

INFLUENCE OF COATING PIGMENT CHEMISTRY AND MORPHOLOGY ON THE CHROMATOGRAPHIC SEPARATION OF OFFSET INK CONSTITUENTS

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ABSTRACT

This work is aimed at characterising the chromatographic action of some typical paper coating pigments in relation to the separation and fractionation of offset printing ink components during absorption into the coating void structure, with particular emphasis given to the chemical and structural parameters of the pigments.

The separation phenomenon was studied experimentally using primarily large-scale model systems based on a modified thin-layer chromatography method. The separation of the ink constituents was detected directly from the absorption path using Fourier Transform Infra-Red (FTIR) microscopy. The coatings were characterised for their physical properties using mercury porosimetry, and the absorbing fluids for their viscosity and surface energy. The ink-coated paper contact on the realistic scale

was evaluated using the concept of ink-on-paper tack development. Coating pigments used in the work included typical paper coating grade ground calcium carbonates, fine clays of different origins, as well as talc and precipitated calcium carbonate. The choice of pigments provided the possibility to investigate independently the chemical and physical aspects of pigment properties on the constituent fluid separation. Ink chemicals included representatives of the most typical offset ink components; namely mineral oil, linseed oil, ink resins and ink pigment. A blend of mineral and linseed oils was used as the main test fluid.

The differential interaction or adsorption-desorption on the pigments leads to separation of the mixture of mineral and vegetable (in this case linseed) oils as they are absorbed into the pigment coating structure, where the more polar linseed oil is preferentially retarded in the structure composed of the more polar pigments. The degree of the separation is directly proportional to the surface area of the pigment within a group of chemically and morphologically identical pigments. It is also affected by the surface chemistry of the pigment but more so in comparing dispersed and undispersed pigments, and polar versus non-polar rather than between the chemically different hydrophilic dispersed pigments. Pigment morphology strongly influences the macroscopic flow behaviour due to changes in physical porous structure (pore size, porosity, tortuosity). The macroscopic flow behaviour, which is affected by all of the above-mentioned structural and chemical parameters of both the solid and liquid phases, proved to be a universal parameter determining the separation efficiency of the oils by affecting the retention time. Added ink resins in the oil mix retards the overall absorption rate of the oils, but does not affect the separation tendency of the oils in most of the cases studied, except in cases where less polar pigments or dispersions are involved. Adding latex into the coating structure, on the other hand, creates an additional gradient for separation of the oils as oil diffusion into the latex provides further selectivity.

INTRODUCTION

Ink setting on coated paper involves a number of complex mass transfer mechanisms, which all influence the printing operation and the final print quality. The predominating mechanisms are determined by the properties of the absorbing fluid phase in relation to the geometry and surface energy properties of the coating structure. The rate and final result of the absorption depends on the ink composition and the separation of the fluid components from the remaining viscosifying ink layer [1], and of the properties of the coating matrix. The spatial distribution of the ink constituents in the ink layer itself as well as in the upper-most few micrometers of the coating layer determine the print density and gloss. Another potential cause of heterogeneous distribution of ink constituents is differential ink spreading at the ink-coating interface. The uneven and non-optimal distribution of these components can be contributing factors to printing defects like print mottle (both density and gloss related), chalking, failure in ink-surface adhesion during tack development and print-through [2].

The absorption of the ink fluid phase is driven by permeation forces acting between the coating porous structure and the absorbing fluids, and by the polymer matrix associated with binders and co-binders in the coating layer. Research on ink absorption behaviour on coated paper has concentrated very strongly on the effect of the coating on the absorption dynamic and has thereby neglected the relative and competitive properties of the absorbing fluid(s). The multi-component nature and the significance of the fractionation of the ink constituents during absorption have, nevertheless, long been realised [4–7].

In our previous work, we showed that a pigmented coating chromatographically separates the individual components of an offset ink as it is being absorbed [8]. It was demonstrated that the ink resins and pigments are mostly excluded by the size of the molecules and particles from absorption, yet a multi-component fluid composing of different oils and possibly some low molecular weight fractions of the ink resins absorbs readily into the coating structure. The absorbing fluid mixture components were found to be most effectively fractionated by the coating pigments. The coating latex, on the other hand, was found to form another gradient for the separation of the ink components, as the association of the ink oils and coating latices is strongly dependent on the particular properties of these chemicals [9].

This work here concentrates on the characterisation of some typical paper coating pigments in relation to the properties that lead to separation of the fluids in multi-component inks. In particular, the pigment chemistry and morphology are studied.

THEORETICAL BACKGROUND

Boundary conditions for offset ink separation during ink setting

Offset printing inks are highly viscous dispersions consisting of solid ink pigment (10–20% by weight), dissolved resins (20–40% by weight) and miscellaneous additives (0–10% by weight) in an oil-based carrier phase (30–50% by weight). The resin-oil compatibility is the first prerequisite in choosing the suitable resins and oils. The real choice is, however, made on the basis of the desired end-product properties and cost, as well as taking into account practical functionality issues. Usually several different types of resins and oils are needed to meet these requirements. In most cases a large molecule size hard resin is used (typically modified rosin esters or hydrocarbon resins), which require heating to high temperature for solution in the oils. Additionally, alkyd resins are intensively used. These include a large variety of polyester type polymers, which are blended/dissolved in a vegetable oil (typically ~50% oil content). In most cases a combination of a mineral oil and a vegetable oil, usually linseed, soya or vegetable oil esters, are added to the formulation in order to meet the solubility, rheological and ink setting/drying requirements. The ink pigments are fine solid particles insoluble to the resin-oil varnish. Most of the offset ink pigments are hydrophobic organic particles in a size range of ~0.01–0.5 μm produced from petroleum chemicals [10,11].

Paper coatings are composite structures of pigments (50% by volume), binders (20–30% by volume) and air (25–35% by volume). These structures are often anisotropic as a result of pigment morphology and/or directional application and drying forces. Pore sizes in coatings range from less than 0.02 to 1.0 μm , the average being approximately 0.1 μm . Polar pigments, such as calcium carbonate and clay, form the major part of such porous structure matrices. The paper coating pigments are practically non-porous particles possessing fairly low surface areas in the order of 10–20 m^2/g . Water soluble polymers are added in levels of 0.5–2 pph (parts per hundred by weight of pigment) to improve the operational properties, such as rheology and water retention, of the coating colours during the coating application. Latex (typically including styrene, butadiene and acrylic copolymers) addition levels of 10–20 pph are used in offset papers to bind the coating pigments to each other and to the basepaper. The polymers affect the packing of the pigments by flocculation in the wet state and, especially during the drying stage of the coating structure formation, by causing shrinkage and inter-particle bond formation. They also contribute to the coating chemical properties by lowering the effective surface energy in papers [12] where concentration of binder polymer may be high and by contributing amphophilic properties where

significant quantities of surfactants and stabilisers are used which tend to concentrate on the coating surface.

In offset printing, an ink film of 0.25–3 μm thick is transferred onto the coated paper surface from the printing blanket. With approximately 50% oil in the ink and 25–50% porosity in the coating the total absorption length of the ink solvent is thus also in the order of 0.25–3 μm . Therefore, the whole coating structure, which usually is 5–15 μm thick, is not completely saturated by the absorbing ink fraction and can normally be discussed independently of the absorption properties of the basepaper. However, there are likely to be cases in light weight and in multicoated grades where basepaper or pre-coating respectively play an important role, especially when preferential pathway absorption may result in deeper penetration than would be expected from the simple saturation calculation [13]. The separation and absorption of the low viscous fluid phase of the ink is known to occur after the printing nip [14]. Therefore, no external force or pressure gradient is present in the absorption which is solely driven by the permeation difference between the absorbing fluid and the coating structure. The overall absorption rate of the bulk fluid in the coating structure thereby sets the time limitation for the possible rate-determined separation phenomena by determining the retention time in contact at the fluid front. In actual multi-color printing, the very short-time absorption is, naturally, of most interest as the printing speeds continue to increase, but the overall ink setting takes minutes and the final consolidation, i.e. distribution of the ink chemicals in the ink and in the coating layers, is known to last for days.

Ink setting through absorption

Two mechanisms have been identified as the major driving forces for absorption in a coating structure; these include capillary absorption and diffusion into the coating binders. The capillary absorption phenomenon, relating to coated paper, is considered to be the predominating mechanism and it has been a subject of a number of fundamental investigations [15–23]. In addition to the capillary-driven absorption mechanism, diffusion of ink solvents into the latex component of the coating layer is known to play an important role in the ink-coating interaction [8,24–27]. The ink solvents have been shown to diffuse into the latex, to cause swelling and even to dissolve the latex, thereby to cause structural changes in the coating structure, and to affect the mode and rate of ink setting.

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 [28,29].

$$h^2 = \left(\frac{r\gamma \cos\theta}{2\eta} \right) t, \quad (1)$$

where h is the penetration depth, t time for penetration, r the equivalent hydraulic pore radius of a single capillary or the effective mean value of the radii in a porous matrix, γ the surface tension of the absorbing fluid, η its viscosity and θ the three phase contact angle between the fluid and the solid at the free surface with air.

The quadratic law of liquid movement as a function of time is moreover a general statement of the laminar flow of Newtonian liquids in a single capillary or in a bundle of capillaries (presenting a simplified model for a porous structure), and was already discovered by Darcy in 1856 [30]. Also the parameters describing the contribution from the fluid properties (γ/η) is a general relationship found by a number of researchers in different fields as reviewed by Geiss [31]. Experiments conducted in model systems with single solvents or oils in coatings support at least a generalised form of the Lucas–Washburn theory [15–17,20]. However, in all practical studies of ink absorption on coatings contradictory behaviour is found [2,5,32,33]. Disagreement on the influence of pore size of the substrate is widely discussed suggesting the inability of a sole average parameter to account either for the complex porous structure or the detailed physico-chemical nature of the absorption dynamics. In many cases the experimental parameters of the absorbing fluid are adjusted or neglected. An improved model taking into account the viscosifying ink layer was suggested by Schölkopf et al. [1]. In other work by Schölkopf et al. [23], the Bosanquet equation [34] was employed to consider the inertial effect in absorption into a porous network consisting of a range of pore sizes, matching for the first time the experimentally determined liquid-solid interaction with the observed rate of absorption into a compacted porous structure, whilst maintaining the constant parameters of surface energy.

Practical complications of conducting fundamental research on the parameters and mechanisms influencing absorption in porous structures include the need for reliable measurement of several influencing variables and the fact that many of the variables are inter-related. For example, the surface free energy characterisation of powders cannot be conducted with any simple method (such as static contact angle measurement), but requires methods that are influenced by absorption dynamics in a structure generated from the powder, such as dynamic contact angle measurement from sessile droplets on pellets or IGC (inverse gas chromatograph). Chibowski [35] and Siebold [36] among others have used a thin-layer wicking approach to identify the

polar and non-polar surface free energy components of pigments. They use the Lucas–Washburn equation for calculating the contact angle between the porous structure and well-defined liquids by observing the absorption rate of the liquid.

When observing the absorption wetting line as a function of time, i.e. following the visual liquid front, a draw-back is clearly seen in that the absorption volume follows a gradient of saturation level toward the absorption front. For the wetting parameters to be determined from the Lucas–Washburn equation, the whole porous structure is assumed to be necessarily filled with liquid. However, the apparent gradient of saturation indicates that this is not so. This is known as the frontal gradient in the field of thin-layer chromatography [31]. Additionally, the pre-adsorbed layer of the liquid on the solid surface through the volatility of the liquids is very significant for the result. Another difficulty is associated with the characterisation of the porous structure properties. Many of the methods used in paper science are indirect end-property related measurements like gloss, air permeability or printability, which do not reveal information concerning the real porous structure parameters like pore size, porosity, connectivity etc. Direct methods include imbibition, which again relates to the absorption properties of the porous structure and a well-defined absorbing fluid, and microscopical/spectroscopical techniques. Mercury porosimetry has gained wide acceptance also in the characterisation of coatings, but several considerations must be taken into account in the interpretation of the data, as demonstrated by Gane et al. [37].

Aspects of multi-component mass transport in porous media

The major difference in the transport of multi-component fluids in porous media, compared to the single-component system, is that during multi-component transport the differential molecular level physico-chemical phenomena occurring at the boundary of the solid and liquid phases become important. These differential interactions with the solid are unique for each component in the liquid mixture and lead to the fractionation of the liquid components. This, on the other hand, is the particular cause of the dynamic changes in the bulk liquid absorption character as both stationary and liquid phase properties alter (surface tensions, viscosity, contact angle etc.) during the course of absorption. This leads to non-linear absorption behaviour and explains partially why the models derived for single-component systems do not fully apply in more complicated systems like ink-coating interactions.

Multi-component transport in porous media is present in many industrial applications, for example in catalysis, in chemical reactors, in oil recovery and in chromatographic processes, of which liquid chromatography resembles

most closely the case of ink-coating interaction. Chromatographic processes encompass a group of separation techniques for analytical, preparative and research purposes, where the general feature is that a mobile phase flows along a stationary phase and the different components of the mobile phase are retarded to different extents. This feature is realised in a number of different process technical solutions mostly including practices where the sample fluid components are separated with the help of an external carrier solvent and the sample is introduced to the system as a pulse feed. More resemblance to the case of ink-coating systems is represented by the *frontal analysis* mode, where the sample to be separated is introduced to the system as a step change and it continues to flow in the porous matrix as such [38,39]. This frontal analysis technique has quite limited use for the modern chromatographic applications (more so in continuous fixed-bed chemical separation reactors), and in the chromatographic sciences it is mainly discussed as a defect resulting from a multi-component carrier solvent separating undesirably during the analysis procedure (solvent demixing, autochromatography [31,38–41]).

As already indicated, even the single-phase flow in porous structures is a very sophisticated process and difficult to predict by theoretical means with sufficient correlation with reality. The theoretical description of separation processes, on the other hand, includes another order of magnitude more complex differential equations. Most of the equations derived for chromatographic operations are derived for specifically designed cases, and are therefore of limited applicability in systems relevant to our scope of interest. Also, reference to chromatographic separation during non-pressurised absorption conditions is only relevant in thin-layer chromatography. This is why the theoretical equations on the chromatographic applications are not presented here, and some aspects are only discussed in a qualitative manner.

Separation mechanisms and factors affecting separation efficiency

The phenomena leading to fractionation of an initially miscible liquid mixture may be (a) preferential *adsorption* on the liquid-solid interphase, (b) *partition* based on solubility difference between the bulk liquid and an adsorbed thin layer of liquid, (c) *size-exclusion* (permeation) in which molecule size is the separating factor, or (d) *ion-exchange* relying on ionic strength differences. In practice, a combination of several mechanisms is often present, and all could take place also in the case of an ink absorbing in a coating structure. The dominating mechanism for separation, its direction and efficiency depend on both the solid and the liquid phase properties [31,38–41].

The direction of the separation refers to the arrangement of the most and

least retained components. In so-called normal or straight phase chromatography systems, the stationary phase of the system is polar and the mobile/carrier phase is a non-polar organic solvent. Thereby polar molecules are attracted to the solid phase and retained in the system. In reverse phase systems the solvent is more polar than the solid matrix and thereby the less polar components are retarded [31,38–41].

The activity of the solid phase surface contains two components; namely a surface energy contribution and a surface area contribution, both of which are directly proportional to separation efficiency. The particles used in chromatography are larger in size compared to coating pigments, and have significant internal porosity within the particles and therefore high specific surface areas (~200–1000 m²/g). As a very few pigments are of practical interest for chromatography, namely silicas, alumina and modified silicas, the surface energy parameter is mainly discussed in relation to the pre-adsorption of the mobile phase components or diffusive vapours on the solid surface. The physical porous structure influences the absorption rate of the solvents and thereby influences the volumetric capacity, resolution and the rate of separation. Basically, large surface area with moderate size and rather narrow particle size distribution solid phases are considered favourable [31].

In the most commonly used modes of thin-layer chromatography the carrier solvent is an active component of the separation system, its properties being of equal importance for the system performance as those of the solid phase. In the frontal analysis mode though, where no carrier phase is present but the components separate from the original solution, the miscibility/solubility of the liquid components is the dominating factor. The order of increased retention in normal phase adsorption chromatography for organic compounds is: saturated hydrocarbons, olefins, aromatic hydrocarbons, ethers, esters~aldehydes~ketones, alcohols and carboxylic acids [31,39–41].

Chromatographic separation of printing ink constituents

The use of the chromatographic theory to explain the absorption behaviour of pigmented inks, such as offset ink, has not been used intensively prior to our work [8]. Separation phenomena are, however, demonstrated and acknowledged to be of importance in printed media [4–7]. The origins of liquid chromatography are in the fractionation of coloured components like soluble dyes. The chromatography of soluble dyes is thus very well-established, and this knowledge has been implemented to explain the separation during absorption of ink-jet inks [42], which are more often one-phase systems based on soluble dyes.

Although the applicability of the chromatographic theory for pigmented inks is hindered by the insolubility of the pigments, chromatography finds applications also in the analysis of such inks. Chromatographic analysis of printing inks has importance in forensic sciences, in the study of historically valuable works, in quantifying the toxicity of inks etc. [43–50]. Chromatographic techniques for the printing inks are usually used as the first and preparative stage of the analysis, and it is usually followed by thermogravimetric or elemental analysis of the separated substances [47]. The publications even on the analytical side are, however, quite sparse and the information gained is of limited use in the prediction of printing ink performance.

Most of the offset ink components themselves are mixtures of molecularly different substances. For example mineral oils (or petroleum distillates) are composed of a wide range of alkanes in the order of C_7 – C_{24} as well as paraffinic, naphthalenic and aromatic components. Vegetable oils, on the other hand, include a variety of different fatty acids. The fractionation of these has also been the subject of interest and moreover a challenge for the chromatographic sciences. The separation of these oils is thus possible [39], but hardly relevant to offset printing of coated paper. Polymers, or ink resins also contain a wide distribution of different molecule size polymers. The fractionation of polymeric materials by molecular weight, on the other hand, using permeation chromatography is quite commonly applied for analysing alkyd resins. This mechanism may also have significance in the case of the resin fractionating during ink setting.

EXPERIMENTAL APPROACH

Materials and sample preparation

(i) Pigments and binders

The main variables under study here are the pigment chemistry and morphology. Ten commercial coating pigments were chosen. These included a series of ground calcium carbonates (GCC) differing in their mean particle size (HC60, HC90 vs. SC)¹ and in their particle size distribution (SC vs. CC)¹. Other pigments included fine clays of English, U.S. (SW95, AG respectively)²

¹GCC Products of the Hydrocarb (HC), Setacarb (SC) and Covercarb (CC) families, and co-structure pigment (V40) supplied by Omya AG, Postfach 32, CH-4665 Oftringen, Switzerland.

²English clay Suprawhite (SW) and US secondary clay Alphagloss (AG) supplied by Imerys, St. Austell, Cornwall, England.

and Brazilian origin (AM90)³, talc (C10)⁴, a precipitated aragonitic calcium carbonate (A40)⁵ and a special co-structure pigment of talc and GCC (V40)¹. Principally, all the pigments were tested as dispersed according to the supplier's instructions or pre-slurred by the supplier. The clays and the carbonates, thus, include approximately 0.1–0.3 pph sodium-polyacrylate dispersant equivalent. The talc and talc-carbonate co-structure were pre-dispersed products. The influence of the pigment dispersing agent itself was investigated by comparing a dispersed and an experimental dispersant-free quality of a ground calcium carbonate (CC vs. CC-pure). The work concentrated on characterising the chromatographic separation properties of the dispersed pigments alone, but they were also all tested in combination with a constant amount, 10 pph by weight of pigment, of a commercial styrene-butadiene coating latex (DL940, particle size 0.15 µm, Tg 22°C)⁶. Also a series of different addition levels of latex was studied with two of the pigments, a fine GCC (HC90) and the English clay (SW95). A detailed description of the pigment properties given by the pigment suppliers along with the abbreviations used in this and later text is given in Table 1.

The pigment slurries were coated with and without binder on glass plates

Table 1 Coating pigments and their properties.

Product name	Pigment type	Particle size <2 µm	%w/w <1 µm	BET area /m ² /g
HC60	GCC	60	36	7.1
HC90	GCC	90	62	12.4
SC	GCC	97	80	16.1
CC	GCC	95	75	9.8
SW95	English Clay	92	81	15.0
AG	US clay	94	83	21.0
AM90	Brazilian Clay	97	95	17.4
C10	Talc	46		4.8
V40	Talc + GCC	85	63	8.8
A40	PCC	median particle size	0.4 µm	10.0
CC-pure	GCC undispersed	95	75	9.8

³Amazon clay (AM) supplied by Kaolin International B.V., De Bleek 11, 3447 GV Woerden, Holland.

⁴Finntalc (C10) supplied by Mondo Minerals, Laurinmäenkuja 3B, FIN-00440 Helsinki, Finland.

⁵Opacarb (A40) supplied by Speciality Minerals, FIN-21600 Parainen, Finland.

⁶DL940 is a latex from Dow Suomi Oy, PL117 FIN-00101 Helsinki, Finland.

with a laboratory draw-down coater using a blade geometry. The pigment-only coatings were dried at room temperature, whereas the coatings containing latex were dried at 80°C for 30 minutes in order to ensure realistic latex film-formation. This procedure resulted in an applied coating layer of approximately 100 g/m². For the ink tack printability tests the coating colours including the latex binder were coated on a synthetic non-permeable basepaper⁷ with a rod and dried at 80°C for 5 minutes to give a coat weight of approximately 12 g/m².

(ii) Porous structure determination

In order to characterise the physical porous structure of the dry coating layers, the coating suspensions were additionally coated onto a non-porous polyester film the same way as the synthetic papers. These coated films were then analysed with mercury porosimetry (Micromeritics, Autopore III), and the results were corrected for sample vessel expansion, mercury compression as well as for sample skeletal compression effects, as proposed by Gane et al. [37]. The support polyester film was confirmed to be non-porous by mercury porosimetry analysis, however it showed to be highly compressible at high pressures. This compressibility was subtracted from the result by the correction for skeletal compression. The porosity values were recalculated from the measured values of sample vessel volume, total sample volume and mass, proportion of the coating vs. support, density of the polyester film and volume of intruded mercury into the sample. The porous structure properties of the thin-layer coatings including the mean pore size and porosity values measured are gathered in Table 2.

(iii) Fluids/ink formulations

A 50/50 mixture (by weight) of commercial grade linseed and mineral oils⁸, which is one of the most commonly found ink vehicle mixtures, especially in sheet-fed offset inks, was used as the test fluid phase for studying the separation of ink oils in the coating structure. The mineral oil was a low aromatic oil with boiling point of 280–310°C. Each oil, and mixes thereof, were analysed for surface tension using a Krüss Digital Tensiometer K10T with ring-configuration. The viscosities were also measured with a Paar Physica rheometer at low shear rates (<100 s⁻¹). All properties were measured at 23°C. The oils are seen to be miscible, i.e. they form to a close approximation a single phase solvent for the ink as indicated by the nearly linear change in viscosity and surface tension as a function of the proportion of oils (Figure 1).

⁷Synthetic basepaper, Synteape® is a trademark of Arjo Wiggins, Itäranta 7 FIN-02110 Espoo, Finland.

⁸Sicpa Oy, Myllypuronkatu 30, FIN-33330 Tampere, Finland.

Table 2 Porous structure properties of coating structures.

Pigment	Porosity /%	Median pore size/nm	Pigment + 10 pph latex	Porosity /%	Median pore size/nm
HC60	23	256	H6D1	15	250
HC90	28	103	H9D1	24	115
SC	18	75	SCD1	12	81
CC	21	110	CCD1	24	160
SW95	24	147	SWD1	19	110
AG	30	53	AGD1	19	60
AM90	30	56	AMD1	18	76
C10	29	290	C1D1	8	276
V40	22	200	V4D1	19	191
A40	27	127	A4D1	26	137
CC-pure	16	303		–	–

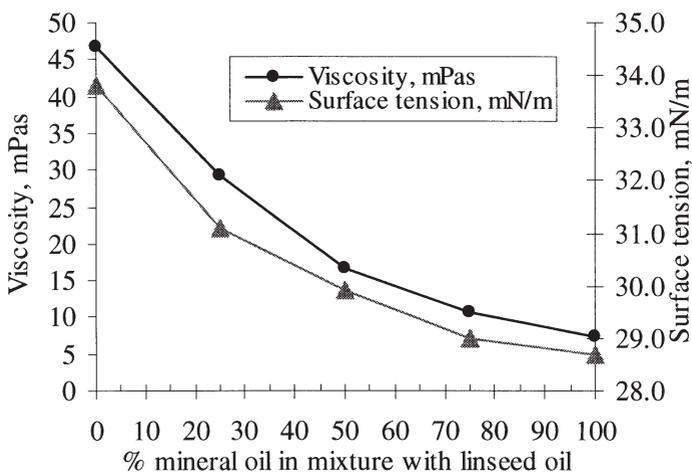


Figure 1 Miscibility of mineral and linseed oils as indicated by viscosity and surface tension values.

A typical linseed oil-based alkyd resin and a large molecule size rosin were used as representative resin polymers as an additional step toward an ink formulation. The separation of the linseed/mineral oil mixture within the model structures was studied first applied as a pure oil blend only and secondly in the presence of the ink resins, and finally with a composition containing a cyan ink pigment. For the ink tack/setting test, a specially manufactured ink including the same resins and the 50/50 blend (by weight) of the same oils was produced incorporating an additional cyan pigment⁸. The level of ink resins and pigmentation follow those given in Table 3.

Table 3 Test fluid/ink formulations expressed as % by weight.

Mineral oil / %	Linseed oil / %	Alkyd resin / %	Rosin / %	Cyan pigment / %
50	50			
37	37	20	7	
34	34	6	17	9
22	22	10	30	16

Absorption and separation on model structures – thin-layer chromatography

A modified thin-layer chromatography approach [8], TL-method, was applied to detect the separation of the ink constituents on an enlarged scale. The coated glass plates, as described above, were cut into approximately 3 cm x 10 cm size platelets. A scale of 1 mm graduation was marked on the sides of the platelets and the samples were conditioned at constant temperature and humidity (23°C and 50% RH) before usage. The test fluid was first inserted in a thin-layer chromatography chamber, whereafter the coated glass platelets were placed vertically in the chamber. The initial level of liquid was approximately 0.5 cm and the level of rising liquid front was observed as a loss of opacity, seen as a progressing translucency as a function of time, using a light source to study the absorption kinetics.

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 cm⁻¹ proved to be the most useful analytical method for the TLC 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 upper-most point at which oils are present is detected by the presence of a strong peak at approximately 2925 cm^{-1} representing the organic compounds. The mineral and linseed oils can be separated only by the difference in the carbonyl absorbance at approximately 1740 cm^{-1} , which is very strong for linseed oil but not present in the case of mineral oil. The separation of the oils is, thus, only detectable as the absence of linseed oil meaning that this method is only applicable to cases where mineral oil absorbs further than linseed oil. This, however, is seen to be the case with all pigments as they are hydrophilic and apparently retain the more polar linseed oil preferentially to the non-polar mineral oil. The separation character of an absorptive-substrate system is presented quantitatively as a separation %-value, $s\%$, equation 2.

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

where $s\%$ is the separation percentage, L_t the total absorption length and L_i the absorption length of component i .

The value of $s\%$, therefore, represents separation efficiency independently of total absorption. The absorption and separation experiment was repeated three times for each coating and fluid/resin mixture combination, and the average of these was taken. A standard deviation of approximately 10% was found.

Absorption was allowed to proceed for approximately 20 hours. This long time-scale was chosen to ensure that the separation had reached equilibrium, as the separation was seen to be initially strongly time-dependent but to eventually stabilise as seen in Figure 2. The separation character of the pigments measured after equilibration, therefore, gives values, which are essentially independent of measurement time. This time-dependent effect is suspected to be related to the differential pathway dynamic identified by Gane et al. [22] and accentuates the separation tendency over short times associated with certain fine, short pore structures within the network – an observation of clear practical implication when considering thin layers of applied inks in which the effect of separation could be expected to be strongly heterogeneous on a short timescale.

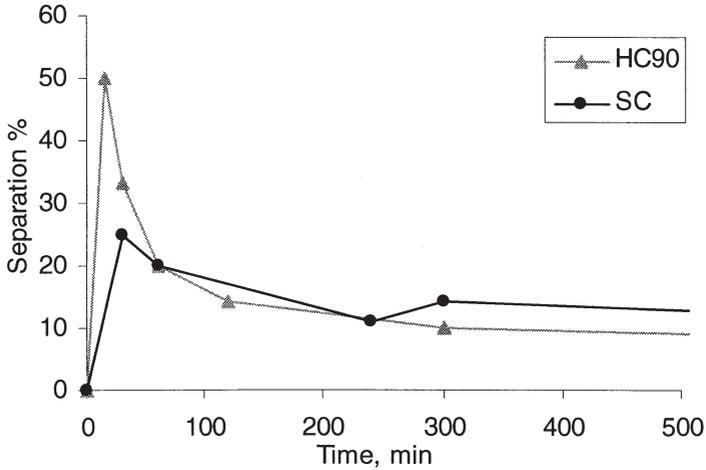


Figure 2 Time-dependency of ink oil separation.

Ink setting

The Ink-Surface-Interaction-Tester (ISIT⁹) was used to study the ink setting character of the well-defined ink on the different coating substrates. In this method the tack force development of the ink, freshly printed on the coated paper, is detected as a function of time. It thus provides an analysis of the tack behaviour from the initial tack rise caused by the ink fluid phase absorption into the porous coating structure until the final consolidation of the ink layer through the various mechanisms of polymerisation and adsorption of resins. A more detailed description of the device hardware and analysis procedure is found in the publication of Gane and Seyler [2]. A standard level of ink application was attained using an IGT ink distributor. Three repetitions were performed for each ink-coating combination during a maximum of 20 minutes of elapsed time from the initial application of the ink to the distributor. A printing speed of 0.5 m/s and nip pressure of 50 kgf were used. These conditions result in approximately 1 g/m² of ink being transferred onto the paper.

⁹ISIT is a product name of SeGan Ltd., Perrose, Lantyan, Lostwithiel, Cornwall PL22 0JJ, U.K.

RESULTS AND DISCUSSION

Influence of pigment morphology and coating structure on the separation of ink oils

The specific pigment surface area (m^2/g) is a critical parameter describing the chromatographic separation activity of the solid phase, especially if controlled by an adsorption-desorption mechanism. In Figure 3, the separation of the oils is plotted against the BET-surface areas of the pigments. In the widely accepted BET-method [51] the specific surface area is defined by measuring the number of nitrogen atoms (for which the atom cross-section is known) adsorbed as a monolayer on the sample surface at the temperature of liquid nitrogen. The series of dispersed ground calcium carbonates is seen to follow very well a linear relationship, where increased available surface area leads to increased separation. Even the dispersed precipitated calcium carbonate (aragonite) fits onto the same linear plot as that of the dispersed ground calcium carbonates (calcite).

Looking at all the pigments as a single group, increased separation is generally found with larger specific surface area, but the pigments of different chemistry and shape do, however, deviate from the linear relationship established for the dispersed carbonates. This deviation could be related either to the surface energy/reactivity differences between the pigments and/or to their

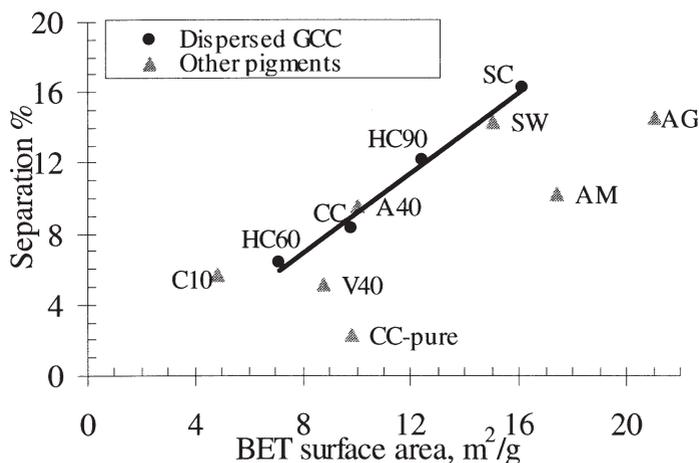


Figure 3 Dependence of the separation of mineral and linseed oils on the pigment packing structures. The line shows the dependence on the surface area of dispersed carbonates.

differential packing. The pore structure formation character of the pigment particles is strongly affected as the pigment shape changes from blocky to very high aspect ratio particles, for example from blocky calcite or low aspect ratio secondary clays to high aspect ratio English clay, or from undispersed aggregates to dispersed single particles, and by the particle size distribution of the pigment with the same individual particle shape.

The particle shape difference between blocky calcite and needle-like aragonite, as seen above in Figure 3, is insufficient to induce this deviation effect. Based on this finding, packing anisometry is assumed to be a minor factor in itself when considering the long time-scale separation at equilibrium unless combined with either surface energy and/or surface area differences which can affect interaction or flow. At shorter times, however, if we consider a proposed preferred pathway dynamic [22] there will be a tendency initially to expose the higher surface area finer pores at the fluid front. These, in turn, will therefore exert a greater separation as a function of surface area. Thus, packing effects, which change the pore size distribution, will be likely to dominate separation behaviour at short time-scales. Similarly, packing differences that strongly retard the wetting front absorption rate by viscous drag will effectively include this short time-scale relationship occurring continuously at the fluid front with the higher surface area regions of the structure acting differentially at each stage of the absorption such that the cumulative effect is likely to be seen over longer time-scales. These issues are now investigated further in the following sections.

Influence of pigment surface chemistry on the separation of ink oils

The pigment surface energy can affect the separation of ink fluid constituents in two different ways. On the one hand, the pigment surface energy influences the affinity/adsorption tendency of a particular component of the liquid mixture at the liquid-solid interface. On the other hand it affects the bulk rate of absorption of the fluid by affecting the contact angle and thereby the wetting between the solid and the liquid. If separation occurs, the absorption rate should thus change as the composition of the absorbing fluid changes.

In order to study the influence of surface energy on the separation of the ink oils independently of the individual pigment particle morphology, a “pure” specially produced dispersant-free carbonate (CC-pure) was compared with the dispersed equivalent having exactly the same particle size distribution. The pore size distribution will change significantly when comparing an undispersed flocculated/aggregated system with a fully dispersed one (see Table 2). Therefore, this methodology alone cannot extract independently the surface chemistry effect from the wetting pathway dynamic as

defined by the packing characteristic, but is valid in respect to constant particle surface area.

The use of a sodium-polyacrylate dispersant increases the pigment polar surface energy and, as a result, makes the pigment surface more hydrophilic. Due to the electro-negativity imbalance between the sodium ion and the carboxylic group on the acrylic polymer, the surface also becomes hygroscopic. As seen in Figure 4, the increased hygroscopy and/or change in packing characteristic effectively increases the separation of the oils.

The comparison of differently dispersed coating pigments in respect to their surface energy is hindered by the many intractable problems related to the measurement of the surface energy of powders as discussed in the theory section. As the pigments used here are of technical grade, and therefore contain a variety of impurities, values found in the literature for pure single crystal surfaces are assumed in detail likely not to apply. Additionally, it is difficult to subtract the influence of the pigment morphology, i.e. the shape and particle size distribution and pigment packing parameters, and the effect of absorption occurring simultaneously with wetting leading to sub-surface spreading and subsequent assisted surface wetting.

According to the wetting rate data, derived from observing the wetting front, the porous structure properties of the coating layer were shown to play a more important role in the absorption transport kinetics than the surface energy effects when comparing the different pigments. Increased rate of the

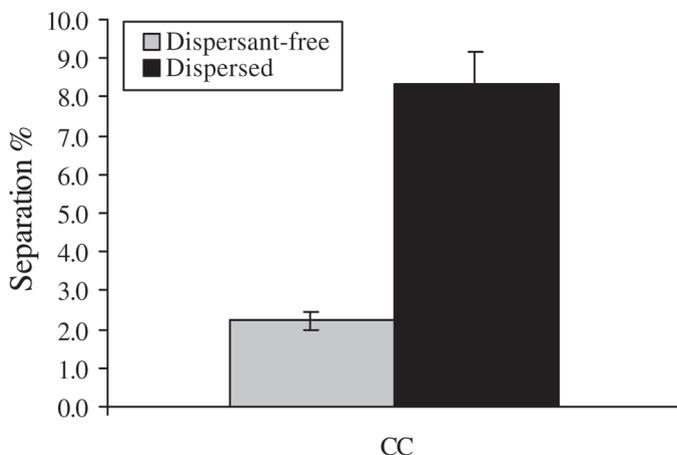


Figure 4 Influence of the pigment surface energy on the separation of ink oils.

absorption front was seen to strongly correlate with increased pore size of the coating. Calculated values for contact angle using the Lucas–Washburn approximation were very similar for all pigments, a slightly lower value was calculated for the American and Brazilian clays and non-dispersed pigment. The same was seen with pure mineral and linseed oils as well as with the oil mixture.

An indication of the surface energy contribution of the different pigments on oil separation, however, can be revealed by dividing the separation value with the surface area as the surface area was shown to be linearly proportional to the separation efficiency within a given chemical group of similar morphology (Figure 3). As indicated in Figure 5, the separation efficiency of the pigments increases in the order: *undispersed GCC*, *dispersed Brazilian clay* and *co-structure talc-carbonate V40*, *dispersed fine U.S. clay*, *dispersed fine English clay*, *dispersed GCC* and *dispersed aragonitic PCC*, and *dispersed talc*. The separation efficiency values of the four GCCs and the aragonitic PCC are rather similar, supporting the original proposal of surface area controlling the separation within a chemically similar group. The separation efficiency of the talc-carbonate co-structure V40 is similar to that of clay supporting the comparison made by Gane et al. [52] that this co-structure emulates in some respects the action of clay in respect to both rotogravure printability and matt/silk offset print rub resistance. The dispersion of talc alone is a unique case in itself, as the dispersant markedly differs

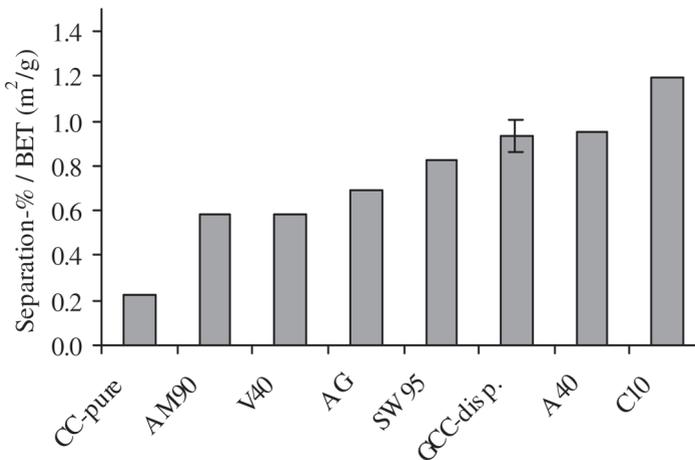


Figure 5 Influence of the pigment type on the separation efficiency of ink oils.

from that used for the other pigments in that it incorporates a necessary surfactant wetting agent to render the naturally hydrophobic talc surface hydrophilic and therefore compatible with water-based dispersions.

We therefore conclude that the minor surface energy differences between the various fully dispersed pigments is not a dominating factor in respect to the separation phenomenon, but that there must be another mechanism which may be related to the observed rate of permeation of the wetting front.

Rate of absorption and residence time: influence on the separation of ink oils

Capillary absorption in a porous structure is influenced both by the physical porous structure character as well as the surface chemistry relationship between the solid and the absorbing fluid. The absorption rate data, when taken as the slope of wetting front distance against time in these thin-layer coatings, are seen to be nearly linear despite the separation of the components as seen in Figure 6. Faster long-time penetration is seen with increased pore size in the structure, as predicted by the Lucas–Washburn equation, but is also affected by the pore size distribution, tortuosity and pigment surface chemistry.

In Figure 7 the separation efficiency is shown as a function of the absorption rate constant of the particular coatings. The absorption rate constant is determined as the slope from the relationship presented in Figure 6, and thus

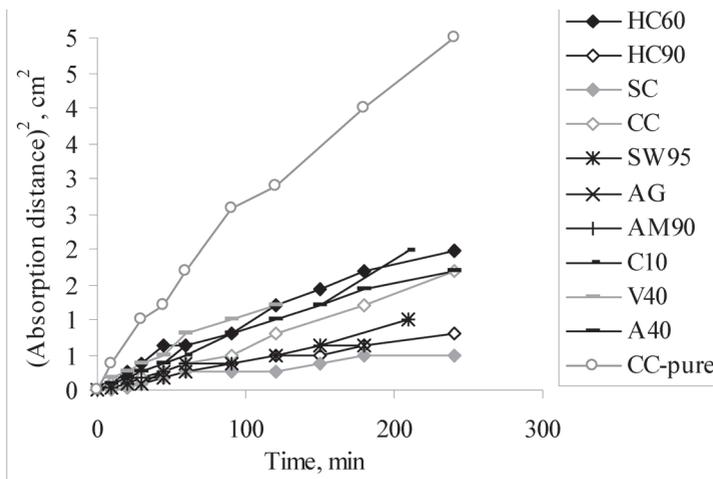


Figure 6 Linear square root of time dependence of absorption distance.

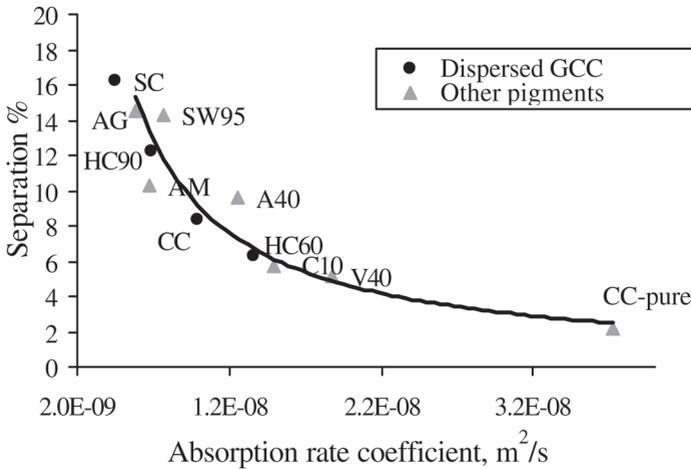


Figure 7 The universal curve of separation of linseed and mineral oils as a function of absorption rate.

has units of m^2/s . As the rate of wetting front absorption increases, the separation of the ink oils is reduced. The relationship is not linear, the separation approaches zero as the absorption rate approaches infinity.

Faster movement of the absorption front means reduced residence time per unit surface area for separation. This is apparently the critical universal parameter for the separation over the range of pigments studied here. The effect of residence time supports the action concluded in the previous sections, namely the greater separating action of the higher surface area pores involved in providing the greatest driving force for absorption when resistance to flow is at its highest in low permeability structures. This universal parameter also includes the effects of surface chemistry, packing, particle shape factor and, therefore, pore size distribution and pore morphology.

Influence of ink resins on the separation properties

So far, we have discussed the separation of two initially miscible oils during absorption into a structure based on dispersed coating pigments, and in one case an undispersed pigment. In adding typical ink alkyd and hard resins into the 50/50 mixture of mineral and linseed oils, the separation of the oils in the porous structures formed of either carbonate or clay was found to follow the same trend as was seen when no resins were present in respect

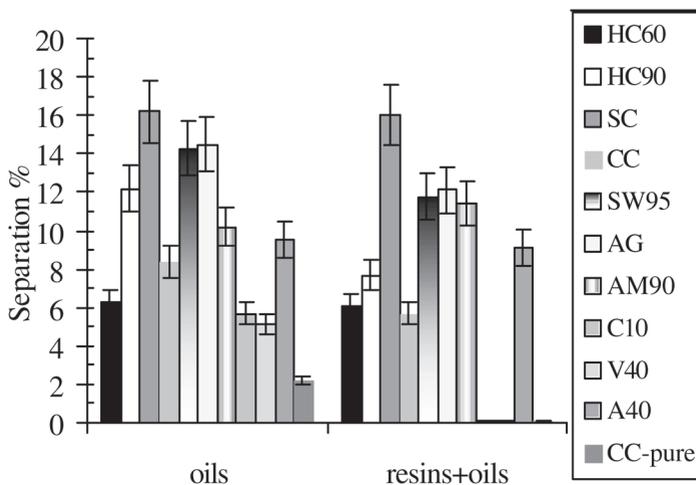


Figure 8 Comparison of the mineral and linseed oil separation character with and without the presence of ink resins.

to both the coating pigments and also quantitatively (Figure 8). Thus, the oils separate from the varnish readily as a complete 50/50 mixture while the ink resins are excluded from absorption, i.e. the permeation of resin into the coating pores is effectively restricted by the size of the resin molecules [5,8], such that the oils behave as a separate phase and there is little or no interaction between the resins and the coating pigments in the bulk of the structure. The preferential retention of linseed oil by the ink resins found in previous experiments [9] does not show in this case.

A major difference in the separation when ink resins were added was found, however, with the talc, the talc-GCC co-structure and the undispersed GCC. In these cases, no observable oil separation occurred when ink resins were added, whereas the oils separated in the absence of resins (Figure 8). We must remember that the measurement method by FTIR microscope views only the absence of linseed oil in comparison with the wetting front position. It does not eliminate the possibility that mineral oil is completely excluded from or retained by the surface structure. This cessation of separation in respect to advancing mineral oil could be explained either by the inability of the large pore size, highly permeable structures to effectively separate the ink resins from the fluid. This is, however, opposed by the fact that separation is not affected from the addition of ink resins in the case of the large pore size HC60 pigment. Another explanation could be that the non-polar mineral oil

has sufficient residence time to become adsorbed onto the talc component and the less polar undispersed carbonate due to the slower absorption rate in the presence of the flow resistive resin structure concentrating on the outer surface. This observation correlates well with the long term resin-controlled surface tack setting phenomenon described by Gane et al. [52] for the talc-GCC co-structure seen as characteristic of improved resistance to print rub. Despite the high oil separation efficiency in the presence of dispersed talc seen with the oils alone, the mechanism is transformed into one of complete oil or differential mineral oil retention and adsorption when the resins are present.

In an earlier study it was also shown that the proportion of mineral and linseed oils present in the oil mix has a significant influence on the degree of separation in the structure [8]. Hence, the ratio of oils delivered into the bulk of the structure, as either a function of retention by the excluded resin or retention of oil and/or solved resin by the surface layer of the structure will play a crucial role in the separation phenomenon.

Looking at the absorption dynamics of the oils absorbing from the resin-oil mixture in Figure 9, it is clearly seen that the absorption of the oils requires a certain time before the actual absorption rate increases in most of the systems. The resins have retention ability towards the oils as the resins

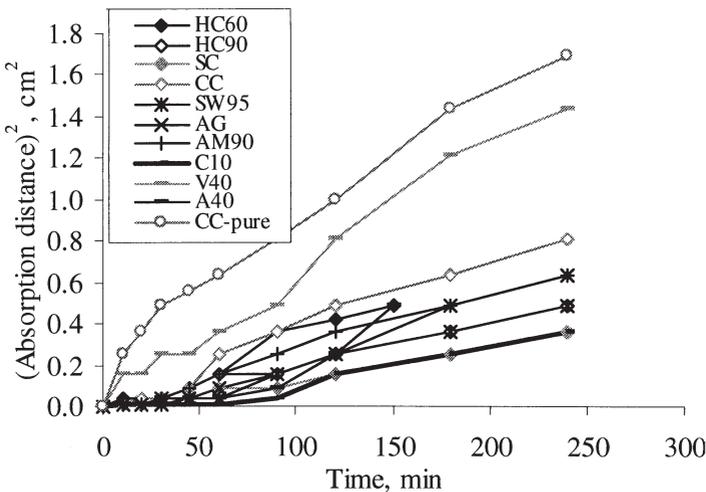


Figure 9 Absorption kinetics of an oil mixture separating from a varnish on different coating structures – note the region of initial slow absorption for most systems except that of the talc-GCC co-structure and that of undispersed carbonate.

initially form a stable solution with the oils, i.e. a varnish. This is seen as a region of very slow absorption, or nearly zero, in the absorption curves, thereafter the absorption proceeds following approximate square root of time dependency. The region of initially slow absorption is different for the different pigments, but the equilibrium absorption rate has initiated within 60 min in all cases. As an exception, a clearly defined slower region is not observed for the talc-GCC co-structure nor the undispersed GCC, but, compared with the plain oil absorption, still a significant drop in the rates of absorption is seen. This is again interpreted as a strong apolar affinity/adsorption due to the undispersed nature of the talc held within the co-structure [52]. Again, as absorption proceeds it follows an approximate square root of time dependency.

Influence of coating latex on the separation of ink constituents

Addition of latex binder into the coating formulation at an addition level of 10 pph by weight of pigment changed the absorption and separation character in the thin-layer chromatography experiments drastically with all pigments. The rate of absorption dropped significantly. Nevertheless, the oils were still seen to be absorbed from a resin-oil mixture. The pore distribution of the coatings did not change dramatically although an overall decrease in porosity is detected, as the pigment is still a major and dominating structural component in a coating containing 10 pph of film-formed latex (see Table 2).

Separation of mineral oil ahead of linseed oil within the structure was no longer detected. We again must remember the limitation of this observation in that this only means that we could not detect the faster transport of mineral oil in respect to linseed oil and does not preclude that linseed oil may in fact be transported faster than mineral oil. This confirms earlier work in which it was seen that this latex type preferentially absorbed linseed oil driving the linseed oil front further into the structure than in the case of pigment only [8,9]. The differential interaction or diffusion of the different ink oils into the latex counterpart of the coating structure creates another possible mechanism for the chromatographic separation of the ink components, which resembles the principles used in gel-permeation chromatography. The long time-scale of the experiment to achieve spatial resolution allows extensive swelling of the latex (as a function of oil-latex interaction), thereby blockage of the coating pores, preventing further absorption. The limits of the spatial resolution of the FTIR microscope system are also not good enough to differentiate between the absorption regions associated with latex and pigment separately.

A fine GCC and an English clay were further tested for the addition limit at

which separation can still occur. This limit was found to be 4 pph for the clay and 6 pph for the calcium carbonate as seen in Figure 10. The fact that none of these coatings were calendered means that the permeability is at a level relevant to that of matt papers. Clearly, the permeability of gloss papers would be much less, and, if we accept the finding that permeability in relation to residence time at the fluid front is the key to the oil separation mechanism, we cannot exclude the possibility that the separation mechanism could still exist at higher latex levels in gloss papers.

Ink setting on coated paper

Ink setting was studied on coating structures formulated with the same coating pigments as used in the separation studies with a constant amount, 10 pph of latex, in order to see the effects of the ink component separation in the ink setting. The coatings, as previously described, were made onto a synthetic non-absorbent basepaper to eliminate any effects due to differences in coating holdout, migration of fluid components into the basepaper etc.

A well-defined ink containing a 50/50 blend of mineral and linseed oils as the ink vehicle was used with the same resins as previously studied together with an additional cyan pigment. The results of the ink-coating interaction measured as tack development (Figure 11) are thus comparable in relation to the ink contribution and the latex-ink interaction and should only depend on

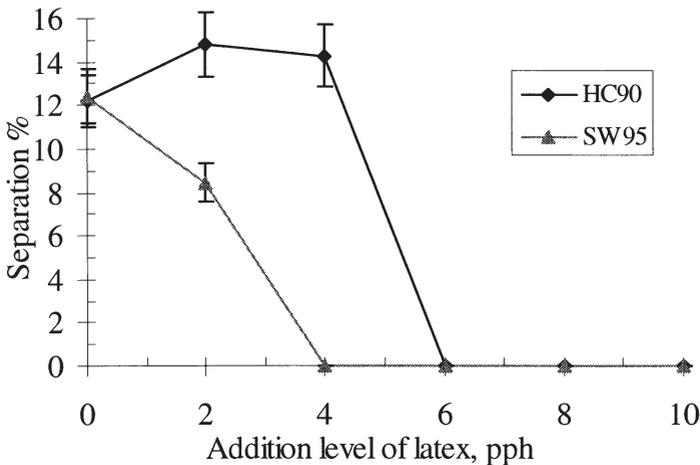


Figure 10 Separation of ink oils in the presence of coating latex.

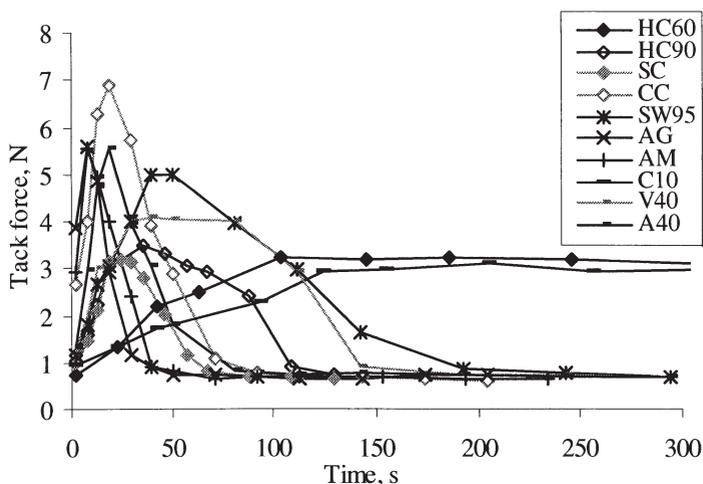


Figure 11 Ink tack cycle/setting for the different pigment coating structures containing 10 pph of styrene butadiene latex.

the structural and chemical interaction between the absorbing portion of the ink, the coating pigment and the pigment pore structure modified in relation to a fixed amount of latex.

Faster separation of ink oils from the ink is seen with reduced pore size in the coatings as indicated by increased slope of ink tack rise in Figure 12. The relationship is, however, seen to be affected by a number of other parameters as well. The effect of the pore size distribution is shown to be significant as the narrow pore size distribution structure created by the CC-pigment deviates from the otherwise linear correlation of the GCC series. Also the shape and chemistry of the pigment affect the rate of oil removal from the ink, but additionally the differential separation characteristics may contribute to the setting character.

The absorption rate measured here with the ISIT-test is not to be confused with the observation made using the TL-method in which the faster moving fluid front was associated with coatings of higher permeability in the case of pigment structures (Figure 6). As mentioned already in the theory section, this inverse correlation of the effect of pore diameter on absorption dynamics observed in model structures (and predicted theoretically) and in real ink-coating interaction has attracted a lot of research efforts. The faster apparent absorption of the oil phase into larger pore size structures in the TL-method was also indicated when observing the oil

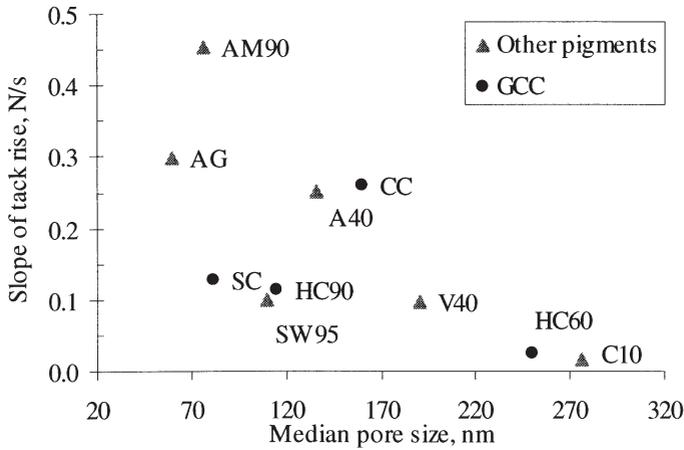


Figure 12 Ink tack cycle/setting for the different pigment coating structures containing 10 pph of styrene butadiene latex.

absorption from a full ink composition, i.e. including ink resins and pigment. Thus, the ink composition is *not* effecting the apparently reversed absorption rate behaviour. The key to this confusion probably lies in the definition of the fluid front in the Lucas–Washburn equation. The theory assumes saturation of the void structure such that the position of the fluid front is itself a measure of the volume of fluid absorbed. As we discussed earlier, the structure is not necessarily saturated. If we consider the observations made by Gane et al. [22], where it was seen that the penetration of a fluid is anomalously deep in the case of highly porous samples, indicating incomplete filling of the pore volume available, we see that penetration distance cannot be assumed to be a measure of absorbed volume. Schölkopf et al. [13] go on to explain this by inertial differentiation of different pore sizes excluding some combinations of large pores. The tack of an ink is, however, related to the actual absorbed volume of oil, and therefore the two must not be confused, i.e. the properties of the ink respond to the volume of oil loss into the coating whereas the TL-method observes only distance travelled by the oil front.

CONCLUSIONS

The separation of offset ink constituents was quantified in respect to the coating pigment chemical and morphological characteristics using a thin layer chromatographic method identifying the fluid front and its composition by a combination of direct white light illumination and separate analysis by FTIR microscopy techniques. Separation of ink oils into polar and non-polar components was observed to occur within a pigment coating structure, with retardation of the polar component. Different pigments behave differently. In our observations, dispersed calcium carbonates of different single particle crystal morphologies form a simple relation in respect to chromatographic oil separation as a direct function of pigment specific surface area. Undispersed pigment, dispersed clay pigments of different origin and talc containing formulations develop a variety of surface chemistry and pore structure effects all affecting the observed chromatographic separation of the oils. The permeability to the wetting front observed in terms of the rate of progress of the wetting front, as it affects residence time in relation to pigment surface area, is shown to be the universal controlling parameter for the fractional separation of the oils over the wide range of structures studied.

The action of resins in an offset ink is seen as a retardational effect on the initial and long term absorption, and differentiates further the various pigment chemistries and structures. Highly porous permeable structures do not have the capillarity necessary to remove oils so effectively from the resins except in the cases where high affinity through apolar interactions is introduced into the structure either by using oleophilic talc in a co-structure with carbonate or by the omission of sodium polyacrylate dispersing agent.

Inclusion of a typical styrene butadiene latex, suitably heat dried, increases the imbibition rate of the slightly polar linseed oil. At levels above ~4 pph by weight in uncalendered coating structures, the chromatographic separation in favour of mineral oil transport is no longer seen. However, the effect of the latex on ink setting through the preferential latex-driven absorption of the slightly polar linseed oil, swelling and pore closure, is observable in respect to offset ink tack measurements when including ink pigment within the ink formulation. Study of the rate of wetting front progress, using the thin layer chromatography method, showed that the rate determining step in respect to tack rise of a complete ink is determined by the capillarity of the coating. This capillarity is seen to be greater in the case of low permeability fine pore structure coatings or in the case where non-polar affinity is introduced into the surface chemistry properties of the coating. It can be concluded, therefore, that observing the wetting front only during absorption into highly porous structures ignores the likely unsaturated nature of these structures.

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Transcription of Discussion

INFLUENCE OF COATING PIGMENT CHEMISTRY AND MORPHOLOGY ON THE CHROMATOGRAPHIC SEPARATION OF OFFSET INK CONSTITUENTS

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All the work you have presented here relates to cold offset printing. You provided us with further understanding of ink components separations looking at pigments. What is striking from your results are the structural effects on the shape of the pigments or the pore distribution provided by the pigments. For instance, the fact that the slope of the ink tack decreases with the mean pore size is a very interesting result. To move closer to heat-set offset, the time delays between and ink setting should be in the order of one to two seconds (from first printing unit to heat-set oven). So if you would extrapolate your work to these time delays, do you believe that the actual ink structure would still have such an importance? Or would it resume to a mere paper surface effect and nothing more; i.e. paper roughness and ink coverage with a minor effect of offset ink constituents separation?

Sanna Rousu

I believe that the mode of absorption – how the oil separates initially, as well as the penetration depth will affect the final drying by evaporation as well as the depth of the separation – how the oil separates initially from the ink.

Patrick Gane

Patrice, you've raised a very important issue here, and I think it indicates that one has to understand the ratio of timescales of different coating structures

Discussion

while absorbing ink vehicle and the question is whether it is possible to have zero interaction, which is what you are saying when we had large pores, and still have a satisfactory print? In some cases that may be possible. I think the danger is where you sit halfway, you're getting some interaction, but it is not necessarily on the right timescale for the printing and we see this for example where we consider matte coatings in sheet offset or where we consider particle size distributions that are extremely steep – where we do not have the fast-acting pores. In those cases, we end up with problems of print-rub and so on, but I think the direction of this work is to try to understand what role does chromatographic separation play in these phenomena like print-rub, and do we really need the action of ultra-fine pores or at least a controlled amount of them? In the case of heat set, the temperature increase reduces the viscosity of the ink and they absorb faster. Residence time is the universal parameter for chromatographic – faster absorption gives shorter local residue time.

Tetsu Uesaka Paprican

When you benchmark different pigment systems, in terms of percent separation, is it really appropriate to measure the in-plane separation rather than the thickness direction separation because many of the pigment systems have sometimes quite strong anisotropy, the separation properties are different between the in-plane and thickness direction, because of the pigment orientation. Particularly after calendaring although it is not calendared in this study. When you look at the in-plane direction only, perhaps your conclusion maybe quite different for separation among the different pigment systems? The result you obtained by measuring in-plane separation maybe different from the reality that we are really interested in, which is the thickness direction separation. Is this relevant to the actual separation of any oil in the ink system in actual offset printing processes?

Sanna Rousu

With the different blends, it will affect the whole macroscopic absorption rate and thereby also the specific interactions and the separation phenomena and that will probably be different. The ink layer on the surface does not know in which direction the separation occurs. Our study is to show that surface chemistry effects a separation.

Patrice Mangin

From your results, I believe there is a kind of chromatic effect into the

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separations and the blends of different pigments wouldn't affect too much, unless you find and I haven't seen it in the data, that the shape of the pores would also affect this kind of separation – which is not what you've been doing.

Sanna Rousu

Through affects to absorption rate, it will affect the separation.