

SEPARATION OF OFF-SET INK COMPONENTS DURING ABSORPTION INTO PIGMENT COATING STRUCTURES

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SUMMARY: The objective of this research was to relate the mode of absorption of the offset ink mobile phase into a pigmented paper coating layer with particular emphasis on the chromatographic properties of that layer. Rate of absorption along with the separation of the ink fluid components during absorption into coating structures was investigated. This fundamental information serves to gain understanding on the optimisation of ink - paper coating interactions for successful printing operation and printed product quality.

Ink absorption and phase separation from the ink and within the coating structure were studied on an enlarged scale both from an infinite liquid (super)source and with a limited absorptive to substrate ratio. Coating structural variables included both physical structure and chemistry. Known blends of typical sheet-fed offset ink ingredients, namely mineral and vegetable oils and alkyd and hard resins, were used as absorptives and characterised for their physical properties. The penetration paths of the different components were detected by microscopic FTIR-analysis and a visualisation method using iodine.

Separation of all the investigated ink components was detected in contact with and within the porous coating. Even the apparently miscible mixtures of linseed and mineral oils were found to separate. In pigment systems containing only dispersant and soluble binder, non-polar mineral oil absorbed further. As the level of latex content was increased in the coating structure the separation was either arrested or reversed. This is probably a result of decreased surface energy and preferential interaction of latex with linseed oil. The absorption length of ink binders was found to be rather short, but oils, especially mineral oil was easily separated and absorbed further from mixtures thereof. Both the physical and chemical properties of the coating and the ink were found to influence the absorption and separation mechanism of the ink components.

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INTRODUCTION

Demand for increased productivity and quality as well as environmental considerations urge ink and paper manufacturers for continuous development of their products. In practice, ink and paper chemists tend to work independently of each other and the success of the printing operation and print quality is in the hands of the printer often on a trial-and-error basis. However, the optimisation of the printing process for increased product quality, economy and ecology requires knowledge of the basic phenomena involved in the process. In particular, the increasing use of pigment coated paper in high-quality printed products has made the fundamental understanding of the interactions between ink and coating layer components an essential prerequisite.

In pigment coating the surface structural properties of paper are upgraded for improved optical and printing performance. The main constituents of a 5 - 15 μm thick coating layer are pigments (~50 % by volume) and polymers (~20 - 30 % by volume), which form the skeleton for the presence of the third key component; air (~25 - 35 % by volume). Air is present in the form of small pores in a broad distribution of shapes, sizes and surface chemistry. Pore sizes in coatings range from 0.02 to 1.0 μm . Polar pigments, such as calcium carbonate and clay, form the major part of the porous structure matrix, but water soluble polymers and latex have shown to decrease the effective surface energy significantly (Lundqvist 1996).

In offset printing, an ink layer or layers of 0.25 – 3 μm is applied on the coating surface. Offset inks are highly viscous paste-like materials, which are formulated by dispersing solid colour pigment (10 – 25 % by weight) into a resin (20 – 40 % by weight) and oil (30 – 50 % by weight) based varnish. Desired ink tack, setting, final gloss and colour fastness are principally attained by the proper selection of pigment, resins and oils. The main constituents of a typical offset ink varnish are mineral oil, vegetable oil, alkyd resin and hard resin. The mineral oils are weak solvent power non-polar petroleum distillates of varying boiling point and aromatic content. They are mixtures of paraffinic, naphthalenic and aromatic hydrocarbons in the C_{16} - C_{18} range. Vegetable oils and their derivatives are increasingly used due to their

diverse properties as ink solvents and binders, and on the other hand for their environmental soundness as a renewable resource. Linseed oil is the most commonly used drying oil, which is slightly polar and chemically reactive due to its double bonds and ester linkages. Alkyd resins are used intensively in offset inks due to their good wetting potential, good binding ability, low cost, easy usability and possibility to manufacture tailor-made resins for customers. Chemically, alkyd resins are polyesters formed by esterification of polyhydric alcohols and polybasic acids in the presence of a vegetable oil or oil derived fatty acid. The vegetable oil content of the final product is usually greater than 50 %. Most common hard resins used in offset inks are natural colophon resins and synthetic hydrocarbon resins. These resins require heating to high temperatures to achieve solution in oils (Owen 1990).

Ink - coating interactions have significance in both the initial ink transfer from the printing plate and in the first stages of ink drying as well as later in the polymerisation phase for smear and rub resistance (Gane and Seyler 1994 a and b). Regardless of the primary drying mechanism of ink on paper, absorption is an important stage of drying in all cases as it results in the initial setting and enables the subsequent colours to be printed. Optimally, only a certain fraction of the ink, namely the low viscous vehicle, absorbs into the paper while pigments and resins remain on the surface. However, it is unknown which, and to what extent, ink components are absorbed from different ink compositions on varying substrates. In addition to the ink and coated layer properties the printing conditions such as temperature, pressure and contact time naturally have an impact on the possible interactions of ink and coating. In coated paper grades the pressure conditions exerted on the blanket, ink and coating prevent absorption of ink constituents at the printing nip (Oittinen 1976). Absorption is thus driven by thermodynamic interactions between ink and coating layer and by capillary forces. Even though the actual printing process itself is fast, absorption can continue for hours especially in the sheet-fed offset process.

Capillary absorption of ink vehicle is often treated mathematically with the general equations of fluid transport in porous media, in most cases using the Lucas-Washburn equation, 1 (Lucas 1918, Washburn 1921).

$$\frac{dh}{dt} = \frac{rg \cos q}{4hh} \quad (1)$$

where h penetration depth,
 t time of penetration,
 r pore radius,
 g surface tension,
 q contact angle
 h ink fluid viscosity.

The quadratic law of liquid movement as a function of time is moreover a general statement of the laminar flow of Newtonian liquids in single and porous structure capillaries. Experiments conducted in model systems with single solvents or oils in coatings support at least a generalised form of the Lucas-Washburn theory (Gate, Windle 1976; Lepoutre 1978; Ranger 1981; Elftonson, Ström 1995). However, in all practical studies of ink absorption on coatings contradictory behaviour is found (Gane, Seyler 1994; Donigian et al. 1996; Xiang, Bousfield 1998; Ström 1999; Preston et al. 2000). Disagreement on the influence of pore size of the substrate is widely discussed suggesting the inability of a sole average parameter to account for the complex porous structure. In many cases the experimental parameters of the absorbing fluid are adjusted or neglected. An improved model taking into account the filter cake formation of ink pigment was suggested by Xiang and Bousfield 1998. In the work of Schölkopf et al. 2000 the Bosanquet equation (Bosanquet 1923) was employed to consider the inertial effect in absorption matching for the first time the experimentally determined liquid-solid interaction with the observed rate of absorption into a compacted porous structure.

In order to treat ink absorption in a paper coating layer in a more realistic way the absorptive should be treated as a multi-component system. In multi-component transport through porous media physico-chemical phenomena occurring at boundaries, such as adsorption, diffusion and evaporation should be considered. These phenomena are the particular cause, on the molecular level, of dynamic changes in absorption character as both stationary and liquid phase properties alter as absorption proceeds. Multi-component transport in porous media can be found in many applications, for example in catalysis, in chemical reactors, in oil recovery and in chromatographic processes. Liquid chromatography is well established for soluble dye systems and has also been considered in absorption studies resembling ink-jet inks (Donigian et al. 1998). However, chromatographic mechanisms namely adsorption, partition, size-exclusion etc. have not been used to explain the absorption behaviour of pigmented inks although similarities and also applications are found in the analytical models of such inks (Szekely, Baumgartner 1979; Fuller 1985; Erhan 1992; Aginsky 1993; Nazli 1994). Separation phenomena are, however, realised in these systems. Hattula and Oittinen 1982 discussed the separation of K&N ink constituents in coated paper. In the work of Ström 1999 model ink constituents were

fractionated and analysed with permeation chromatography. Wickman et al. 1998 analysed the separation of ink constituents by detecting ink chemistry change during ink setting. The separation phenomena of offset ink components in contact with a waterless offset plate has also been reported (Lanet, Gandini 1999).

The physico-chemical interactions between ink and coating components should be determined for the broader understanding of the absorption phenomenon. However, this has been overlooked within the interests of many publications. Alkyd resins are known to adsorb on clay (Johansson 1991) and calcium carbonate surfaces (Wickman 1998), and the adsorption is shown to be affected by the solvent used, the chemical structure and molecular weight distribution of the alkyd and by the adsorbing surface. The interactions between ink solvents and coating latices are also demonstrated (Kelly 1971; Van Gilder, Purfeerst 1994; Triantaphilopoulos, Lee 1996; Van Gilder et al. 2000). Another important aspect consequential to ink – coating interactions is de-inking, which is also a driving force for research on this area (Heimonen 1995; Ben, Dorris 1999).

This study aims at revealing some new aspects of the phenomena involved in offset printing of coated paper, in particular multi-component fluid transport in porous structures. Both absorptives and substrates are well characterised. The experiments are performed on an enlarged scale compared to actual paper – ink dimensions in order to magnify the phenomena. The final aim is to bring out fundamental information which can mainly be applied to prevent print quality defects such as mottle, set-off failure, chalking, show-through etc. Also distribution and spatial variation of ink components influence the optical performance of the print and the printing operation in multi-colour printing.

MATERIALS AND METHODS

Coating components, sample preparation and characterisation

Two types of dry coating structure samples were produced from coating colour suspensions; namely thin-layer coatings on glass plate and macro-scale coating blocks. The chemistry of the dry coating samples was thus known and clearly defined and the physical structure properties were determined using mercury porosimetry. The coating parameters investigated in this study were pigment particle size (three different polyacrylate-dispersed slurry calcium carbonates CC1 - CC3, 60 % < 2 µm, 90 % < 2 µm, 97 % < 2 µm respectively of product names Hydrocarb 60, Hydrocarb 90 and Setacarb, respectively, produced by Omya AG) and chemistry (calcium carbonate vs. English clay EC, 92 % < 2 µm, with product name Suprawhite 95 from Imerys Ltd.). Also the influence of water soluble co-binder (carboxymethyl cellulose CMC, FF10 from Noviant) and latex addition level (0 – 15 pph based on 100 parts by weight of pigment) were investigated. The CMC grade used was of low viscosity and the latex used was a typical styrene-butadiene offset latex with glass transition temperature of 22 °C (DL940 from Dow Chemicals).

Thin-layer coating structures were prepared from the pigment suspensions using a motorised laboratory draw-down coater with blade configuration having an adjustable gap. Glass plates were coated and dried either at room temperature or for latex containing structures at 80 °C in order to ensure film-formation. Pure latex films were coated in the same manner for latex – oil interaction tests, and dried at 80 °C for 30 minutes. In addition to the self-prepared coatings on glass plates a commercial thin-layer chromatography plate (Merck, Silica60) was employed as reference.

Macro-scale coating structures were prepared from all pigment slurries and coating compositions by consolidating wet-colour in a mould on an un-glazed ceramic plate. Consolidation was performed either at room temperature or at elevated temperature (80 °C) for latex containing structures. As a result, coating blocks of approximately 1 – 2 cm thick and 3 – 4 cm diameter were produced. Homogeneity of the structure was confirmed by grinding the outer surface and checking the observable texture using microscopy.

Mercury porosimetry analysis was performed using a Micromeritics Autopore III apparatus. Data were handled with a standard procedure of corrections for mercury compression and sample carrier expansion. In addition a correction for sample compression was made using Pore-Comp software (Gane et al. 1996).

Model ink components, sample preparation and analysis

Offset model inks consisting of oils, oil mixtures and oil-resin mixtures were prepared using typical commercially available raw materials. Typical representatives were selected from each of the main components present in offset ink varnish, namely mineral oil (Bp 280 – 310 °C), linseed oil, linseed oil-based alkyd resin and a modified colophon resin. The dissolution of the resins was conducted by an ink manufacturer, thus guaranteeing suitable homogeneity.

The model inks were analysed for surface tension using a Krüss Digital Tensiometer K10T with ring-configuration. The viscosity was measured with a StressTech rheometer at low shear rates ($<100 \text{ s}^{-1}$). Both were measured at $23 \text{ }^\circ\text{C}$. Density of the mixtures was analysed by weighing a known volume of the liquid in a specially predetermined vessel. FTIR-analysis was conducted for pure chemicals and mixtures thereof.

Ink absorption and component separation during absorption

The most significant difference between the two methods employed to study absorption, i.e. thin-layer (TL) and droplet-on-tablet (DT), is the absorptive to substrate ratio. The TL mode represents a case of unlimited liquid super-source, whereas the amount of liquid available for absorption is limited in the DT method. In both methods the coating substrate samples were conditioned at constant temperature and humidity ($23 \text{ }^\circ\text{C}$ and $50 \text{ } \%$ RH) for several days before usage. The absorption phenomenon was observed by detecting the kinetics and by quantifying the spatial location of ink components after absorption.

In thin-layer absorption the absorptive is first inserted in a thin-layer chromatography chamber, whereafter coated glass plates are placed vertically in the chamber. The initial level of liquid is approximately 0.5 cm and the level of rising liquid front is observed through a light source as a function of time. Absorption, showing as a progressive translucency, is allowed to proceed for $5 - 24$ hours, after which the separation of ink components is determined. In the DT-method a droplet of $2 \mu\text{l}$ is allowed to penetrate into a tablet. The ink component separation is subsequently determined from the cross-section of the absorbed droplet in the tablet.

The spatial detection of ink components is challenged by their inherently invisible nature and on the other hand by their chemical similarity. Fourier-transform-infrared spectroscopy (Perkin Elmer Spectrum 2000) with a germanium crystal - microscopy unit at wavenumbers $550 - 4000 \text{ cm}^{-1}$ proved to be the most useful analytical method for the TL plates. The use of the Ge-microscope mode allows the FTIR-spectrum to be obtained directly from the sample without any sample preparation. Thin-layer plates were thus probed from bottom to top in 1 mm steps to discover the change in absorptive chemistry along the absorption path. The separation character of an absorptive – substrate system is presented quantitatively as a separation %-value, $s\%$, equation 2. This value, therefore, represents separation efficiency independently of total absorption.

$$s\% = 100 \cdot \left(\frac{L_t - L_i}{L_t} \right) \quad (2)$$

Where $s\%$ separation percentage
 L_t total absorption length
 L_i absorption length of component i.

In the DT-method the use of analytical methods was hindered by the small quantity of sample and the short absorption path. Therefore, a visualisation approach with iodine vapour was used. The method is based on the reaction of iodine with double bonds of organic compounds. After absorption, the tablet was ground up to the mid point of the absorbed droplet diameter and the tablet was placed into iodine atmosphere for a few hours. The samples were photographed and the spatial location of ink components determined qualitatively.

Absorption behaviour was found to alter greatly in the presence of polymers in the coating structure. Therefore, polymer – oil interactivity was studied separately. The experiments were performed as static gravimetric measurements of oil uptake by a latex or carboxymethyl cellulose film coated on a glass substrate.

RESULTS

Properties of model coatings and inks

It is clearly indicated from the mercury porosimetry data that with larger particle size pigment a more porous structure with larger pores and lower surface area results. Addition of 1 pph of CMC alone increases the porosity and the pore size, resulting in reduced effective surface area. Latex addition results in reduced porosity. Average pore size, on the other hand, increases with small addition of latex. Clay-based structures are more closely packed compared to similar size carbonates if the clay platelets are aligned along the coating xy-plane. Normally, a printing ink will be applied perpendicularly to the platelet surfaces of such aligned samples. The absorption then occurs into the short inter-platelet

entry pores and continues through the void structure following the narrow planar capillaries in the xy-plane as well as progressing through the short capillaries presented in the z-direction into the coating structure. When using the TL method, the fluid encounters the sample edge-on rather than face-on and at first enters differentially more of the narrow planar capillaries. As the structure begins to fill, the statistical entry of these planar slit geometries occurs from one end only rather than from a probability distribution of both ends, as would have been the case with surface printing. This means that there is likely to be a greater viscous drag acting on the fluid counteracting the increased capillarity in the direction of absorption when using the TL method for clays. In the case of the DT method, where within the macro-scale tablet samples clay platelets remain disordered due to the absence of a levelling force in the sample preparation, a more highly porous structure is generated. All results gathered in table 1 are measured from tablet samples except for silica.

The commercial silica thin-layer chromatography plate has a dual distribution of pores, i.e. the silica pigment particles are rather large and poses internal porosity within the particles. Measured porous structure values from the thin-layer coatings showed similar trends, except for the clay-based coating as explained above. The interpretation of the porosimetry of the TL coated glass plates, however, suffers some practical problems. The analysed material is very small compared to the support material, also errors in the absolute values of porosity and average pore size are greater than for the tablet structures. Absolute parameters from porosimetry of the thin layers are therefore considered here to be of limited value. Hence, only porosimetry data from the tablet analyses are presented and subsequently used in the later quantitative correlations.

Table 1. Pore structure characteristics of coatings.

Abbreviation	Composition	Porosity, %	Av. pore diameter, nm
<i>C1</i>	CC1 (60 % < 2 μ m)	31.09	125.08
<i>C2</i>	CC2 (90 % < 2 μ m,)	27.16	47.65
<i>C3</i>	CC3 (97 % < 2 μ m)	27.61	43.19
<i>C4</i>	CC2 + 1pph CMC	30.09	62.24
<i>C5</i>	CC1 + 1 pph CMC + 10 pph LATEX	23.56	184.24
<i>C6</i>	CC2 + 1 pph CMC + 5 pph LATEX	30.32	68.02
<i>C7</i>	CC2 + 1 pph CMC + 10 pph LATEX	19.82	59.75
<i>C8</i>	CC2 + 1 pph CMC + 15 pph LATEX	9.77	27.40
<i>C9</i>	CC3 + 1 pph CMC + 10 pph LATEX	18.50	46.58
<i>C10</i>	EC (92 % < 2 μ m)	34.07	70.88
<i>C11</i>	EC + 1 pph CMC + 10 pph LATEX	29.22	77.58
<i>C12</i>	Silica60 (Merck)	32.78	23.32

Physical properties of the absorptives are summarised in table 2. Surface tensions of all tested oils and oil - resin mixtures are fairly low, ~30 mN/m. Higher values of surface energy for the vegetable oil and resins are a result of their slightly polar nature caused by the carboxylic groups. The viscosity of the mineral oil is significantly lower than that of linseed oil, and viscosity is also increased greatly with added alkyd and hard resins.

Table 2. Physical properties of model inks.

Abbreviation	Composition	Surface tension, mN/m	Viscosity, mPas	Density, g/cm ³
<i>I1</i>	100 % mineral oil	28.7	7.3	0.837
<i>I2</i>	75% min-25 %lin oils	29.0	10.7	0.857
<i>I3</i>	50% min-50 %lin oils	29.9	16.6	0.881
<i>I4</i>	25% min-75 %lin oils	31.1	29.3	0.906
<i>I5</i>	100 % linseed oil	33.8	46.7	0.937
<i>I6</i>	Min40%-lin30%-alk30%	30.0	53.7	0.905
<i>I7</i>	Min36%-lin25%-alk25%-hr14%	30.2	175.0	0.920

The physical characterisation of ink component mixtures reveals also information on the compatibility of ink components. It is seen in figure 1, for example, that the oils do not form ideal mixtures, as the correlations between the various properties and the relative concentrations of the oils are not precisely linear. Therefore, they do not follow Raoult's law exactly, but a very close approximation to it.

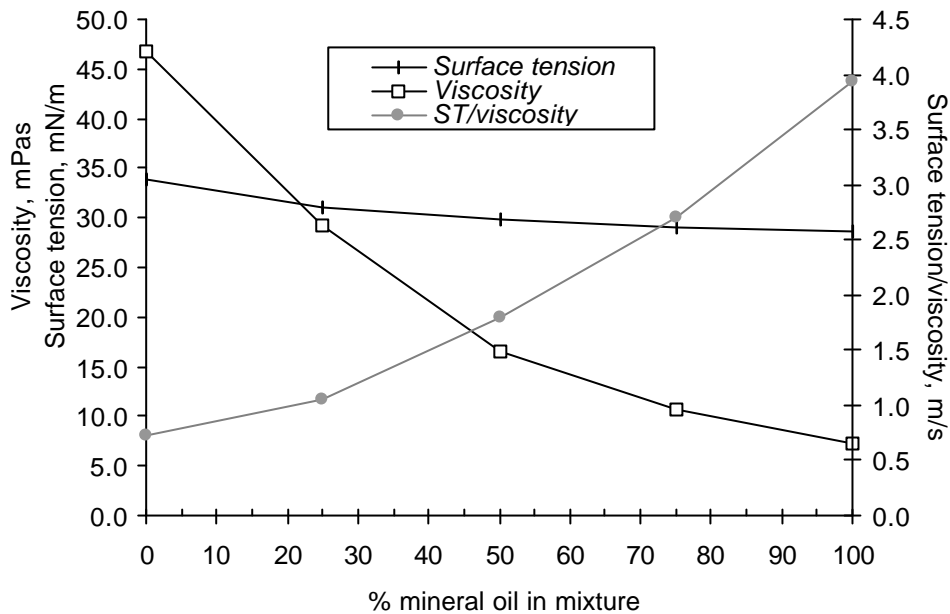


Fig. 1. Viscosity and surface tension of linseed and mineral oils and mixtures thereof.

Organic compounds have strong FTIR-absorption at wavenumbers $2800 - 3000 \text{ cm}^{-1}$, which represents the CH-bonds of organic compounds. Particularly, the peak at 2925 cm^{-1} distinguishes the absorptives from the pigment substrates in the TL-analysis performed. Mineral oil is distinguished from the other components due to the clear absence of a peak at 1740 cm^{-1} , which represents the carbonyl functionality (figure 2), easily definable in the case of linseed oil as a strong IR absorption.

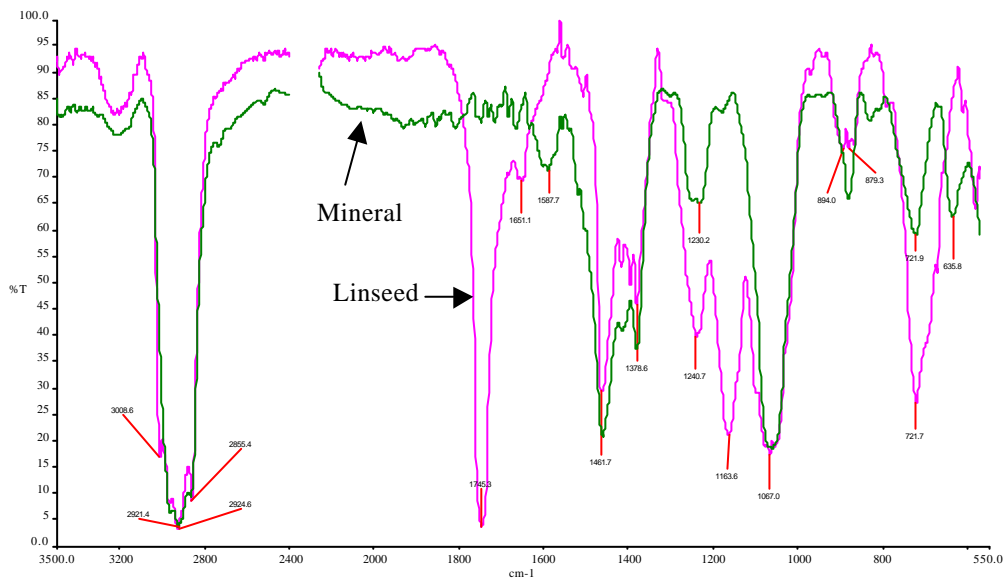


Fig. 2. FTIR-spectra of linseed and mineral oils.

Absorption kinetics

The movement of the liquid front in a thin-layer coating sample was found to approximate to a linear square root of time dependency for all absorptive - substrate pairs as seen in figure 3 for representative tests. Absorption coefficients, i.e. the slopes of the absorption rate curves (h^2 against t) were thus determined and they are summarised in table 3.

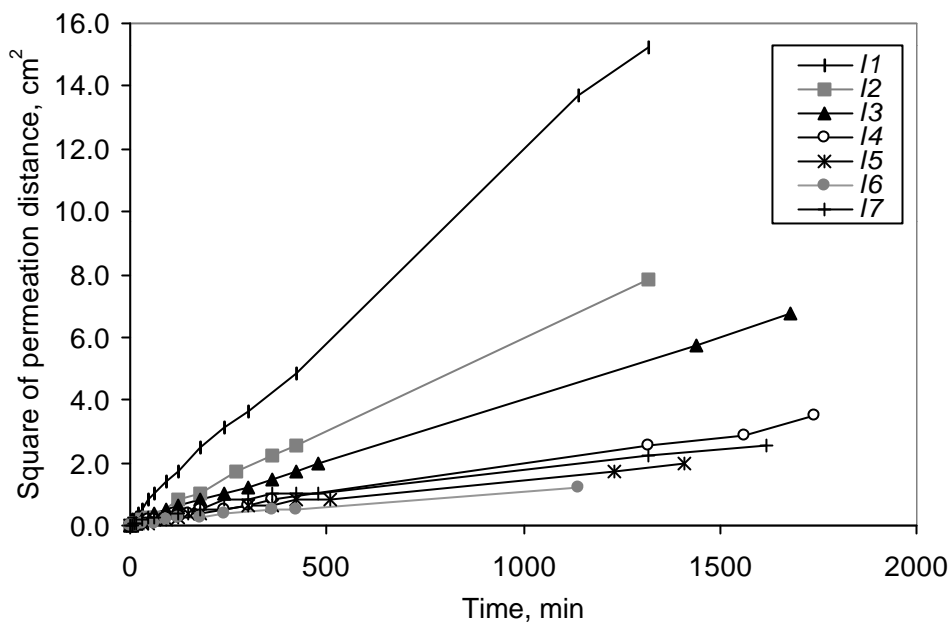
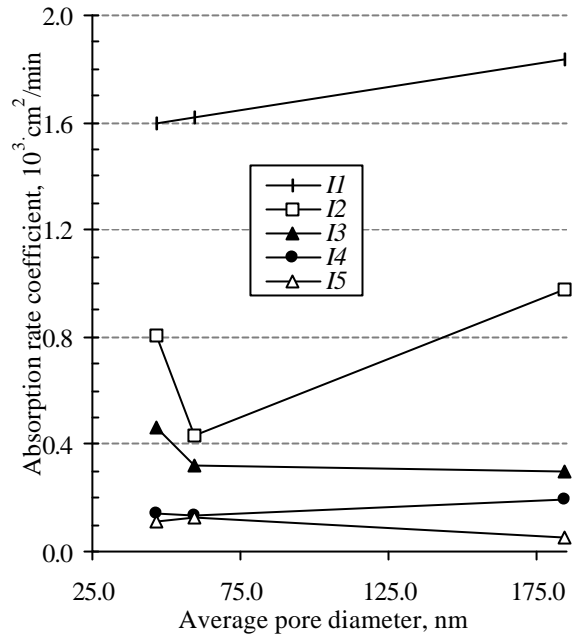
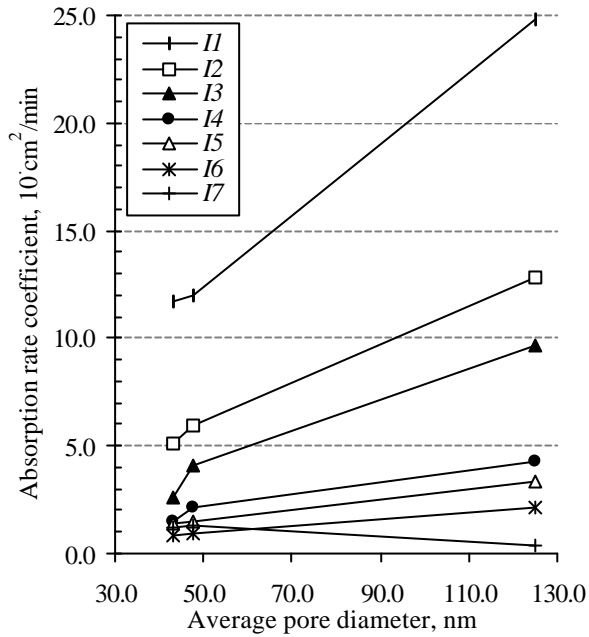


Fig. 3. Linear square root of time dependent absorption of model inks on a carbonate-based structure.

Table 3. Absorption rate coefficients in $10^3 \cdot \text{cm}^2/\text{min}$.

Model ink/coating	<i>I1</i>	<i>I2</i>	<i>I3</i>	<i>I4</i>	<i>I5</i>	<i>I6</i>	<i>I7</i>
<i>C1</i>	24.80	12.11	6.71	4.10	3.38	2.17	0.47
<i>C2</i>	12.00	5.93	3.67	2.16	1.53	0.88	1.48
<i>C3</i>	12.49	4.60	2.28	1.52	1.35	1.03	1.73
<i>C4</i>	8.62	5.90	3.20	2.38	1.47	0.71	1.66
<i>C10</i>	12.05	10.65	6.52	3.32	1.26	1.48	2.10
<i>C12</i>	326.93	300.56	194.28	103.78	51.76	14.22	0.39
<i>C5</i>	1.83	0.98	0.30	0.19	0.05		
<i>C6</i>	3.29	1.06	0.68	0.32	0.17		
<i>C7</i>	1.62	0.40	0.32	0.13	0.13		
<i>C8</i>	1.25	0.70	0.40	0.20	0.43		
<i>C9</i>	1.59	0.71	0.46	0.14	0.11		
<i>C11</i>	1.17	0.36	0.13	0.01	0.05		

Absorption rates are an order of magnitude greater for pure pigment coatings and coatings with just water soluble binder compared to latex containing structures. For given chemistry the absorption rate should increase as the average pore size of a structure increases according to the Lucas-Washburn model, although account must be taken of any change in the number of pores per unit cross-sectional area and their inter-connectivity as the structure changes. This general correlation was found to hold in the case of pure calcium carbonate systems (i.e. for pore sizes $< 0.1 - 0.2 \mu\text{m}$) in all cases except for the most complex model ink, *I7*, containing both types of resins and oils, as shown in figure 4a. With constant amount of latex in a calcium carbonate-based structure the correlation depends on the absorbing liquid, where pure mineral oil, *I1*, gives higher absorption rate with increased pore size but linseed oil, *I5*, an opposite correlation as seen in figure 4b.

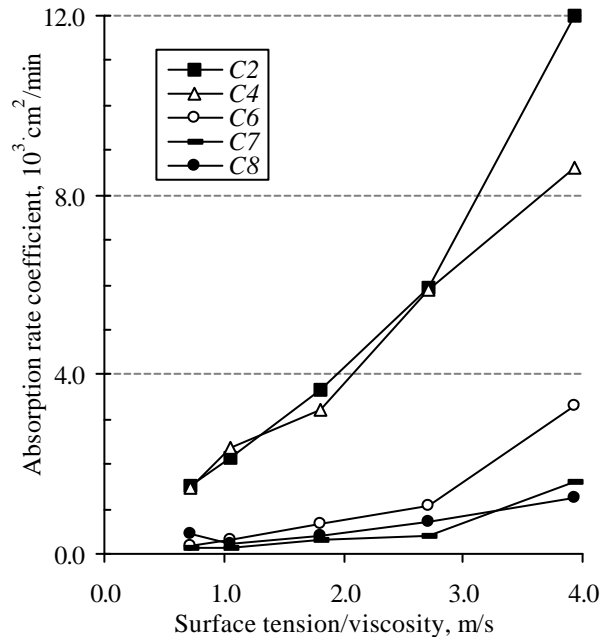
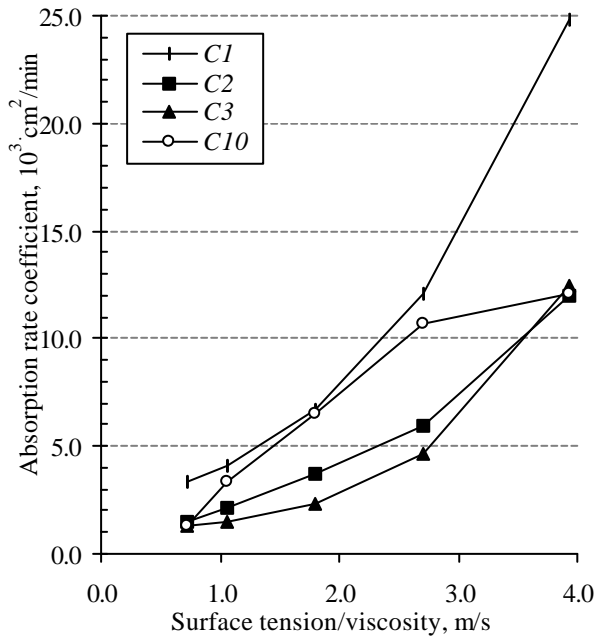


a. Pure pigment structure (C1-C3).

b. Pigment with latex (C5-C7).

Fig. 4. Absorption rate in relation to the average pore diameter of substrate. Model inks I1-I5 present the series of the linseed and mineral oil blends with increasing linseed oil content, I6 is the absorptive containing oils and alkyd resin and I7 contains both oils and both resins.

It has been shown that the flow velocity constant is merely determined by the surface tension – viscosity ratio (gh) rather than either parameter alone (Geiss 1984). This can be viewed in parallel with a Washburn-type absorption constant such that absorption rate decreases with increased viscosity and increase with increasing surface tension of the absorptive. When plotting absorption rate coefficient as a function of gh the correlation should be linear for a given porous substrate. However, in the multi-component absorptives deviation from linearity was found as depicted in figure 5.



a. Pigment structures.

b. Calcium carbonate with added polymers.

Fig. 5. Absorption rate as a function of absorptive properties. Coatings C1-C3 presents the series of ground calcium carbonates of decreasing particle size and C10 is the English clay. Coating C4 contains CMC added to the fine calcium carbonate C2, and series C6-C8 presents the series of addition levels 5, 10 and 15 pph of latex into the pigment/CMC blend C4.

Separation of absorptive components

Ink binders, both alkyd and hard resins, were found to have a negligible absorption length into the coating structure. This is demonstrated in the photograph, shown in figure 6, of the cross-section of absorbed droplets into a tablet structure with the surface tilted toward the viewer. However, both mineral and vegetable oils were found to separate readily from the resins which was also indicated in the absorption kinetic studies. In addition to separation from resins the oils were also found to separate from each other during absorption. As the separation of the oils from each other was thereby reasoned to be one source of non-linear absorption behaviour experiments focused on quantifying separation of mineral and vegetable oils from known mixtures of the two.

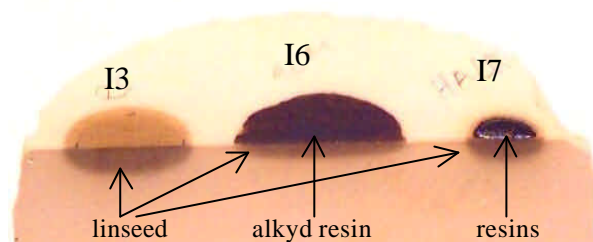


Fig. 6. Separation of oils from resin binder-oil mixture on a calcium carbonate-based coating structure.

In pure pigment structures mineral oil was found to absorb further than the other components. As seen in figure 7 both the ratio of the oils and the coating substrate properties influence the degree of separation. Quite logically the greater the ratio of mineral to linseed oil the greater the difference between absorption length and thereby increased $s\%$ -value. This is also seen in figure 8 in a tablet - droplet sample, where the absorption path of linseed oil reduced as its proportion in the applied mix decreased while the total drop volume and spreading characteristic remain constant. With given coating chemistry, separation is more pronounced as the pore diameter decreases and the surface area increases. More separation occurs in clay- and silica- based structures compared to calcium carbonate-based structures of similar pore size and surface area. Addition of resins into an ink formulation containing equal amounts of mineral and vegetable oils resulted in similar behaviour in respect to the separating media. However, slightly increased values were measured which might be an indication of enhanced release of mineral compared to linseed oil.

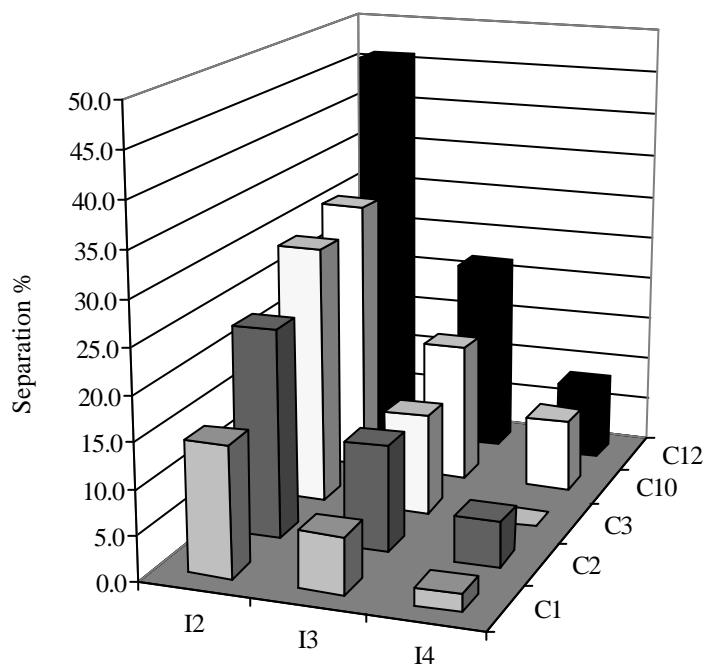


Fig. 7. Separation of linseed and mineral oil on pigment coating structures which do not contain binders. The amount of mineral oil in the absorptive decreases from I2 to I4. Coatings C1-C3 present the series of ground calcium carbonates of decreasing particle size, C10 is the English clay and C12 the Silica structure.

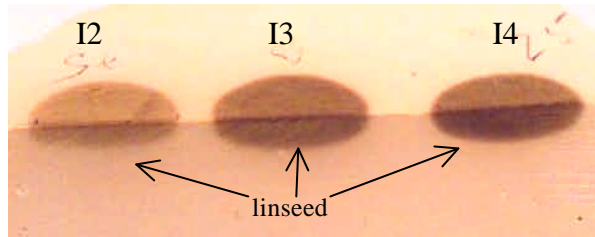


Fig. 8. Separation of linseed and mineral oils in a limited absorptive to substrate ratio. The amount of mineral oil in the absorptive decreases from *I2* to *I4*.

With the addition of latex into the coating formulation the separation behaviour changed in a manner that can not be explained solely by the change in physical porous structure of the coating. Despite the relatively small change in physical porous structure even a 5 pph addition of latex decreased the degree of separation dramatically, figure 9. With 10 pph of latex separation is only detected with a large ratio of mineral to linseed oil and with large surface area.

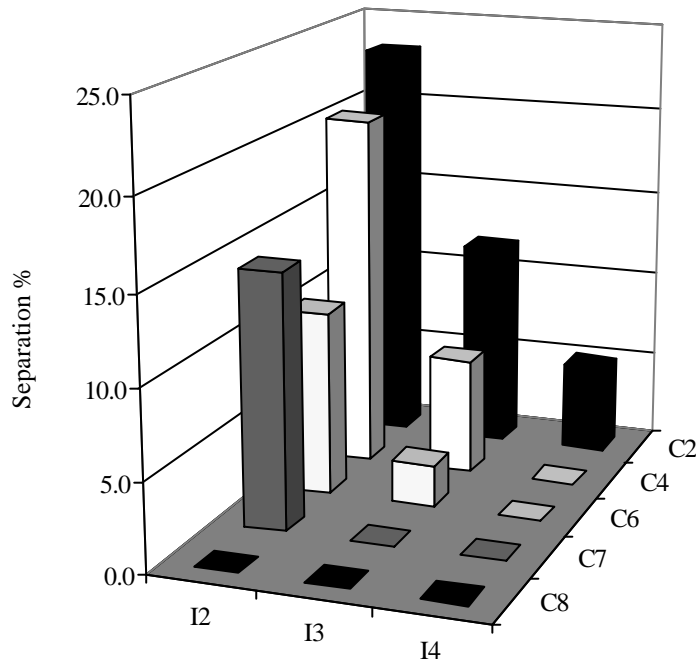


Fig. 9. Separation of linseed and mineral oil on coating structures of varying polymer content. The amount of mineral oil in the absorptive decreases from *I2* to *I4*. Coating *C4* contains CMC added to the fine calcium carbonate *C2*, and series *C6-C8* presents the series of addition levels 5, 10 and 15 pph of latex into the pigment/CMC blend *C4*.

In order to explain the dramatic change in the separation behaviour in the presence of polymers, our first approach was to check whether the total absorption length was insufficient for the separation to occur. Time-dependent separation studies, however, proved that the separation of the oils occurs already in the initial stage of absorption, figure 10, which is also found in actual chromatographic systems (Geiss 1984).

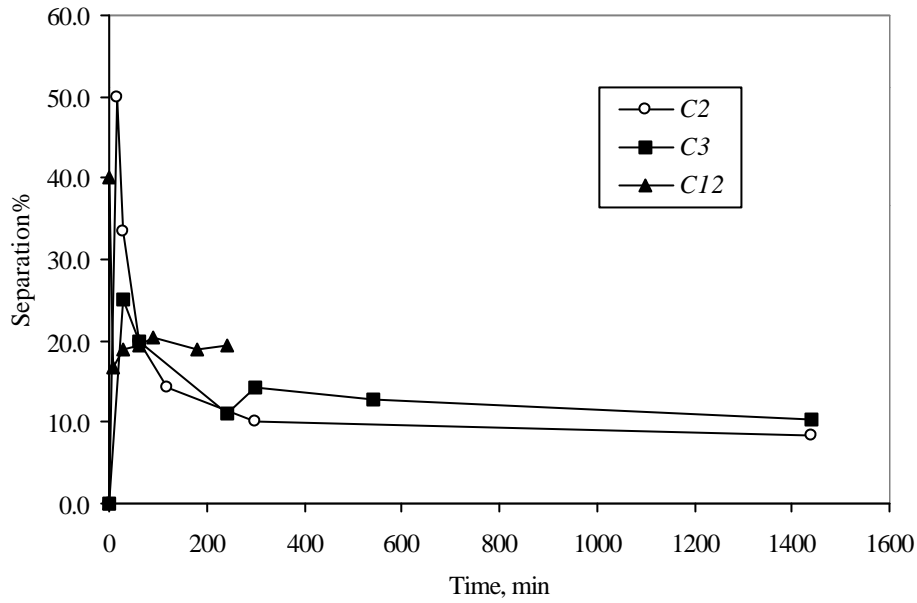


Fig. 10. Time-dependent separation of linseed and mineral oil on coating structures.

Latex Polymer-Oil Interaction

The next step toward explaining the strongly modified separation characteristics with the addition of latex polymers was to determine independently the interaction of latex with the different oils. It was found that linseed oil is absorbed to a significantly higher degree by a latex film compared to mineral oil, figure 11. The absorption was also highly dependent on the latex film drying temperature, i.e. the state of film formation of the latex film. This finding is significant in explaining both the altered absorption kinetics and the change in separation phenomena. Oils did not interact with the carboxymethyl cellulose film.

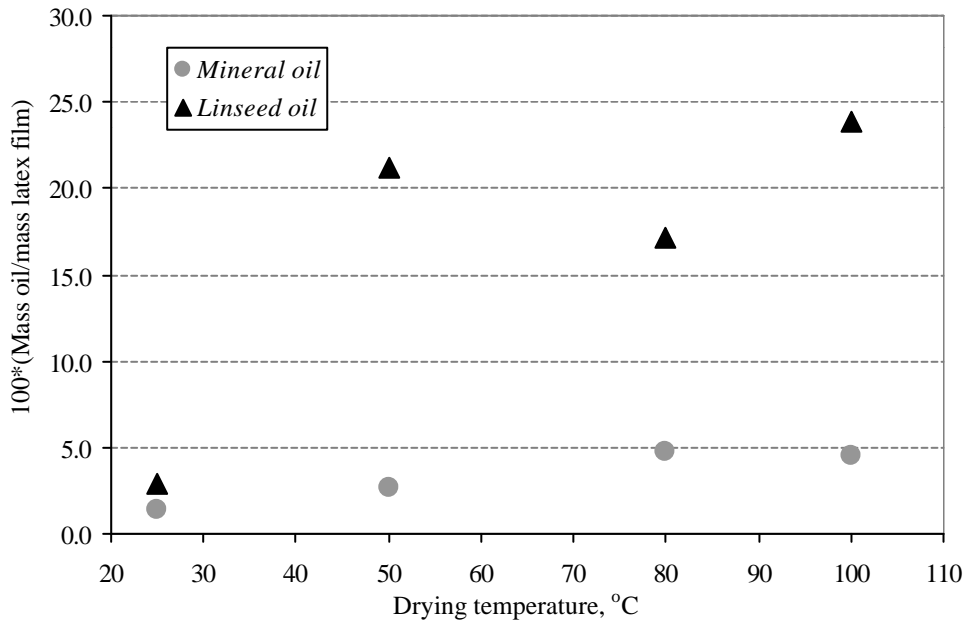


Fig 11. Latex-oil interaction.

DISCUSSION

Movement of the absorption line of offset ink fluid phase chemicals on a thin-layer coating porous structure showed linear square root of time dependency, as depicted by accepting a generalised model of Newtonian fluid absorption in capillaries. However, care should be taken in the interpretation of the data since the apparent absorption line does not necessarily indicate the degree of filling of all capillaries in the structure but is rather a mean value of the menisci height. It was previously shown in a study by Gane et al. (2000) that, despite the ability of all the tested fluids to saturate completely the available pore volume in a pigment structure, the level of individual pore filling at a given time depends on the porosity level, the abundance of fluid and the time of absorption. Given the relative volumes of fluid (~50 %) in a practical ink layer of ~ 0.25-3.0 μm and the available pore volume in a typical coating (25-50 %), the penetration depth assuming complete saturation would also be ~ 0.25-3.0 μm . Clearly, this is far less than the penetration depths used in this macro-scale experimentation. However, if we take the findings of Gane et al. (2000) above, we may consider that the fluid front is progressing by a preferred pathway mechanism being fed by the subsequently filling larger pores in the network. This behaviour occurs at the meniscus front, or absorption line, irrespective of penetration depth and only the rate slows as a result of the extended viscous drag as absorption length increases. In support of this earlier proposition, it was noted in this current work that the absorptive was clearly not homogeneously distributed along the absorption line as a function time. There exists also a concentration gradient along the absorption direction in respect to the degree of saturation (amount of filling of the porous structure) as the meniscus front is approached. This was also seen as deviation from linearity in relation to the absorptive properties. As the components are separated from each other, the surface tension, viscosity and the contact angle do not remain constant during the course of absorption indicating a breakdown of the detailed “constants” in the Lucas-Washburn relationship. Also average pore size was shown to be an insufficient parameter in describing absorption tendency in relation to the porous media. Especially in the presence of latex in the coating structure significant differential interaction was observed with the oils, which influenced the total absorption length and rate. The interaction most probably causes swelling of latex and thereby changes the physical porous structure, which, in turn, might cause blocking of pathways otherwise available for fluid imbibition.

Various separation phenomena are involved in the absorption of offset inks into pigment porous structure. When dealing, as we do here, with practically non-volatile oils the influence of vapour diffusive pre-wetting of the capillary surface can be neglected. Initially the ink pigment particles and high molecular weight ink polymers are excluded mainly by size from absorbing into the fine network of pores in a coating layer (Ström 1999; Hattula and Oittinen 1984). Work of Wickman 1998 suggested that alkyd resin retention is also affected by the strength of chemical interaction with coating chemicals. For the single alkyd and hard resin types studied in this work, the resins are retained at the porous matrix surface and the oil components were easily released from the resin layer for absorption into the porous structure. Although addition of resins to model ink reduced the rate of absorption drastically the degree of separation in the presence of resins was slightly enhanced. This is an indication of effective separation of mineral oil from the composition as linseed oil shows stronger interactions with resins, which was also found by Ström 1999.

Furthermore, our findings showed that separation phenomena proceed beyond the size-exclusion mechanism. Despite relatively similar molecular weight and good miscibility, mineral and linseed oils separated from each other during absorption into porous pigmented structures. Increased separation was detected with increased surface area and with increased surface energy of the substrate. The slightly polar linseed oil was retained preferentially to mineral oil in the polar pigment matrix. As the ratio of mineral to linseed oil increased more effective separation was seen. However, as latex was added and the non-polar nature was thereby reinforced no separation (or possibly reversed separation) occurred. All these findings support adsorption chromatography theory. However, another mechanism is probably involved in the presence of latex in the porous structure. Reduced separation was evident even with such small amounts of latex which are not sufficient to cover the pigment surface completely, i.e. insufficient to change the surface chemistry totally. Therefore, the preferential absorption of linseed oil by latex might be another compelling indication of the potential for reversed separation.

CONCLUSIONS

The main conclusions of this work can be summarised as follows:

- The absorption behaviour of different offset ink oils and mixtures thereof are greatly dependent on their specific properties and should not be treated as one sole fluid but as a separable group of miscible fluids.
- Mineral oil is preferentially absorbed into a polar pigment porous network structure – an effect which can be related to its lower surface tension-viscosity ratio compared to linseed oil.
- Linseed oil is preferentially absorbed into latex films by chemical diffusion.

- Molecule level interactions between fluids and solids are not necessarily identifiable by macroscopically observing absorption kinetics.
- The absorption length of both alkyd and hard resins is short indicating size-exclusion by the fine capillaries of the coating structure.
- High surface area, i.e. small pore size, and increased surface energy of the porous substrate promotes the chromatographic separation of oils. Mineral oil is seen to absorb differentially further into such structures compared with linseed oil.
- Reduced separation, and possibly even reversed separation, of mineral and linseed oils occurs as a function of increased latex content, i.e. reduced surface energy and increased polymer level in the substrate.
- Initial separation of ink components is largely determined by the ink component compatibility for each other whereas coating structure and chemistry are responsible for further separation phenomena occurring during absorption.

Even though the chromatographic separation of ink constituents on coating porous structures was demonstrated here in model systems where the length of absorption is significantly greater than in the initial ink-coated paper interaction on the press we expect that these separation phenomena do contribute to printability and differential print quality. Such printing defects as print mottle (both unevenness in print density and gloss), failure in ink-surface adhesion during tack development and print-through are likely to be related to the differential separation of the ink constituents on and within the heterogeneous coating substrate. These findings are also likely to have significance when considering the formulation of inks, especially when considering the trend to using vegetable-based inks which can be predicted to behave differently in their interaction with coatings compared with mineral oil-based formulations.

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