polystyrene and poly-n-butylacrylate 18.5 $MPa^{1/2}$ and poly-acrylonitrile 26.0 $MPa^{1/2}$. The contributions from specific energies are rather similar for butadiene and styrene, almost solely dispersion energy. A somewhat higher polar and hydrogen bonding energy contribution is reported for acrylate, and considerably higher values are given for acrylonitrile (due to nitrogen) /24/.

There are several shortcomings in the direct use of the solubility parameter concept to predict polymer – liquid interaction. For example, the molecular volume of the solvent is not fully taken into account; solvents with smaller molecular volume are thermodynamically "better" fitting within the polymer network even though the solubility parameter values are identical /22/. Liquid viscosity affects the time needed to reach equilibrium swelling /25/. When predicting the polymer solubility, the degree of cross-linking and the need to take into account the degree of annealing bring further difficulty /23/. Another general problem exists with the accuracy of solubility parameter determination for both liquids and polymers. A large range of values is reported for each of the chemicals presented above depending on the method used /24/.

Diffusion kinetics is another aspect not taken into account by the solubility parameter alone, and which is relevant to most applications of polymer – liquid interaction /26,27/. Polymeric materials permit the transport of most gases and liquids by a diffusion mechanism, which is driven by the activity potential of the solute at the two interfaces /26/. The solute flux or the rate of penetration is determined by the permeability factor and the diffusion coefficient; the former is affected by the concentrations of the initial liquid in contact with the polymer interface and later by the volumetric concentration gradient in the polymer matrix. Diffusion kinetics and polymer – liquid solubility are thus strongly related. The size and shape of both the solvent and polymer molecules are important for the permeation, diffusion kinetics and solubility /28/. Polymer variables affecting the transport include the chemical nature of the polymer, its molecular weight distribution, degree of cross-linking, and degree of annealing. The molecular weight and shape of the solute molecules are relevant properties for the penetrating fluid. According to Sherwood /26/, the rate of transport is greatly enhanced if solution of the diffusing substance causes the polymer to swell.

## Experimental materials and methods

### *Latex properties and coating compositions*

A series of nine well-defined latices were produced in laboratory scale at BASF, (see table 1 in the Appendix). The variables in these model latices were: (i) degree of crosslinking, gel content (%), (ii) glass transition temperature Tg (°C), (iii) chemical composition comparing styrene-butadiene (SB) and styrene-acrylate (SA) latices as well as acrylonitrile inclusion (An) in both SB and SA types. Degree of carboxylation and the quality and quantity of the surfactants and other additives were kept as closely constant as possible. The solubility parameters were calculated from the mass proportion of the monomers and their solubility values, even though this approach neglects factors like crosslinking /24/.

The latices were investigated as pure latex films and as a part of a coating layer structure. The physical porous structure of these coatings was evaluated with mercury porosimetry (Autopore III, Micromeritics) using corrections for sample vessel and mercury expansion as well as sample compression (Pore-Comp, University of Plymouth). Values for pore size and porosity are also given in table 1.

### *Ink oil properties*

Five mineral and vegetable based oils commonly used in offset inks were investigated. Physical and chemical properties of these test oils are described in table 2 in the Appendix. The solubility parameters for aliphatic and aromatic mineral oils and tall oil ester were calculated by determining the value for the heat of vaporisation from an experimental vapour pressure – temperature curve (Fischer Labodest 0601, by Fortum). The oils were first tested as pure oils in contact with pure latex films, and further as added into an ink composition.

### *Latex-oil interaction: gravimetric and dynamic methods*

The equilibrium uptake of a liquid by a latex film was determined gravimetrically. Latex dispersion was coated on a non-interactive polyester film and the film was dried at 80°C for 30 minutes. The weight of a piece of latex coated film of known surface area (2 cm by 2 cm) was measured before and after letting the film imbibe in a super-source of different ink oils. The imbibition time varied depending on the polymer and liquid, and was always continued until no weight change could be observed, thus ensuring that the interaction had reached equilibrium. Excess liquid was wiped from the surface of the film using a soft paper cloth before re-weighing. The weight of the substrate film was subtracted from the final weight, and the result was also corrected for the remaining amount of liquid on the sample substrate surface by performing the same imbibition, wiping and weighing procedure for the substrate film alone. The results are presented as the weight of oil in grammes absorbed by a gramme of latex, which is multiplied by 100 and thus signified as w/w%-uptake. The test was repeated ten times for each oil – latex combination, and the average error was approximately 15 %.

In a real printing situation, time and volume are limiting factors for all interactions. Therefore, the kinetics of the polymer-liquid interactions was studied in addition to the above-described equilibrium, quantitative liquid uptake. This was realised using the concept of tackification of a polymer film in interaction with oil using the Ink-Surface-Interaction-Tester (ISIT6) /14/. A latex film was coated on a synthetic basepaper (Synteape ) with a laboratory draw-down coater (RK Coat Instrument) and dried in an oven at 80°C. A 0.25 mm oil film was applied on the latex surface using an IGT rotogravure roll applicator attached to the ISIT. Directly after oil application, a sequence of tack measurements was performed over a period of 1 000 seconds using the static pull-off method. The level of interactivity is judged from the time of initiation of tack rise and the magnitude of tack. The results are presented as a function of the tack value after 2 seconds, but the discussion is based on the entire tack sequences.

Measuring the tack of the pure latex films, i.e. without addition of oil, showed that some latices, namely the low Tg latices, are tacky as such, whereas other are non-tacky to begin with. The tack curves of the oil – latex interaction with the non-tacky latices always ended in zero tack whereas tack curves with the originally tacky latices ended in a high tack value. The coat weight of the latex film was approximately 6 g/m$^2$ and the amount of applied oil 0.22-0.23 g/m$^2$, thus according to the equilibrium uptake values the amount of oil in the applied film is not able to saturate the whole latex layer. This allows us to conclude that the oil diffused into the latex film as a permeation front eventually leaving the latex surface, and that the observed tackiness does represent the state of the latex as a result of the diffusion.

### *Ink-on-paper tack development*

Ink setting on paper was characterised with ISIT. Six test inks based on the five oils respectively (Appendix, table 1) and additionally one ink containing 50-50 % blend of aliphatic mineral and linseed oils were prepared (by Sicpa Oy). The inks included approximately 45 w/w-% of the respective ink oil, 16 w/w-% of cyan pigment, 10 w/w-% of alkyd resin and 30 w/w-% hard resin. The relative amounts of the oil and hard resin, and thereby the percentile amount of ink constituents, varied slightly depending on the necessary solubility-dependent adjustments that had to be made in the varnish manufacture.

The standard coating pigment was fine ground calcium carbonate (HC90, Omya AG), and the nine coatings contained 10pph of the respective latex by weight of pigment. These were coated on the synthetic, macro-smooth basesheet with a laboratory draw-down coater to a coat weight of approximately 12 g/m$^2$.

The ISIT method provides an analysis of the ink-paper interaction from the initial tack rise caused by the ink fluid phase absorption into the coating structure until the consolidation of the ink layer. The slope, or tack rise rate (N/s), is used as a measure for the mainly capillary-driven ink oil uptake by the coating. A standard procedure of ink application from a roller on the ISIT, pre-inked using an IGT ink distributor, was used for printing onto the coated paper samples, resulting in approximately 1 g/m$^2$ of ink being transferred onto the paper. Three repetitions were performed for each ink – coating combination. A more detailed description of the device hardware and analysis procedure is found in the literature reference /14/.

## Results and discussion

### *Diffusional interaction: latex and oil property effects*

#### (a) Oil solubility parameter and viscosity

The gravimetric uptake of the oils by the nine test latices is presented in figure 3. The order of increased amount of absorbed oil follows roughly the order of increasing solubility parameter, i.e. aromatic mineral (17.7 MPa$^{1/2}$), tall oil ester (16.9 MPa$^{1/2}$), linseed (14.9 MPa$^{1/2}$), rapeseed and aliphatic mineral oil (14.3 MPa$^{1/2}$). The solubility parameter is thus indicative of the total amount of oil that is able to penetrate into the coating latex through chemical association. Thus, higher solubility parameter of oil leads to greater interaction because the solubility parameters of latices are generally higher than for the oils and thus the difference in solubility (delta solubility) decreases.

Fig. 3 Gravimetric equilibrium uptake of oil by latex film for five oils on nine model latices.

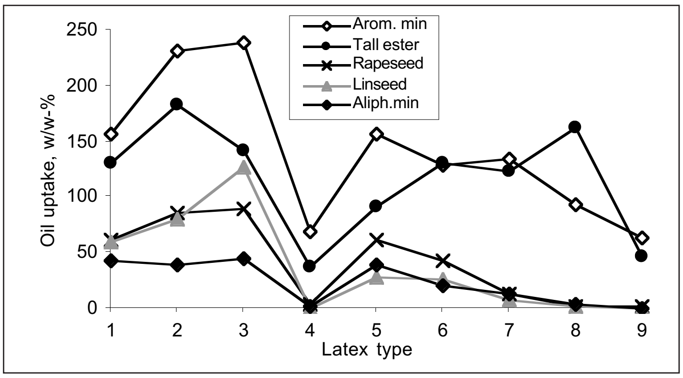
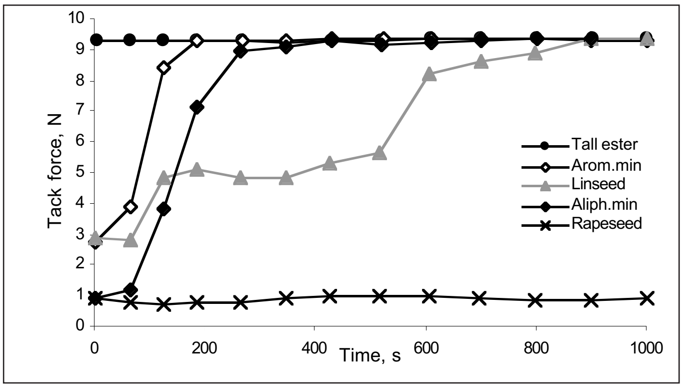


Figure 4 demonstrates the dynamic interaction of different oils with one type of latex (L7) chosen as an example (oils arrange in a similar ranking with all latices). Also in this test, the oil interactivity and solubility parameter were observed to correlate to some extent, however with significant exceptions. Namely, tall oil ester showed very rapid and strong interaction (stronger than aromatic mineral oil). Also aliphatic mineral oil showed respectively stronger and rapeseed slower interaction than expected from the gravimetric measurement. These differences can be explained by the diffusion rate factor, which becomes relevant in this dynamic test. As stated in the theoretical section, diffusion rate is affected both by the solubility factor and solvent phase viscosity, which is indeed verified by these results. Diffusion rates are greater for the low viscous tall oil ester and aliphatic mineral oil, and slower for the high viscous rapeseed oil.

Fig. 4 Dynamic latex-oil interaction measured as tackification of latex film (L7) in contact with oil.

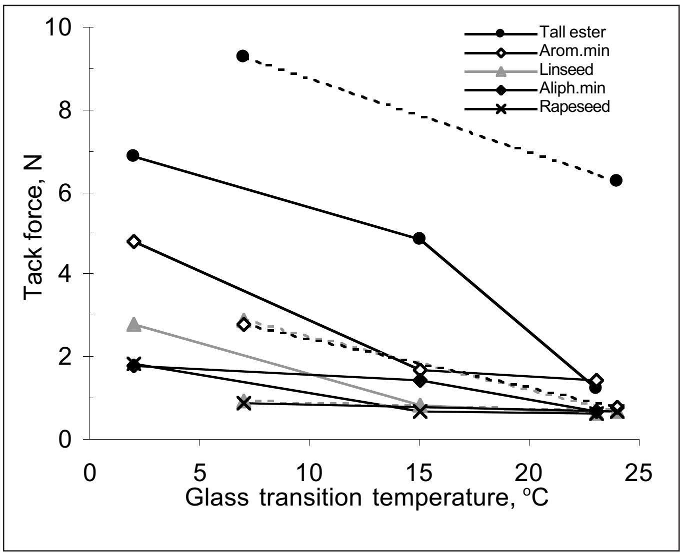


**(b) Latex solubility parameter, degree of film formation and crosslinking**

Latex properties affected the degree of oil interaction similarly in both the gravimetric and dynamic test methods. In the following, the influence of the latex properties on the dynamic interaction with oils is considered (tack value after 2 seconds contact time).

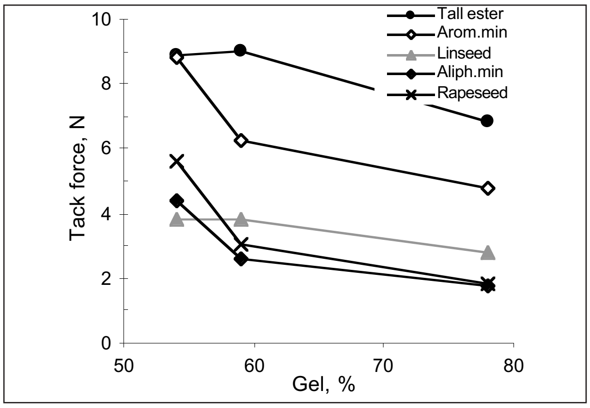
Glass transition temperature, Tg, was shown to influence strongly the degree of interaction with all oils, so that higher Tg led to decreased affinity (figure 5). The same was seen with both SB and SA type latices. In case of SB latex, this could be explained by an increase of the polymer solubility parameter because the proportion of styrene is increased to adjust Tg (butadiene 17.0 $\text{MPa}^{1/2}$, styrene 18.5 $\text{MPa}^{1/2}$). Lower latex solubility parameter should enhance the association with ink oils, because their solubility parameters in turn are generally lower than for the latices. In case of styrene-acrylate latices, the solubility parameter concept does not, however, explain the decrease in association with increased Tg. In a SA latex, increased Tg means increased level of styrene in the co-polymer but this leaves the solubility parameter remaining on the same level (poly-n-butylacrylate 18.5 $\text{MPa}^{1/2}$). This indicates that latex Tg is an indicative parameter to oil association on its own via a mechanism not captured by the simplistic solubility parameter. The behaviour, however, corresponds well with the molecular mobility of the polymer chains, which is more likely the key parameter for the dynamic interaction with oils. In the case of latices with increased Tg (above, or close to, room temperature) the polymer chains were in a more glassy state when interacting with the oils; this then likely entails a slower diffusion of the oils into the latex film.

Fig. 5 The role of latex Tg on interaction with different oils. Points connected with solid lines present SB and dotted lines are SA.



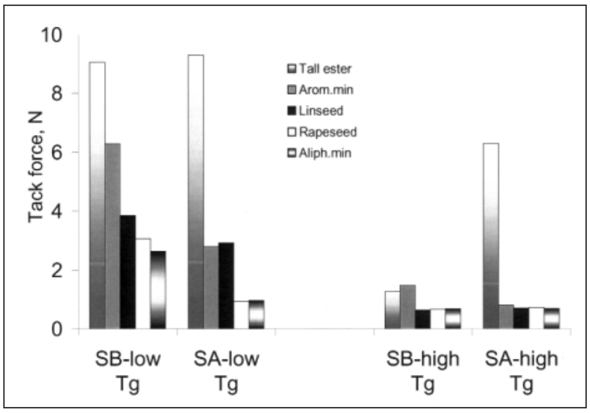
Degree of crosslinking, gel-%, is also indirectly related with oil interaction (figure 6). The higher the gel-%, the greater is the amount of entanglement between the polymer chains (crosslinking), and the less prone is the latex to swelling in contact with solvents. As the ratio of styrene and butadiene is kept constant in these latices, neither the monomer solubility parameter dependence nor the degree of film formation explain the result. The difference is, thus, caused by the proportion of easily swelling material in the polymer film.

Fig. 6 Increased latex gel-% leads to decreased oil association.



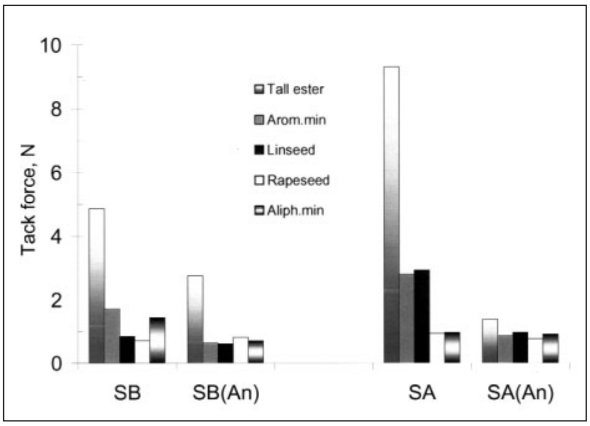
Styrene-butadiene latices are more interactive with oils than styrene-acrylate latices having the same Tg. This is shown in figure 7 at two different Tg's. This can be explained by the difference in the latex solubility parameter along with the change in the monomer composition. Acrylate (18.5 MPa$^{1/2}$), which has a higher solubility parameter value than butadiene (17.0 MPa$^{1/2}$), reacts less with solvents than butadiene. Additional contribution comes from a Tg difference; Tg of acrylate monomer is higher than that of butadiene and thereby the proportion of acrylate in a co-polymer with styrene is higher than in a styrene-butadiene co-polymer of same Tg. This explains why the difference in interaction is great. The only exception here is the tall oil ester for which the interaction is in favour of the SA type latex in high Tg grades.

Fig. 7 SB-latices interact stronger with oils than SA-latices having same Tg; low Tg here is 7°C and high 24°C.



In both SB and SA latices, the addition of acrylonitrile (An) reduces the interaction with all oils significantly, figure 8. The SB(An) and SA(An) co-polymers are not comparable, because the latter has lower Tg. The influence of acrylonitrile addition on reduced oil interaction can be attributed to the increased solubility parameter (26 MPa$^{1/2}$). This influence has been previously reported /19/.

Fig. 8 Acrylonitrile (An) reduces the oil interaction significantly in both SB and SA type latices.



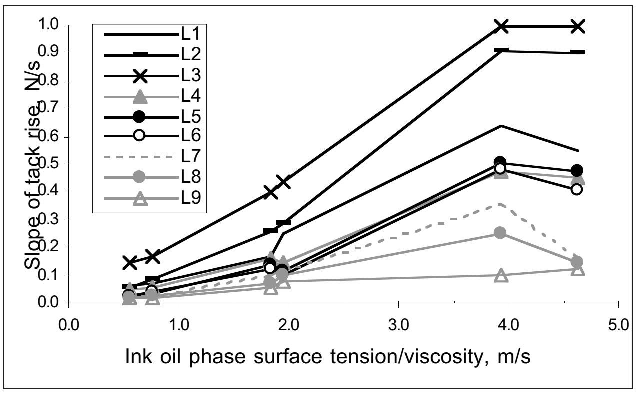
## *Consequences of latex-oil diffusion on ink setting*

### (a) Capillarity absorption vs. diffusional effects

As discussed earlier in this article, capillary absorption is the primary driving force for ink oil phase penetration into a paper coating structure during ink setting at typically low latex addition levels. This is evident from the strong correlation between oil viscosity, or the surface tension/viscosity ratio (figure 1), and ink setting rate, as well as from the relation between the porous structural variables and ink setting rate (figure 2). The observations regarding pure oil – latex association are now considered in the real context of offset ink and coated paper by observing the ink setting dynamics.

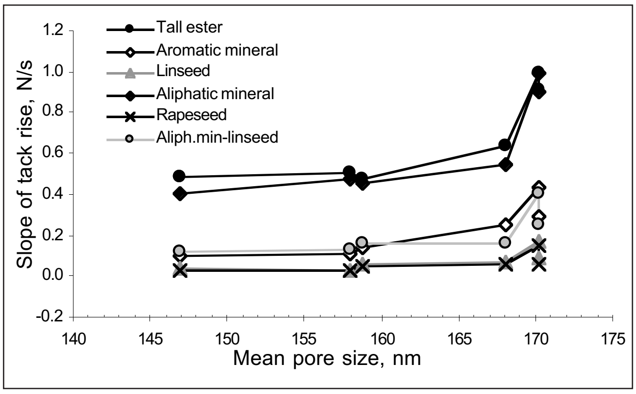
As shown in figure 9, the viscous properties of the ink oil phase also dominate when having a wide range of both strongly and weakly oil-interactive latex types in the coating (10 pph). A slight discontinuity in the correlation is observable at the surface tension/viscosity ratio value of approximately 1.9 m/s, i.e. aromatic mineral oil, and at 3.9 m/s, i.e. tall oil ester, which are the strongly interactive oil types. These kinks can be interpreted as an indication of induced rate of ink tackification and setting due to more intensive diffusion of ink oil into the coating latex. The degree of discontinuity at these points varies depending on the latex grade. Oil solubility/cohesion properties thus play a role at this initial stage of ink setting, although viscous properties strongly dominate.

Fig. 9 Ink setting is mainly controlled by surface tension and viscosity properties of the absorbing oil-phase, but oil-latex interaction is observable with aromatic mineral oil and tall oil ester. L1-L9 are coatings with 10 pph of the respective latex. Ink oils in the order of increasing surface tension/viscosity are: rapeseed, linseed, aliphatic mineral-linseed combination, aromatic mineral, tall ester and aliphatic mineral oils.



As indicated in table 1 (Appendix), and within the scope of the present studies based on uncalendered coatings prepared with a draw down coater on a synthetic basesheet, the average coating structural parameters were not largely affected by the latex type, although the number and distribution of pores are clearly modified by blocking, partial void filling and the differences between latices in controlling the shrinkage properties. [In the case of realistic calendered coatings, these average parameters would be expected to show greater differences as mechanical forces and temperature impact on the compressibility and flowability of the latex.] A correlation between decreasing mean pore size with higher latex Tg was evidenced. In contradiction to the well-acknowledged relationship between increasing ink setting rate with decreased pore size (figure 2), the physical porous structure differences of the coating layer in relation to latex type has no (or very little) contribution on the initial ink setting rate (figure 10). There appears, therefore, an inverse relation between ink-latex interaction and the resulting pore size generated by the use of that latex. The existing large differences in ink setting are therefore discussed in relation to the differential diffusion-driven penetration of the ink oils into the coatings.

Fig. 10 Decrease in pore size caused by the latex choice in these cases does not lead to increased rate of ink oil removal as pore volume and permeability are also changed. Latex is the variable (L6, L5, L4, L1, L3 and L2) in the coating structure at a level of 10 pph.



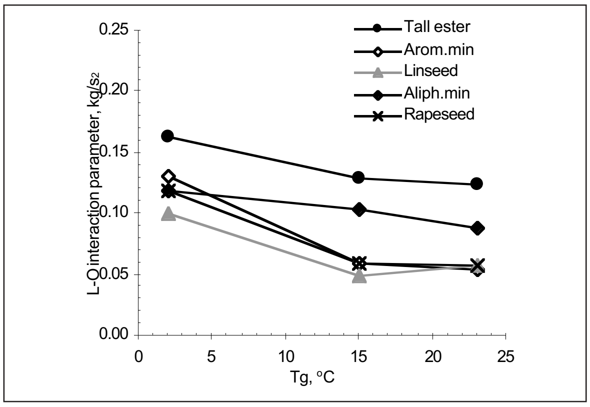
### (b) Influence of latex properties

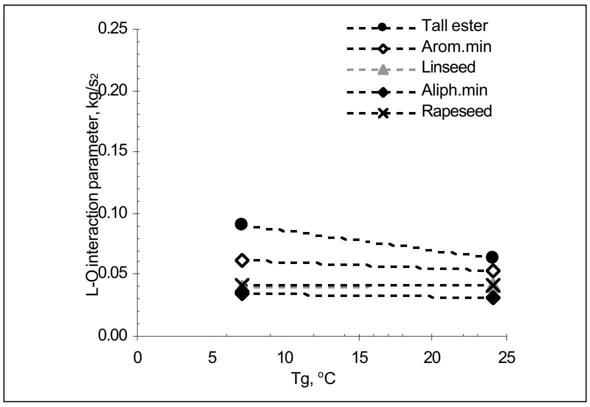
Coating latex choice seems to have a greater impact on the diffusional interactions during ink setting than the oil solubility differences. From the ink side, oil surface tension and viscosity continue to strongly dominate the absorption behaviour. Dividing the slope given by the tack rise rate value with the surface tension/viscosity ratio of the respective ink oil, thus normalising for the dominant capillary-absorption related variables, gives an indication of these relative effects. The ratio of the “slope of tack rise” and “surface tension/viscosity” is thus used as a measure of the observed influence of latex – oil affinity on absorption during ink tack rise. This parameter is referred to as the “L-O interaction parameter” (kg/s$^2$), and, in the following, this parameter will be used to observe the diffusional ink setting mechanism.

In figures 11 a) and b), we note that with increased latex Tg the association between latex and oil is reduced with SB (a), and also in some cases for SA-latices (b). This finding is in accordance with the results from pure latex – oil interaction tests, and thus proves that the differences in the diffusional properties of the latices are the cause for the variations in ink setting. In respect to oil properties, the order of increased ink setting rate does not follow the order of increased diffusion rate in the case of the fast SB-latices, but does so in the case of the overall slower setting SA-latices. This is the first shown indication of the time-dependency of the diffusion versus capillarity-driven ink oil penetration. Diffusion-driven penetration is slower, which is seen to be significant only if the main driving force, i.e. the capillarity-driven absorption, takes a longer period of time. It is also shown here that the dynamic diffusion properties are more relevant in the realistic ink setting situation than the quantitative measure of oil absorption into pure latex (tall ester faster than aromatic mineral oil). The time-dependency of the latex-oil interaction will be addressed later.

Fig. 11 The role of latex Tg on latex-oil interaction observed in the slope of tack rise: (a) represents SB- latices and (b) SA-latices.

(a)

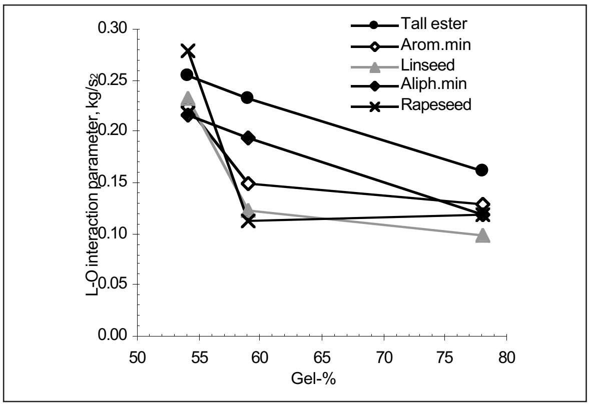




(b)

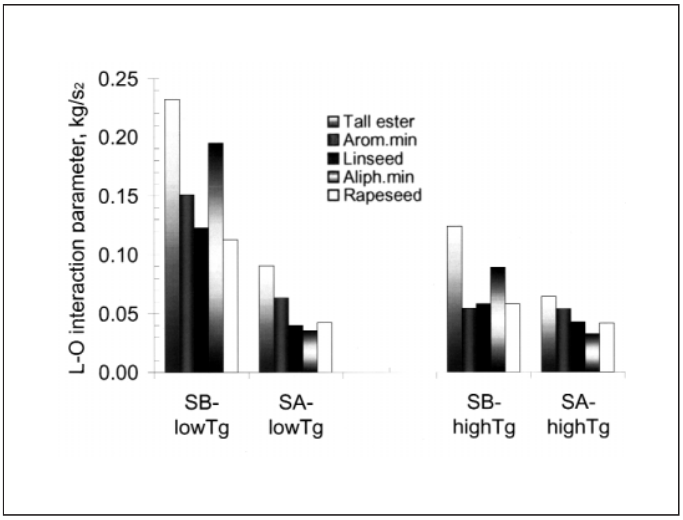
The degree of crosslinking of the latex polymer affects the ink setting rate on a pigmented coating surface in the same way as observed in the pure oil-latex interaction test. With a reduced amount of crosslinked polymer, enhanced solvent uptake is observed. Again we see that for the fast set of rather low Tg (~6 °C) latices, the inks do not follow the expected order, i.e. the order of increased diffusion. Namely, the low viscous aliphatic mineral oil again shows more interaction than expected. This supports the above-mentioned explanation of the influence of relative rates of diffusion and capillary-driven transport.

Fig. 12 The role of latex gel-% on the latex-oil interaction parameter in real time ink-coating contact.



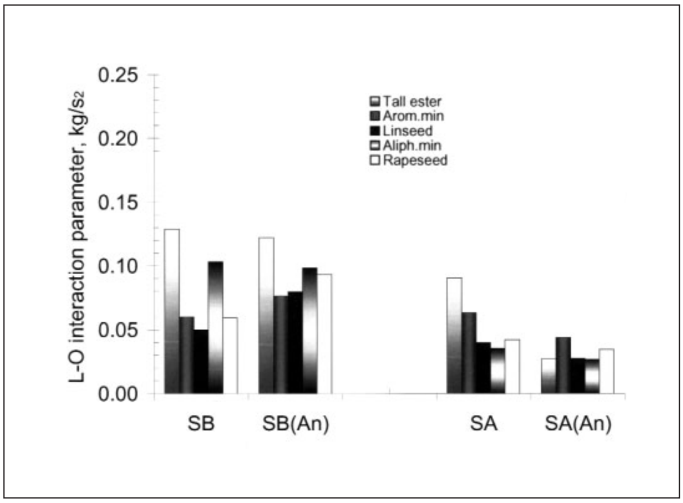
Styrene-butadiene latices are more affected by diffusion-driven ink tackification than the corresponding styrene-acrylate latices with all the different types of ink oils, as seen in figure 13. The differences between the inks are again not as might be expected, especially in the case of the low interactive aliphatic mineral oil based ink. The data show that time-dependent diffusion is more important in actual ink setting situations than the gravimetric total equilibrium uptake previously discussed.

Fig. 13 SB-latices are more interactive than SA-latices with same Tg. Low Tg here is 7°C and high 24°C.



Acrylonitrile was previously seen to reduce the interaction with ink oils through increased difference in the solubility parameters. This is also seen in the real ink – coating situation in the case of SA-based latices, as seen in figure 14. For the SB-latices, however, this is true only for some inks. One explanation for this might be the difference in the gel-% of these otherwise comparable types of lattices, which would indeed here favour faster absorption with the SB(An) type, as the gel-% showed to have a strong impact on the ink setting rate.

Fig. 14 Reduced oil uptake in presence of acrylonitrile is demonstrated for the SA type of latex, and for the SB type with some inks.



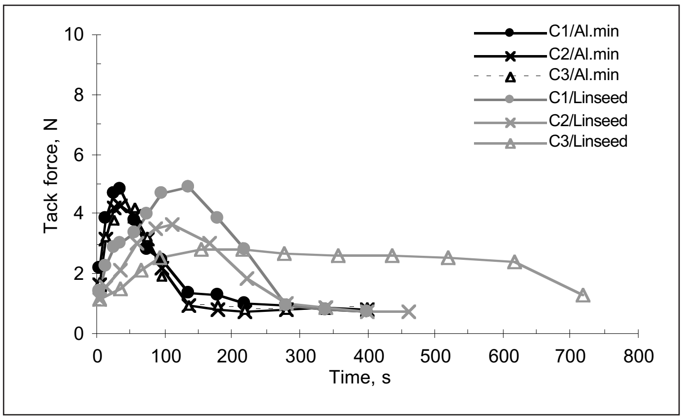
Overall, the initial absorption of the ink oil phase into coating structures, containing latex as the variable, corresponds with the results from time-dependent pure oil-latex interaction. This proves that it is the bulk diffusional parameters of the latex that mainly cause the ink setting differences in competition with the surface chemical wetting or structural changes in the coating layer. From the ink side, the diffusional contribution is also strongly time-dependent.

**(c) Time-dependency of oil-latex interaction**

As already evidenced above, the consequences of the latex-oil interaction on ink setting are strongly interdependent. First of all, the latex-oil interaction itself is time-dependent and this is seen to be more important for ink setting dynamics than the quantitave swelling of the polymer by the liquid. Secondly, the degree to which the latex – oil interactivity affects ink setting rate is determined by the boundary conditions set by the kinetics of the capillary-driven absorption. This is especially important for the contribution made by the oil type. Capillary-driven absorption is largely dependent on the viscosity of the ink oil and thereby this has a dominating role in how significant the diffusion properties (solubility+viscosity) are in affecting absorption.

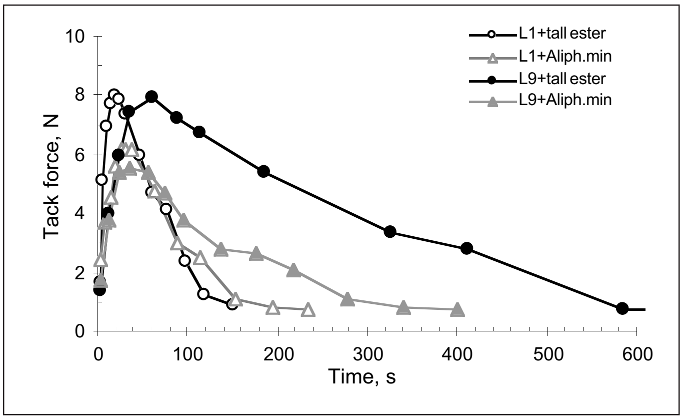
Due to the relative time-dependency factor of these various kinetics, the latex-oil interaction can become important at a later stage than during the initial absorption, i.e. later than the initial slope of tack rise. As a demonstrative example, figure 15 shows the whole tack sequence for the low viscous, low interactive aliphatic mineral oil and the higher viscosity, slightly higher interactive linseed oil, respectively, on three different coatings with variable latex grade. It can be noted that the mineral oil based ink shows very similar behaviour with all coatings. In contrary, the behaviour of linseed oil is very different across all coatings, which could not have been predicted from just looking at the difference in latex – oil interactivity. Due to the high viscosity of the linseed oil, and thereby slower absorption rate, the oil has sufficient time to interact with the coating latex.

Fig. 15 Highly viscous linseed oil based ink absorbs slower by capillary-forces, and has, therefore, more residence time to interact with the coating latex compared with the fast absorbing aliphatic mineral oil based ink. C1-C3 are fine GCC based coatings with 10 pph of different commercial latices as variable /5/.



Another example of the time-dependency of the latex-oil interaction effect is demonstrated in figure 16. Tall oil ester has very rapid initial tack rise rates due to the combined effect of low viscosity and high latex-interaction, but in many cases very long total ink consolidation times. Tack decline, i.e. ink consolidation, is less affected by latex-oil interactivity in the case of an aliphatic mineral oil based ink, which has nearly identical viscous properties as tall ester (surface tension/viscosity) but much less interactivity with latices.

Fig. 16 The influence of latex-oil interaction may affect ink consolidation. Tack decay may be strongly extended due to intensive swelling and blockage of pores in the coating structure in the case of high oil-latex association under certain capillary absorption conditions.



## Conclusion

Altering the coating chemistry by changing the latex type in the coating layer significantly affected the ink oil penetration during ink setting. This effect was influenced both by the latex and ink oil type. Coating latex thus generates a gradient for differential absorption of ink oils into the coating layer. As latex is a major component in the coating by volume its contribution to the pore structure level properties is of significance. However, the diffusional interaction of latex and oil, at least in uncalendered coating structures, competes with any inherent pore size distribution changes, occurring as a result of the latex presence. Practically, therefore, differences in interaction with inks when changing coating latex tend to come from the dominance of diffusion-related chemical interactions.

The degree of ink oil diffusion into latex depends on the properties of both phases. Generally, a larger solubility parameter of the oil coming from, for example, aromatic hydrocarbons in mineral oils and from polar/reactive groups in vegetable oils is responsible for greater diffusion into a given latex. Additionally, factors like oil molecule size and its viscosity affect the rate of diffusion, which is more important in the dynamic rate-determined ink setting process than the quantitative equilibrium swellability of the latex. In respect to latex, the solubility parameters of the monomers, i.e. the latex back-bone chemistry, are indicative of the interactivity with ink oils. However, the degree of crosslinking and Tg, or film-formation, are equally significant. Decreased solubility parameter (butadiene < styrene = acrylate < acrylonitrile), decreased crosslinking, i.e. lower gel-% and lower Tg, lead to greater association with ink oils.

Diffusion is overall a slower process than capillary-absorption when considering fine pore coating structures and therefore its significance in ink setting depends on the general absorption dynamics of the system. This is mainly dominated by the mean pore size of the coating structure and oil viscosity. Diffusion is, however, on occasion found to play a role even in the initial stages of ink setting, thus in some cases competing in absorption dynamic with the main capillary absorption force. The significance of latex-oil interaction cannot, therefore, be predicted in real ink setting situations from the equilibrium in pure oil – latex interaction alone. In some cases, even with moderately or even low interactive latex-oil combinations, and especially with highly viscous oils, the diffusion-related influence in ink – coating contact may come into play in later stages of ink consolidation. Instead of speeding up the ink drying, this type of interaction may contribute to reduced final consolidation of the ink because of blockage of coating layer pores due to latex swelling.

Recognising that the dynamic diffusional interaction between offset ink oils and coating latices of varying types imparts a differential distribution of ink oils in a coating layer is important in understanding the ink drying and consolidation behaviour. The distribution pattern of offset ink components in the print film and coating layer is likely to be relevant in finishing operations of offset pre-printed paper, especially in respect to print rub or during subsequent laser or ink-jet personalisation, varnishing, folding etc.

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## Appendix

Table 1 Latex properties, coating layer porosity and mean pore diameter for 100 pph GCC coatings with 10 pph of corresponding latex.

| Abbreviation | Monomers | Tg / °C | Crosslinking / gel-% | Solubility / $MPa^{1/2}$ | Porosity / % | Mean pore diameter / nm |
|---|---|---|---|---|---|---|
| **L1** | **SB** | 2 | 78 | 17.3 | 29.9 | 168 |
| **L2** | **SB** | 6 | 59 | 17.3 | 28.9 | 170 |
| **L3** | **SB** | 1 | 54 | 17.3 | 27.3 | 170 |
| **L4** | **SB(An)** | 12 | 70 | 18.0 | 25.1 | 159 |
| **L5** | **SB** | 15 | 78 | 17.4 | 25.1 | 158 |
| **L6** | **SB** | 23 | 77 | 17.5 | 26.9 | 147 |
| **L7** | **SA** | 7 | 65 | 17.9 | 29.2 | 159 |
| **L8** | **SA** | 24 | 59 | 17.9 | 29.8 | 152 |
| **L9** | **SA(An)** | 6 | 79 | 18.7 | 27.8 | 159 |

Table 2 Physical properties of offset ink test oils.

| Oil | Viscosity / mPas | Surface tension / mN/m | Density / g/cm3 | Solubility parameter / MPa1/2 |
|---|---|---|---|---|
| **Aliphatic mineral** | 6.1 | 28.5 | 0.83 | 14.3 |
| **Aromatic mineral** | 16.3 | 31.6 | 0.92 | 17.7 |
| **Tall ester** | 8.0 | 31.4 | 0.88 | 16.9 |
| **Linseed** | 45.1 | 34.0 | 0.93 | 14.9 /24/ |
| **Rapeseed** | 59.5 | 32.3 | 0.92 | Not found |