

DIFFERENTIAL ABSORPTION OF OFFSET INK COMPONENTS ON COATED PAPER

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ABSTRACT

In this work offset ink setting on coated paper was investigated, the main emphasis being on the influence of the chemical interactions between the ink and coating components. The differential absorption of the ink components from different ink formulations on a series of well defined coating layers of various chemical and physical character was studied.

Ink – coating interaction was studied as tack development of the ink during a time period of 3 seconds to 15 minutes after impression on coated paper using the SeGan Ink-Surface-Interaction-Tester (ISIT) device. Inks were developed progressively from a simple oil fluid phase to a pigmented ink by the addition of a known amount of each ink chemical one at a time. The ink compositions and components were characterised for their physical properties, namely for viscosity and surface tension. Model coatings were prepared in the laboratory by hand-coating on synthetic base paper following the same procedure as that of the inks, i.e. starting with binder alone and then progressively adding cobinder together with a variety of pigments, firstly a fine ground calcium carbonate, then comparing this with a coarse ground calcium carbonate and finally with the structure formed using a clay.

The main contributing factors to the ink consolidation and setting behaviour are the release of the fluid components from the ink composition, absorption of the released fluid into the porous structure as well as its diffusion into the polymer matrix of the coating layer and adhesion of the ink resins to the coating surface. Experiments showed that the rate of ink setting is highly dependent on the properties of the fluid phase separating from the ink composition. The compatibility of ink chemicals for each other, on the other hand, determines the type and quantity of the released fluid or fluid mixture. Preferential interaction of the different oils with coating components was also seen to influence the rate of ink setting. The information gained serves to enhance the understanding of the prevailing mechanisms and importance of the variables influencing the ink – coating behaviour and illustrates the chromatographic separation effects that take place in the pigment and latex structure matrix and how they influence the surface properties of the ink during and after the printing process.

Keywords: Coating – ink interactions, chromatography in porous structures, differential absorption, printing, offset ink tack.

INTRODUCTION

High productivity and improved printed product quality place pressure on the stringent demands for product development of both paper surface properties and ink formulations. The fundamental understanding of the interactions between these highly complex systems, namely ink and paper coating, is the basis for enhancement of the quality and profitability of the printed medium. In addition, this knowledge is essential to meet the increasing

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environmental obligations, such as efficient material utilization, reduced emission of volatile organic components and enhanced de-inkability.

Offset ink setting is known to result mainly from capillary imbibition of the ink fluid phase into the coating porous structure. Pressure balance and inertial effects between the highly viscous paste-like offset ink and the fine porous structure coating layer prevent pressure driven penetration at the printing nip /1/. Additionally, chemical diffusion of the ink fluids into the polymer matrix of the coating layer is also known to be an important factor in ink transfer, setting and final consolidation. However, the contribution of the ink properties, and those of the absorbing proportion of it, to ink absorption and thereby to ink setting have not been studied systematically.

In our previous work, we defined the non-linear absorption behaviour of offset inks on coating porous structures resulting from the differential separation of the absorbing multi-component ink fluid phase in the interactive pigment – latex coating matrix /2/. The objective of the present study is to observe the significance of these fundamental findings using pure fluids in the more realistic case of a complete offset ink and in respect to the ink - coating interactions as monitored through ink tack development. The work includes chemically and physically well-characterised systems in order to understand the actual mechanisms resulting in the observed behaviour, whilst maintaining realistic levels of industrial chemicals.

We establish a programme of experiments starting with simple oils and their interaction with latex binders and then with a coating colour based on fine ground calcium carbonate using different levels of binder. Progressively, other ink components are added to identify their effects on the combined interactions of inks and binders in the same given pigmented coating. Finally, the effects of coating structure are studied by changing the pigment particle size and type.

BACKGROUND

Offset Ink Chemistry and Formulation

Offset printing inks are highly viscous dispersions in which the solid pigment particles are dispersed in an oil based varnish consisting of dissolved resins and miscellaneous additives. Ink pigments (10 – 20 w/w-%) are insoluble fine particles, which give the ink its visual identity and contribute most to the cost of the ink formulation. Resins (20 – 40 w/w-%) are used to bind the pigment particles to the paper, to give gloss and to control rheological properties. The oil based carrier phase (30 - 50 w/w-%) provides necessary fluidity to the ink and, due to its progressive loss into the coating, determines the ink setting and drying mechanism. In addition to the main components, inks include a variety of additives (0 - 10 w/w-%), such as waxes, filler pigments and oxidation control aids /3,4/.

Offset ink pigments must have the highest possible colour strength characteristics due to the thin printed colour film (0.25 – 2 μm). They also must disperse well into the binder – solvent system, and be hydrophobic in order to prevent interaction with the fountain water. Most offset pigments are synthetic organic particles in a size range of ~ 0.01 - 0.5 μm produced from petroleum chemicals. Ink pigment particle sizes, and the pigment shapes vary from round to needle-like and platy, thereby also contributing to the rheological behaviour of the ink /4/.

Mineral oils (or petroleum distillates) used as solvents in the offset inks vary in boiling point and aromatic content. They are generally weak solvent power, non-polar and non-drying fluids composed of paraffinic, naphthaenic and aromatic hydrocarbons in the C_{16} - C_{18} range /3,4/. Vegetable oils and their derivatives are increasingly used as solvents and binders in offset inks due to their diverse properties, and on the other hand for their environmental soundness as a renewable resource. Vegetable oils are slightly polar mixtures of fatty acids like linolenic, oleic and linoleic acids. Their properties vary in drying and binding ability depending on the number and nature of double bonds present. The extended use of purely vegetable oil based inks has been prevented due to the generally slow setting behaviour and problems associated with de-inkability. However, vegetable oils can be easily modified by, for example, esterification to induce the desired behaviour /3,4/.

An oleoresinous vehicle, including a hard resin and a drying oil alkyd, is used in most offset inks /3,4/. The benefits of alkyd resins include good wetting potential, good binding ability, low cost, easy usability and possibility to

manufacture tailor-made resins. Chemically, alkyd resins belong to the group of polyesters as they are formed by esterification of polyhydric alcohols and polybasic acids. High functionality (ester, hydroxyl, carboxyl groups) results in strong intermolecular forces and high viscosity. The alkyd resins used in inks are typically medium or long oil type, meaning that they contain more than 50 % of a drying vegetable oil. The most common hard resins used in offset ink formulations are high molecular weight modified rosin esters (colophony resins) and modified hydrocarbon resins. The hard resins require heating to high temperatures to achieve solution in the oils, which allows an additional step for the control and modification of the ink varnish by temperature control. The most important parameter of the hard resin, in effect, is its solubility toward the vehicle, where vegetable oils or alkyds have a greater solubilizing effect compared with the mineral oil distillates. Optimum performance of a hard resin includes high stability (solubility), but also proper solvent release for fast ink setting.

Ink – Coating Interaction in the Printing and Setting of Ink

Ink transfer at the nip

The ink and paper variables determining the success of the initial ink transfer at the printing nip include surface energy character, paper roughness and rheological properties of the ink. The most common correlation used to describe the transfer of ink from an offset printing plate to a virgin paper surface is the Walker-Fetsko equation /5/. Generally, a split factor of 0.5 is reported for coated papers, which is an indication of even split of ink between the paper and the printing plate. Ink transfer on the subsequent nips of multi-colour printing depends on the absorption character of the fountain water in the non-printed areas, and on the setting or tackification properties of the ink on the previously printed areas of paper. It has been demonstrated that the significance of the ink – coated paper interactivity on ink transfer is small in the first nip compared with the effect in the secondary nips /6/.

Ink setting

After transfer onto the paper, ink changes to a semisolid, touch-proof state referred to as ink setting. In general, fast setting of the ink is crucial in multi-stage printing processes in order to prevent set-off, excessive ink spreading and penetration. However, traditionally a too-fast ink setting is often cited in problems of carry-over ink piling and low print gloss, due to the rapid tackification of the ink /7/, its subsequent build-up on printing blankets leading to back-trap mottle, and the poor levelling of the ink after the film split in the printing nip /8/. However, more recent studies have shown that promoting good wet ink adhesion to the paper surface under conditions of high tack may be of dominant importance in preventing back-trap mottle /9,10/. This approach may well allow more freedom in the future for developing faster setting inks. Clearly, the process of ink setting has to be well controlled for high resolution, high print density and mottle-free print quality.

On coated paper, capillary driven absorption of the low viscous phase of an offset ink is considered to be the main mechanism of ink setting. The capillary absorption phenomenon relating to coated paper has thus been a subject of a number of fundamental investigations /11-16/. More recent studies include the model of Xiang and Bousfield discussing the filter cake formation mechanism of the ink components /17/, and the work of Schölkopf et al. taking into account the factor of inertial flow /18/. The most recent link between in-situ fluid loss and the rheological properties of the ink has been proposed by Gane et al. /19/. In addition to the capillary driven absorption mechanism, diffusion of ink solvents into the latex component of the coating layer is acknowledged to play an important role in the ink – coating interaction. The ink solvents have been shown to diffuse into the latex, to cause swelling and even to dissolve the latex, thereby influencing the ink setting rate /20-24/. In addition, interactions of the alkyd resin with the surface chemistry of the coating pigment was shown by Wickman /25/ to influence the setting rate, and adsorption of the alkyd onto the pigment, in the case of calcium carbonate, was seen to be inversely related to the level of dispersant previously adsorbed. This latter observation has significant implication in the case of coating pigments, the surface chemistries of which are greatly determined by the high levels of adsorbed anionic dispersant which are differently distributed depending on the pigment type and crystal morphology.

In general, the research on ink absorption or setting concentrates on the determination of the coating chemistry and structure parameters involved, while the parameters of ink composition are not often discussed. In many cases a single-component absorptive is studied, neglecting the complex multi-component nature of real inks. Although the separation of the ink constituents during absorption is realised both in paper science /25-27/, and, for example, in the

forensic characterisation of inks /28/, the degree and mechanisms of separation have not been systematically investigated nor related to print performance.

Final ink consolidation

The ink layer is considered dry when it is effectively rub-proof. Primary ink drying mechanisms of offset inks, during and after the latter stages of fluid loss, are evaporation and oxidative polymerisation. In heat-set offset printing the proportion of volatile oils (along with water from the paper as a side effect) are removed in hot air foils after the printing units, after which the final consolidation is achieved by cooling the paper over chilled rolls setting the thermally initiated polymerisation. Sheet-fed offset inks set by oxidative polymerisation of the drying oils and alkyds, which takes hours and continues for months after printing. Polymerisation is commonly accelerated using oxidative metal-ions or absorbing oils in the ink formulation to concentrate the ink faster, or by the use of IR or UV drying. Long term chemical changes on the one hand result from continuing polymerisation reactions and by-product formation, and on the other hand from the solvent residues (up to 15 %) remaining in the ink layer /3,4/.

The Concept of Ink Tack

Intrinsic ink tack

Intrinsic tack is here defined as the tack of an ink before it contacts paper. We should, therefore, discuss this property before embarking on the complexities of ink-paper interaction as manifest by the ink-on-paper tack which in contrast to the intrinsic tack includes the fluid loss, roughness and adsorptive properties between ink and paper.

The tack of an ink is a measure of the force required to split an ink film, and thereby describes the cohesivity or stickiness of an ink while the ink remains fluid. Tack is a property of great practical value in multi-stage high-speed printing, where the tack of the formerly printed ink must be held greater than that of the ink printed in the preceding station in order to assure ink transfer and prevent ink piling. In general, tack should be as great as possible for ink transfer and print sharpness. A restriction to this, especially on coated paper, is that the tack must be below the critical point at which the ink will pick the paper at the required printing speed, especially in the later printing stations of a multi-colour press.

Tack is closely related to the viscosity of the ink, and it is therefore subjected to changes as a function of non-Newtonian rheological behaviour in the dynamic shear and stress conditions during the printing operation. Tack thus varies with speed, time interval and temperature. The measured value of tack is also largely dependent on the film thickness and geometry of the testing roll. The intrinsic tack of an ink is quantitatively measured using tackmeters consisting of two rotating rolls. In many cases tack is measured as a function of time in order to gain information on the press stability of the ink and its setting behaviour in respect of ink properties /3/.

Tack involves mainly the viscous behaviour of the ink fluid phase. In respect of ink formulation it is thus the resin, vegetable oil/alkyd and distillate choice that contribute most to tack. Ideally, ink viscosity should be as high as possible compared to tack, which can be adjusted to a high degree by the solvency balance between the hard resin and the petroleum distillate /4/. Fig. 1 illustrates the time-dependent nature of the intrinsic tack of an ink, which is indicative of the stability in this case of different types of ink varnishes /3/. In commercial inks usually a compromise of these characteristics is preferred.

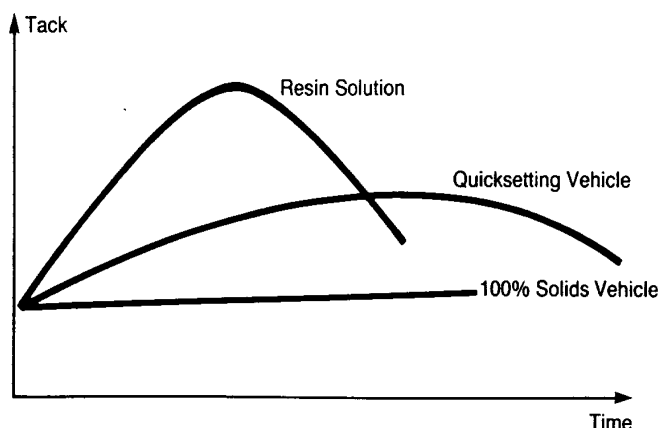


Fig. 1 Offset ink varnish stability measured as time-dependent intrinsic tack behaviour with a twin-roll tackmeter. “Resin solution” refers to a mixture of hard resin and mineral distillate, “100% solids vehicle” to a hard resin - vegetable oil/alkyd varnish and “Quicksetting vehicle” to a varnish of hard resin, vegetable oils/alkyd and mineral oils /3/.

Ink-on-paper tack

Measurement of the time – dependent ink-on-paper tack development directly after being printed on coated paper is important in the prediction of paper performance with particulate ink. After progressive solidification and immobilisation of the ink, the tack-on-paper changes from a purely cohesive property of the ink to a competitive separation between internal cohesion and adhesion to the paper and, progressively, to the test surface, respectively /9/. Tack development on coated paper is thereby mainly a measure of ink fluid phase transport into the paper coating layer. This phenomenon has been studied to a large extent with several types of devices in order to relate the coating structure and chemistry properties to printing performance /9,17,29,30/. However, in all of these previous studies constant but ill-defined inks have been used and the role of ink chemistry thereby has not previously been discussed.

The methodology for this ink-on-paper tack measurement is discussed in the following section.

MATERIALS AND METHODS

Formulating the inks and their constituent oils

Mineral oil (Bp 280 – 310 °C), linseed oil (oil from flax seeds) and a tall oil ester (esterified oil from pines) were selected as representatives of the most important groups of offset ink oils. The characteristic features of the ink oils are presented in Table I. The vegetable oils show higher surface tension values due to their slight polarity resulting from the carboxylic groups of the fatty acid constituents. Linseed oil has significantly higher viscosity compared with the mineral and the esterified tall oils, which have nearly the same viscosity. The properties of the mineral – linseed oil mixtures change almost linearly as a function of the oil ratio indicating virtually complete miscibility.

Table I Properties of the ink oils.

Oil	Surface tension, γ / mN/m	Viscosity, η / mPas	γ/η / m/s	Density, ρ / g/cm ³
Mineral oil	28.7	7.3	3.9	0.84
Mineral75%/Linseed25%	29.0	10.7	2.7	0.86
Mineral50%/Linseed50%	29.9	16.6	1.8	0.88
Mineral25%/Linseed75%	31.1	29.3	1.1	0.91
Linseed oil	33.8	46.7	0.7	0.94
Tall oil ester	31.4	9.0	3.5	0.88

Oils were studied at first alone in respect to interaction with latex, and subsequently as a component of an ink or ink varnish composition. A typical linseed oil based alkyd resin was chosen, and a high molecular weight modified colophon resin was used as a representative of the hard resin group. Model ink and vehicle formulations were pre-prepared and supplied by a printing ink manufacture, thus ensuring proper dissolution of resins and degree of ink pigment dispersion. In the non-pigmented varnishes, the alkyd/hard resin-ratio and the oil/resin-ratio were kept constant and corresponded to the ratios present in the model inks. The tested oil types and approximate compositions of the varnishes and inks are gathered in Table II. The oils were characterised for their surface tension (Krüss Digital Tensiometer K10T, with ring-configuration) and viscosity properties (StressTech¹, with shear rates < 100 s⁻¹) (Table I).

Table II Model ink compositions, where the values present the w/w-% of component in the mixture.

Abbreviation	Mineral oil	Linseed oil	Tall ester	Alkyd resin	Hard resin	Pigment
OM	100					
OL		100				
OT			100			
HM	60				40	
HL		60			40	
HAM	53			12	35	
HAL		53		12	35	
IM	44			10	30	16
IM75L25	33	11		10	30	16
IM50L50	22	22		10	30	16
IM25L75	11	33		10	30	16
IL		44		10	30	16
IT			44	10	30	16

Formulating the Coatings

Coating variables included pigment particle size and chemistry, latex addition level and type. All coating chemicals were of commercial grade and used as supplied. The coating colours were prepared in the laboratory and coated with a table-sheet coater to a coat weight of approximately 12 g/m² on a synthetic paper substrate (Syntepe). The coated sheets were dried in an air dryer at 150 °C and calendered in four nips at a linear load of 62 kNm⁻¹ at 90 °C. The coating compositions along with the abbreviations used in later text are gathered in Table III. All coating colours contained additionally 1 pph of a low viscous carboxy-methyl cellulose as thickener. The latices were studied as pure latex films (6 g/m² on Syntepe) as well as in pigmented coating formulations.

Table III Coating compositions: the values refer to the quantity of a chemical in respect of pigment (pph), FC=fine ground carbonate, CC=coarse ground carbonate, EC=English clay, SB=styrene-butadiene latex and SA=styrene-acrylate latex.

Abbreviation	Calcium carbonate (90 % < 2 µm)	Calcium carbonate (60 % < 2 µm)	English clay (90 % < 2 µm)	DL940 (Tg 22°C)	DL920 (Tg 13°C)	DL980 (Tg -7°C)	S360D (Tg 5°C)
FC/SB22-10	100			10			
FC/SB13-10	100				10		
FC/SB22-5	100			5			
FC/SB22-15	100			15			
FC/SA5-10	100						10
CC/SB22-10		100		10			
EC/SB22-10			100	10			
SB22				100			
SB13					100		
SB-7						100	
SA5							100

¹ StressTech is a product name of ReoLogica, Lund, Sweden

ISIT ink-on-paper tack tests

The Ink-Surface-Interaction-Tester (ISIT²) was employed to detect the tack force development of the inks and varnishes on the model coatings as a function of time. This method provides an analysis of the tack behaviour from the initial tack rise caused by the ink fluid phase absorption into the structure until the final consolidation of the ink layer. A more detailed description of the device hardware and analysis procedure is found in the publication of Gane and Seyler /9/. A standard procedure of ink application using the IGT ink distributor was used for the application of the model inks and varnishes on the coated paper samples. This includes an initial distribution time of 3 minutes of an ink volume of 0.3 ml on the distributor rolls and 1 minute transfer time to the printing disc. 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. In order to apply a constant and small amount of plain oils onto the latex films and coatings an IGT gravured cylinder was employed designed to deliver a film thickness of 0.25 µm.

The interpretation of the tack curve is shown schematically in Fig. 2 /24/. The tack rise is controlled by the finer pore structure in the coating and the interpolymer absorption of oil in the latex. The tack maximum is related to the microsmoothness of the coating surface and to the adhesion of the ink to the coating. The tack decay rate determines the consolidation/setting of the ink and depends on the oil drainage into the total pore volume actually available to the permeating oils, and, as we shall see later, the level of tack decay can be influenced by the diffusive interaction between oil and latex. The available pore volume is a complex function of the preferred pathway wetting of the oil /31/ and the resistive structure build-up of the ink in contact with the coating surface.

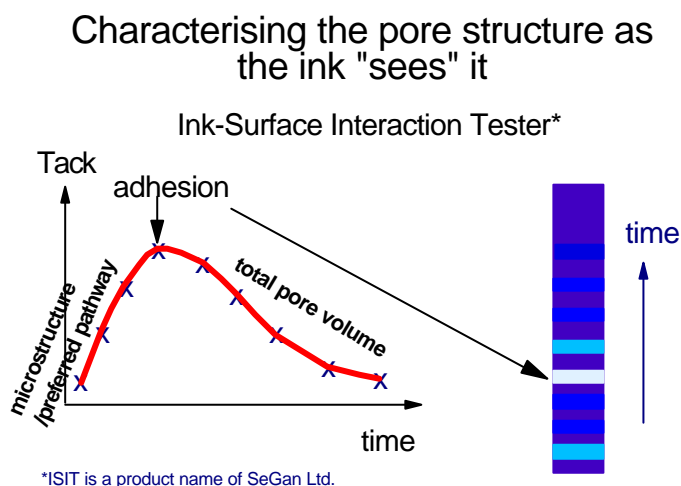


Fig. 2 Schematic interpretation of the tack curve /24/.

RESULTS AND DISCUSSION

Ink-on-paper Tack Force Development as the Indicator for Interaction

(I) Latex film - Oil Interaction

The significance of latex – oil interactions on the tack force development was studied at first independently of coating structure. The degree of interaction of pure ink oils with pure latex films was seen in terms of the differences in the maximum tack force values, the relative delay in the initial tack rise and consolidation/tack decay during an interaction time span of 1 000 seconds. The degree of interaction was found to depend on both the oil and the latex

² ISIT is a product name of SeGan Ltd., Perrose, Lantyan, Lostwithiel, Cornwall PL22 0JJ, U.K.

type as seen in Fig. 3. With all latex types studied, tall oil ester showed the strongest and mineral oil the weakest interaction, respectively. Greater interaction was seen with reduced T_g of the latex, and with styrene-butadiene rather than styrene-acrylate latex. It must be noted, however, that the latices used were of commercial grade and the differential behaviour might be a result of other parameters than just the glass transition temperature, or acrylate vs. butadiene chemistry. For example, latex polarity and polymer chain linearity have been shown to be important in relation to solvent interaction /21,22/.

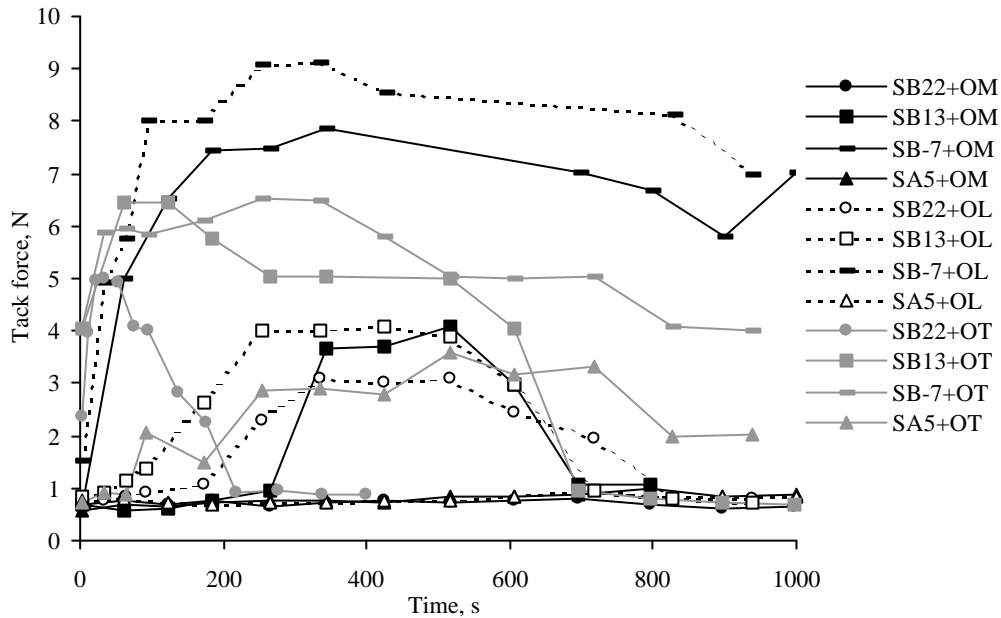


Fig. 3 Oil – latex film interaction.

(II) Ink – Latex plus Coating Pigment Interaction

(a) fixed latex level

The influence of the latex–oil interaction on tack development in a pigmented coating composition was studied using a single coating pigment based on the fine ground calcium carbonate including 10 pph of the various latices in turn. No tack was observed when using pure oils on these coatings.

The same coatings were then used to study the interaction with the various inks. The tack curves resulting from the ink – coating interactions are illustrated in Fig. 4, and we first discuss these in relation to the latex film – oil interactions shown previously in Fig. 3

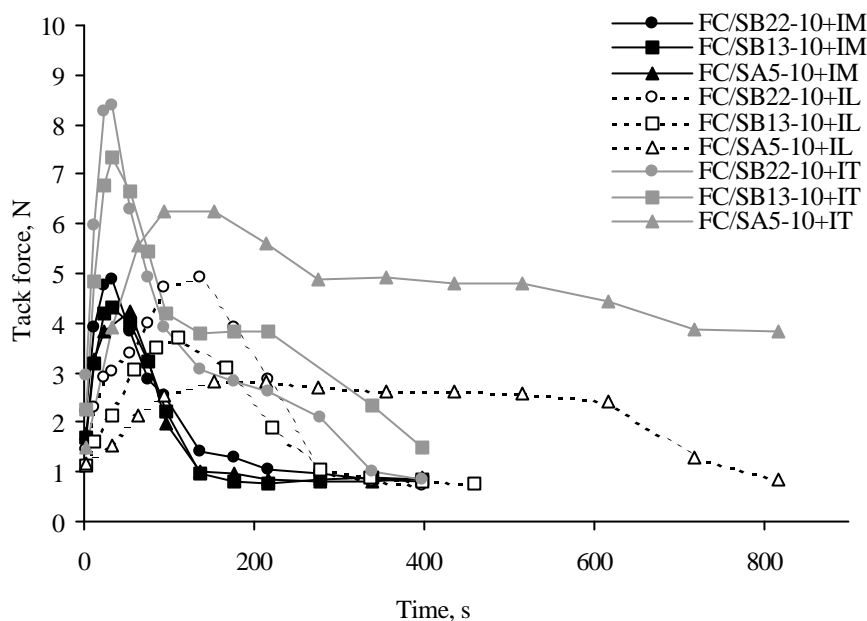


Fig. 4 Influence of latex type on ink-on-paper tack development as a component (10 pph) of a fine carbonate based coating.

It is seen that the mineral oil based ink is insensitive to the latex type used, which is to be expected in light of the lower level of mineral oil – latex tackification. Even the previously detected reaction of mineral oil with the latex having relatively low T_g is too slow to have any consequence over the other mechanisms.

In the case of the vegetable oil inks, the ink – coating interaction is seen predominantly as delayed tack decay. The maximum tack values for a given ink correspond in this case, at 10 parts of latex or less, to the micro-roughness of the coatings – see Table IV below.

(b) increasing latex level

The rate of ink setting and tack decay decreases with additional higher levels of one of the latices (SB22) with all ink types, as seen in Fig. 5. This SB latex is chosen due to its somewhat lower interaction level with the oils to increase the sensitivity to coating structural changes arising from the latex addition level, and thereby helping us to differentiate pore-related effects from diffusive interaction.

In the case of mineral oil, the reduced setting rate and delayed tack decay with additional latex is explained by the overall reduced porosity and, hence, less available pore volume in the structure. It is also worth mentioning that the reduced pore size in this case, i.e. resulting from the latex addition, does not result in increased rate of ink setting as is the case when altering the pore size with pigment choice. The latex therefore acts to block pores or reduce their connectivity.

With linseed oil also, reduced structural absorbency, as a function of the increasing latex level, probably causes the reduction in the rate of ink setting with latex addition up to 10 pph. However, with 15 pph of latex an additional contribution from the latex – oil diffusion can be seen.

Diffusion-driven tack behaviour with the tall oil based ink is clearly demonstrated in these tests as the rate of initial tack rise remains fast at all levels of latex present, but with the lowest addition level of latex (5 pph) the final tack decay level is relatively higher and lasts longer due to the lack of diffusive media. In the cases of sufficient latex being present (at the higher levels of 10 and 15 pph) the final decay is initially slower but to a lower level and overall shorter lived. This difference is also seen when comparing the behaviour of totally capillary-driven mineral oil absorption and that of diffusion-based tall oil penetration. In this comparison, the initial setting of the tall oil ink

is, however, additionally affected by capillarity as the initial tack rises are comparable for these two similar viscosity oils.

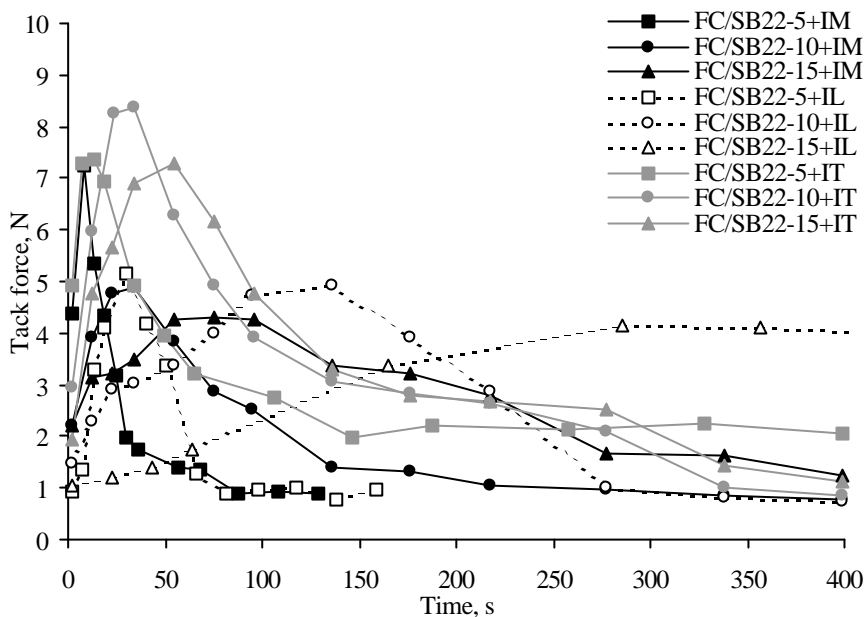


Fig. 5. Influence of additional latex level.

The maximum tack values for a given ink in relation to increasing latex dose do not now correspond only to the micro-roughness of the coatings, as was the case before for fixed lower levels of latex, but begin to demonstrate an additional factor probably due in part at least to the solubility and tackification of the latex.

To understand the effects seen here with the complete inks we move on to break down the various interactions deriving from the individual components of the inks and then later with the coating structural variations relating to coating pigment type and particle size.

(III) Influence of the Ink Components on the Separation of the Fluid Phase

(a) resin and pigment

As learned from the results presented so far and also demonstrated by others /12/, the components separated from the ink dominate the ink setting phenomenon derived from the remaining constituents. In order to get a more in-depth understanding of the influence of the individual ink components on ink-on-paper tack, the tack development analyses were performed for “developing ink” compositions. These were studied on a constant coating containing fine calcium carbonate and 10 pph of a single SB-latex (once again the SB22 with its Tg of 22 °C).

No tack was observed for pure oils nor for oil – alkyd resin mixtures on the coating structure. Even for the case of a varnish of mineral oil and hard resin no tack was indicated, as seen in Fig. 6. This is most probably explained by the poor solvent power of the mineral oil with the hard resin resulting in very fast release of mineral oil. With the further addition of alkyd resin into the mineral oil – hard resin varnish, tack becomes detectable within the time scale of the test. This might be explained by the tackifying effect of the alkyd alone and/or in combination with the hard resin. The release of the linseed oil component from the alkyd resin might have an effect on the detected tack decay. Pigment addition to the mineral ink composition further decreases the rate of mineral oil release (and that of the linseed proportion of the alkyd), which might indicate cohesiveness of the mineral oil with the ink pigment or that of the resins and pigment.

In the linseed oil based formulation tack was already detected in the hard resin – oil varnish. The addition of alkyd resin into the linseed oil hard resin varnish retarded the setting and final drying only slightly, and further addition of

pigment had only a very slight retarding influence (Fig. 6). This is an indication of the stronger compatibility, probably involving acid-base interactions, of the linseed oil with the ink resins in contrast to the poor mineral oil – resin miscibility. This was also mentioned by Ström /27/. It is evident that the tack results from the resins and oils, and suggests that their interaction with the ink pigment is negligible in the case of linseed oil.

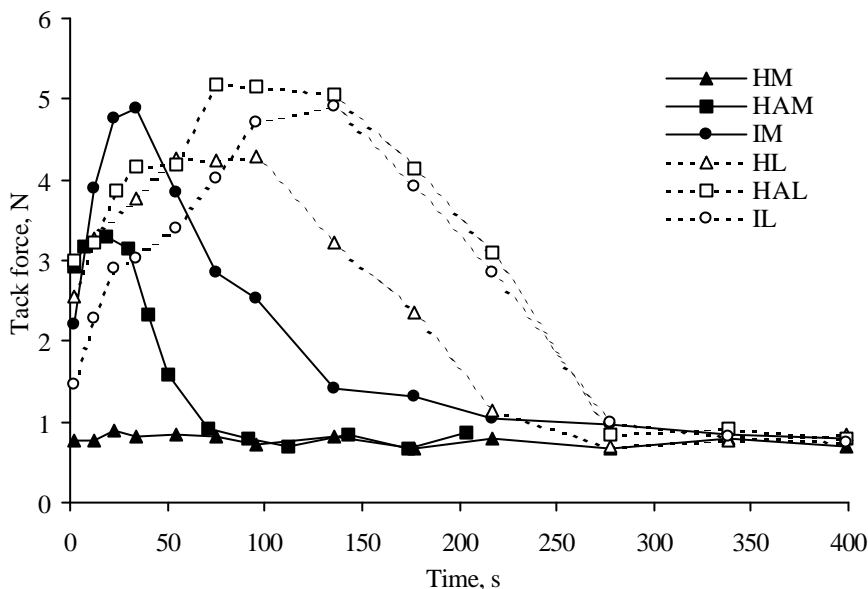


Fig. 6 Influence of ink constituents on tack development (A=alkyd resin, H=hard resin, I=ink, L=linseed oil, M=mineral oil).

(b) capillarity parameters of the oils

In all the coatings tested, increased rate of ink tack build-up was seen with decreased viscosity of the ink oil phase. With constant viscosity, greater surface tension resulted in faster rate of ink setting (mineral vs. tall ester). In general, absorption of Newtonian fluids in a capillary is known to be determined by the surface tension to viscosity ratio of the imbibing fluid rather than either parameter alone /32,33/. This was also indicated in our results in Fig. 7, where we used a chemically similar ink system containing different proportions of linseed and mineral oils as the vehicle on the single coating formulation above, i.e. the fine carbonate with 10 pph of SB22 latex. The surface tension/viscosity values in the figure thus relate to the properties of the ink oil phase. However, when adding the setting rate of the tall oil ester based ink to the same figure it is seen that the linear behaviour is disrupted. This confirms that it is not solely the physical properties of the absorbing oil in relation to a given pore structure that determine the initial absorption rate of the ink vehicle, when measured as ink tack.

The specific interactions of the ink components with the coating layer components (namely diffusion into the latex) as well as mutually with other ink components can be assumed to complicate the straightforward interpretation and acceptance of the linear relationship between the rate of ink tack rise and the γ/η ratio of the ink oil shown in Fig. 7. An additional consideration to the linear relationship found is that, contrary to absorption rate kinetics found in model systems /2/, the ink tack development is an indirect measurement of the absorption rate. It includes additionally the oil release parameter from the ink, i.e. the properties of the consolidating ink composition of which the tack value is actually a measure. This is related to the flow resistance developing within the setting ink, and as menisci are formed, and the solubility and permeability properties of the dissolved polymers within the ink matrix. It has been shown earlier that mineral oil is preferentially released from the ink composition compared with linseed oil thereby supporting the development of the non-linear relationship and separation of ink constituents during absorption found in the previous work /2/.

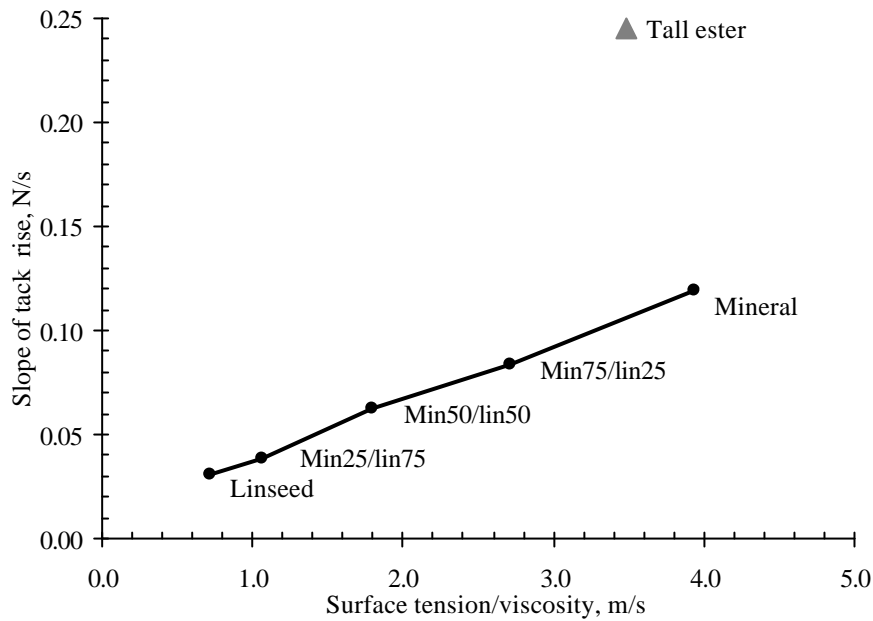


Fig. 7. Slope of tack rise as a function of the surface tension to viscosity ratio of the ink oil phase.

(IV) Influence of coating pigment and structure properties

(a) structural properties of coatings

It has been previously shown that the use of a larger particle size pigment results in both increased porosity and pore size in the final coating structure as measured by mercury porosimetry /2/. The high aspect ratio platelet particles in the English clay gave similar pore size distribution characteristics compared to the similar particle size nearly isometric calcium carbonate particles. As we have seen, increased addition level of latex results in a less porous structure. Latex type on the other hand did not have a profound effect on the surface physical structure of the calendered coatings. It could thereby be stated in the particular case here, when using the synthetic substrate, that the choice of pigment is the factor dominating the physical porous structure character at the 10 pph addition levels of latex binder chosen for study. As the latex level exceeds 10 pph then other factors are observed - as we have already seen above. The roughness values of the coatings are gathered in Table IV.

Table IV Surface roughness properties of the coating structures.

Coating	PPS Roughness, μm
FC/SB22-10	1.41
FC/SB13-10	1.51
FC/SB22-5	1.44
FC/SB22-15	1.45
FC/SA5-10	1.54
CC/SB22-10	1.47
EC/SB22-10	1.39

(b) ink – coating pigment and structure interaction

The pigmented coating formulations based on 10 pph of SB22 latex (+1 pph CMC) were first tested for interaction with the model inks. Faster ink tack rise arises from smaller pores in the coating layer (Fig. 8), which is known from a number of other studies /9,17,27,34,35/. When comparing calcium carbonate and clay of similar particle and pore sizes the latter showed reduced rate of tack rise in the cases of vegetable oils, especially with linseed oil, but an equal tack rise rate in the case of mineral oil based ink. A similar behaviour was seen in direct absorption measurements /2/ indicating either a difference in surface energy between dispersed carbonate and clay – suggesting either that the dispersed carbonate is overall more polar (faster wetting by polar fluids) or that the higher tortuosity of the clay coatings has a greater retarding effect on the more viscous linseed oil (or both). Tortuosity is seen as a major factor controlling the discontinuous absorption dynamic of clay-based structures in relation to the Gibbs hinging effect of intersecting capillaries /36/. Another factor, the previously seen greater chromatographic sorption-desorption for linseed oil on clay /2/, may also play a role.

When considering the tack development curves in Fig. 8 in respect of the ink oil properties, the decreasing rate of initial oil absorption as a function of oil viscosity is clearly evidenced as predicted previously in Fig. 7. It is also seen that the final consolidation of the ink is significantly slower with the vegetable oil inks compared with the mineral oil based formulation. Especially, the prolonged drying of the initially fast interacting tall oil ester based ink stands out. As the tack decay is an indication of the total available pore volume as seen by the ink, this clearly supports the suggestion that the tall oil ester ink interaction is also driven by diffusion of the ink oil into the polymer matrix rather than capillary driven absorption alone into the coating structure. This extra tackification of the latex also plays a role in determining the tack decay and is also supported by the rapid tack increase, which is again related to the combined effect of capillary absorption and diffusion.

The maximum tack force values at the latex level of 10 pph, with each given ink, correspond inversely to the surface microroughness of the coating layer, i.e. highest value is seen with the microsmooth clay coating and lowest with the coarser carbonate. Differences in tack maximum between the inks on the same coatings indicate the adhesion of the ink to the surface. The highly polar tall ester based ink shows almost equally high tack maximum between the clay and the finer carbonate which tends to support the hypothesis of the polar action of the carbonate despite its higher coating microroughness.

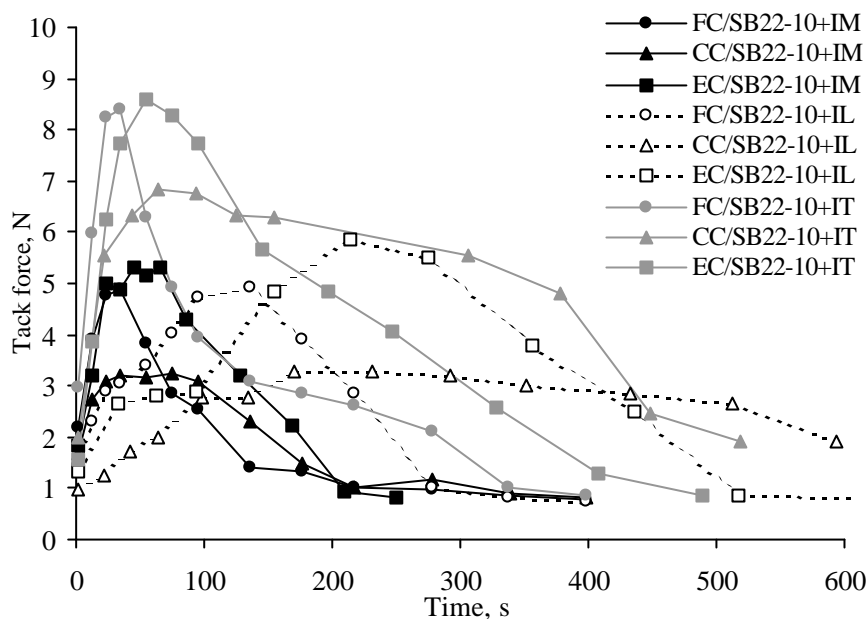


Fig. 8 Influence of coating pigment type on coating structure and tackification using various ink-oil systems.

CONCLUSIONS

Ink tack development on coated paper is a measure of the combined influence of ink fluid phase release from the ink composition, its absorption into the capillaries of the porous coating structure and diffusion into the polymer counterpart of the coating layer. These parameters determine the ink setting and consolidation character of the particular ink – coating system in question, which was successfully studied using time dependent tack development analyses.

In the case where oil – latex interaction is minimised, the initial tack rise or fluid phase absorption from the ink is mostly determined by the capillary flow of the ink vehicle into the microporous coating structure. This is controlled by the viscosity and surface tension characteristics of the penetrating fluid, where the rate of absorption increases with reduced viscosity and increased surface tension of the fluid. Under these circumstances, it can be concluded that the ink setting rate for a given formulation is dictated by the surface tension to viscosity ratio of the separating fluid. In respect of coating structural properties, faster initial ink setting rates result from finer coating structure pores when the binder content is kept constant. Maximum tack is determined by the microsmoothness of the coating and the adhesional properties of the ink in relation to the pigment and latex used.

Ink oil absorption and diffusion into the latex - if present - is manifest both in respect to tack rise and the maximum tack, and by its most observable effect on the final ink tack decay, possibly due to the slower nature of diffusion compared to absorption. In the case of diffusion-based interaction, slower ink tack decay might, however, be influenced by the altered porous structure character of the coating due to latex swelling and thereby blocking the pores and their interconnectivity. The degree of latex – ink oil interaction depends on the character of both the latex and the oil and how much are present in the coating and ink respectively, and how this interaction may also influence the observed tackification of the ink, which includes both fluid loss from the ink and a contribution toward adhesion and tackiness from the latex itself.

The mutual cohesivity created by the ink components determines which components are released from the ink and the rate of their release. The tack of the poor solvent power non-polar mineral oil based ink is largely determined by the volume fraction of resins and resin – pigment combination. The higher solubility and greater compatibility of linseed oil with resins results in greater retention of the oil in the ink, which is an additional factor influencing the slow setting character of the linseed oil based inks.

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