OFFSET INK TACK AND RHEOLOGY CORRELATION: - I: ink rheology as a function of concentration.

P. A. C. Gane
Vice President Research & Development
Paper & Pigment Systems

J. Schoelkopf[1]
Senior Scientist

OMYA AG
CH-4665 Oftringen
Switzerland

G. P. Matthews
Reader in Applied Physical Chemistry

Environmental and Fluids Modelling Group
Department of Environmental Sciences
University of Plymouth
PL4 8AA Devon, U.K.

ABSTRACT

This paper is divided into two parts with the aim to compare visco-elastic structure relaxation of a presheared offset ink with observed ink tack development on a representative absorbent multi-coated paper. The methods used include oscillatory and shear rheometry in part I, and comparison with the SeGan Ink Surface Interaction Tester (ISIT) in part II. By diluting the ink with mineral oil, a plot of viscosity against solids content could be established. The viscosity of the progressively diluted ink was then extrapolated back toward increasing concentration. In this way a relation is developed between the viscous character of the ink at a given concentration and that of the ink as it will be on the substrate, i.e. effectively the ink-on-paper viscosity and solids content in respect to the tack force measurement. This novel approach allows the solids and viscous parameters of the ink to be analyzed as the initial ink setting actually occurs on real papers, as discussed in part II.

Keywords: Ink tack, viscosity, printability, ink rheology, offset printing, substrate absorption.

---

[1] Author to whom correspondence should be addressed

INTRODUCTION

The physical phenomena occurring during and after the application of printing ink in an offset print process are considered to be important factors in achieving desired print properties. Ink vehicle, the continuous liquid phase, is removed from the setting film by absorption into the porous paper coating surface. The dynamics of this absorption are observed as a build-up of internal ink tack (cohesion) from the shortest timescale of fractions of a second up to half a minute or longer, followed by a subsequent decay of ink surface tack (ink-blanket adhesion), often lasting up to an hour or in some cases days. The tack cycle of rise and decay is linked to properties of the final cured ink film, such as print gloss, press runnability and rub-resistance. The control of tack is therefore crucial for the multicolor offset printing process.

It is also important to recognize that on a running press, which has reached equilibrium, the ink retained on subsequent color blankets is aged both over time and in respect to tack. The tack of this blanket-retained ink has been built-up during multiple contacts with progressively setting ink as the print form makes many contacts with the paper. This aged ink cannot be simulated by fresh ink used in rapid timescale test methods. Therefore, tack must be studied over realistically long timescales if the equilibrium press condition are to be simulated realistically. This is especially important when considering the dynamic absorption by coatings coming into contact with such aged ink.

In previous studies we investigated the mechanism of liquid absorption into coating pigment structures (1). We identified the relevance of inertial flow as physically predicted by Bosanquet (2) who expanded the well known Lucas Washburn (3) equation to contain the inertial effect of the liquid mass which has to be accelerated by the wetting force. A 3D plot shows that there exists a time dependent optimum for flow as a function of capillary radius. The consequence is that pores up to a given diameter in a porous network, this diameter being in turn a function of time, fill very fast while bigger features remain by-passed and tend to remain unfilled under conditions of limited supply volumes of fluid as found in the case of thin applied ink films. This promotes what we call a preferential pathway flow (4). The existence of unfilled or by-passed pores is also known from soil science and study with micro models (5). Inertial flow in a glass capillary was observed by Quere using a high speed camera (6). With modifications, we applied the Bosanquet equation to a sequential wetting algorithm for Newtonian fluids in a pore space simulator, Pore-Cor[2], previously developed and described in the literature (7).

Offset inks contain Newtonian liquids as solvents and extenders, but the rheology of the ink itself, especially as it interacts with the paper and the printing press, shows a visco-elastic behavior. The absorption process is itself complex as the porous paper coating structure does not imbibe the whole ink. The liquid phase, the so-called vehicle, is absorbed into the porous structure while the binder/pigment particles, due to size exclusion, remain on the surface, and solvated resins become adsorbed (8). This leads to an effective rise in viscosity of the ink and finally to the formation of an immobilized layer of binder and pigment particles on the coating surface and therefore to a decrease of mobile ink layer thickness (9).

In this first part of the paper we combine methods of rheology to study the relaxation of presheared ink. An extrapolation of viscosity toward higher solids content is derived initially from viscosity data obtained under progressive dilution of the ink with mineral oil. This extrapolated viscosity as a function of increasing solids content is then compared in the second part of the paper with the observed ink tack rise as a function of time as measured on the SeGan Ink Surface Interaction Tester[3] (ISIT) to obtain potentially a predicted volume loss of fluid from the ink as a function of time. The findings are first linked to measurements of the printed ink tack force development on different non absorbent substrates. This permits the analysis of the contribution from mechanisms of ink split, structural rebuild and cavitation. We then go further to analyze the influence of the mobile ink layer thickness as a function of time between printing and subsequent backsplitting on a typical offset paper. A model is then developed to describe the solids and viscous behavior of the ink under the controlled extensional acceleration conditions of the static point ISIT test. Thereby we correlate the single integrated force-time curves, each at a given time after printing, with a process extensional viscosity and hence, via the Trouton ratio, to the observed relaxing shear viscosity of the ink. This novel analysis provides a means of defining the important rheological characteristics of the ink in situ on the paper surface.

---

[2] Pore-Cor is a software program of the Environmental and Fluids Modelling Group, University of Plymouth, PL4 8AA, U.K.

[3] ISIT is a product name of SeGan Ltd., Perrose, Lostwithiel, Cornwall PL22 0JJ, England

THREE BASIC POST-PRINT MECHANISMS

The general framework of mechanisms of a process like printing is the same as for many applications where a multiphase suspension or dispersion is applied onto a solid surface which may be permeable and porous. The framework after initial application consists mainly of evaporation, absorption and curing.

Evaporation, a diffusive process, is dependent on vapor pressure and therefore strongly linked to temperature. The "escape" of volatile fluid molecules results in an increasing solids concentration at the liquid/vapor boundary; a skin formation is often observed.

Absorption on a fine porous substrate happens due to capillary forces where the Laplace pressure of the curved liquid menisci forms the driving force. Also non-Laplacian driven wetting is possible under all kinds of film flow situations. Furthermore, diffusion and effusion also contribute to absorption; the former relates to molecular or particulate transport into a non porous medium, e.g. a cured latex film, the latter is molecular and applies mainly to molecular mixing or exclusion. The consequence is an upconcentration of solid particles at the solid-liquid boundary by size exclusion effects. Even if the size of potential ink particles is much smaller than the mean capillary diameter it is still likely that the ink particles block in pore throats and junctions immediately (10) This increase in solids concentration is actually the build-up of a secondary porous layer, often with progressively reduced permeability due to small void spaces. Only in a potential final stage when liquid menisci are formed at the upper boundary of this ink structure does it start to act as a competitor for liquid with the primary porous substrate.

Curing is a chemical process influencing often the later stages of the first two processes discussed above where the type of curing mechanism furthermore complicates this issue. Oxidative and humidity curing start from the boundary contact layer and are usable only for thin layer applications as access to the inner bulk is dependent on the diffusive permeability of the curing material. Light, from infrared to ultraviolet, electron beam (EB) and heat-induced curing also start at the exposed surface and continue depending on the permittivity of the medium. Only chemical curing, due to any kind of crosslinking or chainlinking reactions, starts everywhere in a medium at a given concentration. The impact of curing is a steady further rise in viscosity and a potential change in temperature, as mentioned before, although it may be only at surfaces exposed to the curing "starter". If this starter is oxygen, it happens in every capillary the polymer fluid enters or remains during the entry of air. The final impact then is the ongoing formation of a network structure resulting in an immobilization and solidification of the former fluid thus reducing the stickiness or exposed surface adhesional properties.

In this work we focus on the offset or lithographic print process where, after the initial pressure impulse applied to both sides of the paper from the printing nip, the above-mentioned three main mechanisms become active in the tackification and setting of an offset ink. Capillary forces and diffusion, plus limited evaporation later in the sequence of heatset web offset, remove the fluid phase from the applied ink layer causing a progressive concentration of solids at first towards the boundary between ink and the surface of the porous substrate and later at the ink surface. The curing, mainly oxidative, occurs ideally after the removal of the fluid components resulting in a solidification of the ink film involving polymerization and setting of resin binder components in the ink formulation. Previous work has shown that the bundle of capillary tubes model is insufficient to model the absorption process. Applying the Lucas-Washburn (LW) equation, assuming a simple bundle of capillaries, often leads to an unrealistic dimension of the effective pore radius and contradicts observation when comparing ink setting on fine gloss coating structures with those of coarser matte coatings. The classical equation of Bosanquet (2) which was virtually ignored for many years since its inception in 1923, includes the effect of inertial retardation of the liquid as it becomes accelerated into the larger pores. Inertia also promotes a regime of flow that is linear with respect to time and takes place first in the finest capillaries. This is in comparison to the square root behavior with respect to time of the LW equation. While this effect in straight capillaries is detectable using high speed cameras it was considered not to be relevant because of the short timescale of its influence, i.e. ~10 ns for water into a capillary of diameter ~ 0.1 µm. In contrast, the effect in a porous network is proposed to be additive. In each single feature of a porous network where the liquid is accelerated, inertia acts over a timescale similar to the pore filling time and leads to a differential in wetting front velocity and position during absorption between the finer and the larger pores. Interestingly, due to observed mass balance in experimental approaches on a macroscopic scale, a proportionality with respect to the square root of time is observed. This observation systematically led to the assumed verification of Poiseuille flow and hence Lucas-Washburn dynamics. However, this overlooked the remaining need for a defined effective capillary radius or surface energy relationship to describe the discrepancy regularly seen between absorption rates for fine and coarse structures, viz. fast ink setting on fine pigmented glossy papers versus slow ink setting on matte papers made from coarse pigments. This issue is discussed further in some detail in recent publications (7), (4). High liquid viscosities shift the time of inertial flow into irrelevant short timescales and low densities decrease the effect of inertia. In the case of offset inks, where the fluid is formed from alkanes in a mineral oil fraction or vegetable oils, the viscosity is in the order of 0.5 - 40 mPas and the density in the order of 730 kgm^{-3}. These fluid properties maintain the relevance of the inertial timescale during the pore selection process within the porous network of a paper coating, i.e. the time taken to fill an isometric pore of, say, 0.1 µm or less, will be of the order of < 10 ns. During this time, larger pores fail to fill due to the inertial lag time of the fluid trying to enter them and so selection in favor of finer pores occurs within the constraints of the available fluid quantity.

Xiang and Bousfield (9) explained a further retardation of absorption into large capillaries by the increased drag offered by a forming filtercake of thickness $\lambda(t)$. The filtercake was assumed to form at the interface between ink and coating surface associated with the large volumes of fluid absorbed by larger pores. However, this would also be inconsistent with the faster setting of inks on finer pore structures if it were the only retardational mechanism.

THE RHEOLOGICAL CHARACTERISTICS OF THE FLUIDS AND INKS

During the print process the ink experiences pressure-induced shear and several stages of film splitting where cavitation and filamentation can occur. The breaking length of the filaments depends on the shortness of the ink, a phenomenological term which is important for the printer. In order to achieve an even glossy ink film the microscopic leveling of the broken filaments is crucial. Failure to level can also be recognized sometimes on a macroscopic level as an orange peel effect. Leveling can happen due to gravity on slow single color presses but more strongly due to spreading forces and due to the elastic relaxation of the induced film split roughness (11). The process is retarded with growing viscosity due to fluid loss and viscous structure rebuild, through oil removal from the ink by substrate absorption. The latter results in a decreasing mobility of the ink layer and the overall phenomenological effects are known as the tack build-up of the ink layer. Roughening may also relate to incorrect concentrations of resins and oil balance in the final stages of setting.

In order to study the behavior of ink, it is of preliminary importance to examine some of the ink’s flow properties. For this purpose a StressTech[4] controlled stress rheometer with a plate-plate geometry (UP40) was used. The plate-plate system permits the measurement of a wide range of viscosities due to its adjustable gap, which we kept at 0.25 mm throughout this work. Offset-inks consist of a liquid-polymer-solid blend of complex rheological behavior. Our main interest was therefore to analyze the viscosity of the ink as a function of oil loss as experienced in the post-print regime on an absorbent substrate. We chose to use a commercial ink, Skinnex cyan 4x73[5] throughout this work. As concentrating an ink is almost impossible to perform uniformly, we investigated ink dilution. By progressively expanding (diluting) the ink with a standard mineral oil, as used in the formulation of offset-inks (Haltermann PKWF 6/9 af), the influence on steady state shear and subsequent structure rebuild was monitored over time as a complex viscosity $h^*(t)$.

The ink and the oil were mixed thoroughly first by hand using a spatula, then under ultrasonic for 5 minutes and final homogenization on the rheometer device itself. For the rheological measurements, a steady shear rate of 360 s^{-1} was used for 180 s and, for the tack measurements, a time of 180 s on the IGT ink distributor before printing was also used for consistency. With our measurement system, increasing shear rates (> 50 s^{-1}) showed an unstable rheological behavior, probably due to centrifugal loss of fluid/measuring system contact. We applied, therefore, a shear-rate of 30 s^{-1}, avoiding such problems. Furthermore, we wanted to obtain data to model the tack rise as measured with the ISIT device. During the ISIT test procedure, as explained later in some detail, and also in a real printing process, the ink is sheared moderately in the nips of the distributing rollers, then split onto the paper where the ”sheared-out” ink structure subsequently starts to relax. During the on-going relaxation, the tack is measured as a function of time after printing.

---

[4] StressTech is a product name of ReoLogica Instruments AB, Lund, Sweden.

[5] Skinnex is a product name of K+E Inks, Stuttgart, Germany.

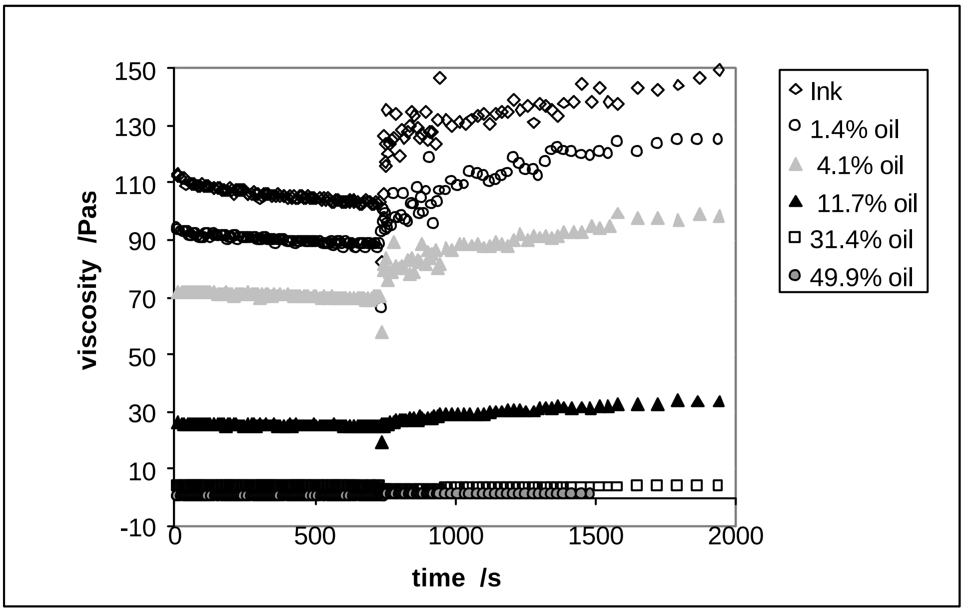

Fig. 1 *Overview of shear viscosity at 30 s^{-1} and subsequent relaxation monitored by stress oscillation in the linear visco-elastic (LVE) regime as a complex viscosity, h*.*

Fig. 1 shows some experimental results over a range of dilutions. The data from the initial range represent the steady shear experiment. We see the shear thinning of the original undiluted ink over an extended period of time. The shear thinning is progressively less pronounced with increasing added oil content. After relief of the shear stress a structure rebuild occurs as monitored by sinusoidal oscillations of the lowest possible strain amplitude (0.5 Pa) and shear rate in order to remain in the linear visco-elastic domain. The underlying phenomena of the sheared ink relaxation are polymer chain rearrangement and re-establishment of interactions of the solid ink particles and the fluid phase. It has to be noted that in the structure relaxation, in contrast to the steady shear experiment, a complex viscosity is measured which contains an elastic contribution.

The relaxation is seen to obey approximately the relation:

$$h^{*}(t) = \left(h^{*}(\infty) - h^{*}(0)\right) \cdot \left(1 - e^{-t/t_{0}}\right) + h^{*}(0) \qquad (1)$$

where t_0 represents the characteristic relaxation time. Eq. 1 was entered into TableCurve 2D* which fits t_0, $h*(0)$ and $h*(\infty)$ to achieve the smallest residue r^2. (This software is used for all curve fittings throughout this paper.) The equation applies well to the measured curves except for the first few data-points where a much faster relaxation process overlays. This initial relaxation may be sample or instrument related. There is evidence of a viscosity drop before recovery and so this could be an inertial effect. However, the first regime lasts only a few seconds. The characteristic relaxation times are seen to trend towards shorter values as the ink oil content decreases. As an example, the blend containing 11.7 w/w% oil is shown in Fig. 2 with a t_0 ~ 500 s.

---

[*] TableCurve is a product name of SPSS Inc.

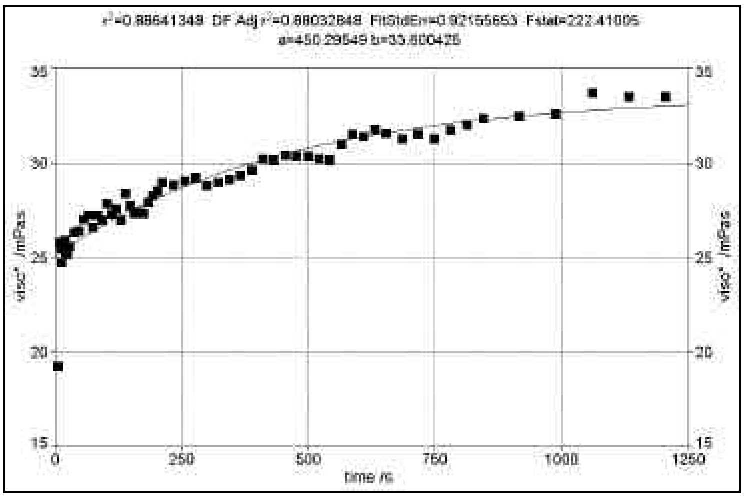

Fig. 2 *Ink structure recovery regime fitted with Eq.1*

The viscosity data for $h*(0)$ are then used as representative values for the subsequent extrapolation to increasing ink solids content, i.e. the regime of oil loss by capillary absorption into the substrate, using an exponential fitting function,

$$\ln h^* = a + b\Delta f_{\mathrm{oil}} \tag{2}$$

where a and b are fitting parameters and Δf_{oil} is the added oil content in w/w% with respect to the sum of the undiluted ink plus the added oil. The resulting curve is displayed in Fig. 3 with the parameters a and b shown, which are used later to compare with the ISIT findings.

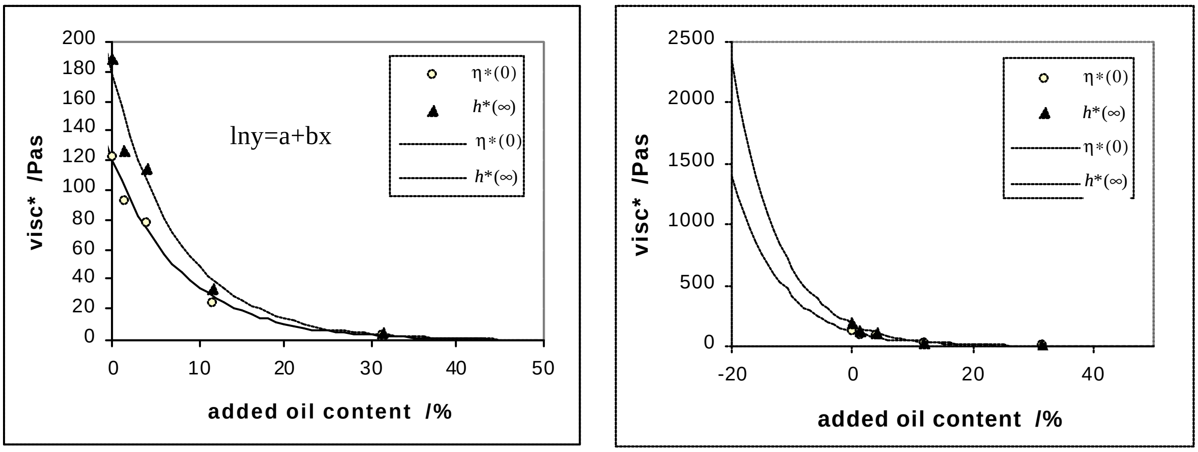

Fig. 3 *Comparison of h*(0) and h*(¥) as a function of <u>added</u> oil content of the ink Df_{oil} (w/w%) - the extrapolation of h*(0) (a=4.78, b= -0.122) , on the right, to reduced oil content, is used as the basis for the viscosity comparison with ink tack measurement in part II of this paper.*

CONCLUSIONS

We have shown that it is possible to describe the rheological relaxation of an offset ink after shearing with an expression to obtain values for the complex viscosity parameters $h^*(0)$ and $h^*(\infty)$. These allow us to predict the viscosity development under conditions of vehicle removal, as occur on an absorbent coated paper, and form the basis for correlating the viscosity of an ink, as a function of solids content, with the ISIT pull-off force-time integral, as will be shown in the second part of this work.

---

[6] Ikonofix is a product name of Zanders Feinpapiere AG (now M-Real) , D51439 Bergisch Gladbach, Deutschland

The methodology we go on to show in part II provides a potential universal tool for workers to study the solids and viscosity properties of a wide variety of polymer and particulate suspensions as they interact with the surface of a substrate.

REFERENCES

1. Gane, P. A. C., Schoelkopf, J., Spielmann, D. C, Matthews, G. P., and Ridgway, C. J., "*Fluid transport into porous coating structures: some novel findings*", Tappi Journal, 85(5), 2000, p1-3

2. Bosanquet, C. M., "*On the flow of liquids into capillary tubes*", Phil.Mag., S6 45(267), 1923, p525-531

3. Washburn, E. W., "*The dynamics of capillary flow*", Physical Review, 17, 1921, p273-283

4. Schoelkopf, J., Gane, P. A. C., Ridgway, C. J., and Matthews, G. P., "*Influence of inertia on liquid absorption into paper coating structures*", Nordic Pulp and Paper Research Journal, 15(5), (2000), 422-430.

5. Bernadiner, M. G., "*A capillary microstructure of the wetting front*", Transport in Porous Media, 30, 1998, p251-265

6. Quere, D., "*Inertial capillarity*", Europhysics Letters, 39(5), 1997, p533-538

7. Schoelkopf, J., Ridgway, C. J., Gane, P. A. C., Matthews, G. P., and Spielmann, D. C, "*Measurement and network modelling of liquid permeation into compacted mineral blocks*", Journal of Colloid and Interface Science, 27(1), 2000, p119-131

8. Rousu, S., Gane, P. A. C., Spielmann, D. C, and Eklund, D, "*Separation of off-set ink components during absorption into pigment coating structures*", Nordic Pulp and Paper Research Journal, 15(5), 2000, 527-535

9. Xiang, Y. and Bousfield, D. W., "*The influence of coating structure on ink tack development*", Pan-Pacific and Printing & Graphic Arts Conference, CPPA, Canada, 1998, p93-101

10. Toivakka, M., Eklund, D, and Bousfield, D. W., "*Simulation of pigment motion during drying*", Tappi Press, Atlanta, GA, 1992, p403-418

11. Xiang, Y., Bousfield, D. W., Desjumaux, D., and Forbes, M. F., "*The relationship between coating layer composition, ink setting rate, and offset print gloss*", CPPA, 1998, p85-91

12. Gane, P. A. C. and Seyler, E. N., "*Some aspects of ink/paper interaction in offset printing*", Proceedings of the PTS Coating Symposium, Munich,1993.

13. Gane, P. A. C., Seyler, E. N., and Swan, A., "*Some Novel Aspects of Ink/Paper Interactions in Offset Printing*", Printing and Graphic Arts Conference, Halifax, Nova Scotia CPPA, Montreal, Canada, 1994, p209-228

14. Adamson, A. W., "*Physical Chemistry of Surfaces*", A. Wyley Interscience Publication, New York, 1990

15. Keiter, S., "*Haftung und Aufnahme von Druckfarben auf gestrichenen Papieroberflächen*", 1998, Diploma Thesis of the University of Dortmund and Private Communication

16. Van Oss, C. J., Good, R. J., and Chaudhury, M. K., "*The Role of van der Waals Forces and Hydrogen Bonds in "Hydrophobic Interactions" between Biopolymers and Low Energy Surfaces*", Journal of Colloid and Interface Science, 111(2, June 1986), 20-12-1985, p378-390

17. Macosko, C. W., "*Viscous Liquids*", Rheology: Principles, measurements and applications, VCH Publishers, New York, 1994, p425-474

OFFSET INK TACK AND RHEOLOGY CORRELATION: - II, determining in real time the solids content of ink-on-paper using the ink tack force-time integral.

P. A. C. Gane
Vice President Research & Development
Paper & Pigment Systems

J. Schoelkopf[1]
Senior Scientist

OMYA AG
CH-4665 Oftringen
Switzerland

G. P. Matthews
Reader in Applied Physical Chemistry

Environmental and Fluids Modelling Group
Department of Environmental Sciences
University of Plymouth
PL4 8AA Devon, U.K.

ABSTRACT

Comparison of visco-elastic structure relaxation of a presheared offset ink with observed ink tack development on a representative absorbent multi-coated paper is made in this part II of a two-part paper. The role of intrinsic ink/rubber blanket adhesion is assumed inherently as a continuous boundary condition. A relation was developed in part I between the viscous character of the ink and its concentration. The individual force-time integrals of the ISIT tack test under constant separation acceleration, known as the ink tack pull-off curves during tack rise, are now used to obtain a predicted volume loss of fluid from the ink on a real coated paper sample, i.e. effectively the ink-on-paper viscosity and solids content. Good agreement is observed between the rheology measurements presented in part I of this paper and the approaches used here based on the uniaxial extensional viscous term applicable during the tack test separation, from which an improved model of the tack-force mechanism is presented. This novel approach allows the solids and viscous parameters of the ink to be analyzed as the initial ink setting actually occurs on real papers.

Keywords: Ink tack, viscosity, printability, cavitation, ink rheology, offset printing, substrate absorption.

---

[1] Author to whom correspondence should be addressed

INTRODUCTION

This work is presented in the context of other studies carried out by the authors investigating the mechanisms of liquid transport into porous model structures made of paper coating pigments [1]. Methods of imbibition [2,3,4], permeation [5] and tack measurements have been applied using pure viscous liquids and also visco-elastic liquids, namely a typical offset ink in diluted and undiluted state [6].

In part I of this paper we introduced a methodology to derive viscosity values for an offset ink during vehicle removal via extrapolation based on measurements performed under ink dilution. In this second part we use these values to compare with data derived from tack measurement and to derive a real time evaluation of ink concentration during tackification on a coated paper surface.

Tack measurements on paper

We consider a commercial offset paper (Ikonofix[2] 150 gm^{-2}). The long timescale tack curve cycle shown in Fig. 1 is averaged from more than 30 single tack curves. We recall once again that the long term tack reflects the equilibrium "ageing" of ink on a real press and that such timescales are indeed relevant to press runnability.

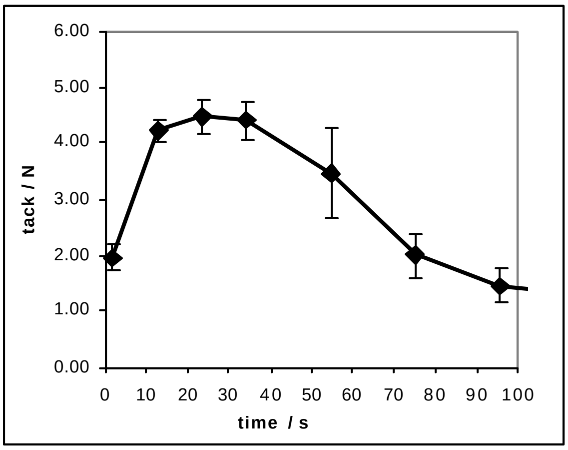

Fig. 1 Overall mean tack curve for test paper.

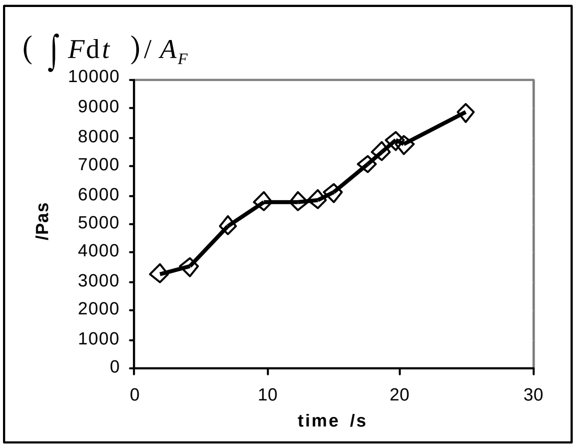

Fig. 2 The tack rise in the form of a "process viscosity", values are shown in Table 2.

It can be seen that the tack rise is completed for this paper in the order of 30 s. This is the regime of interest with respect to capillary oil imbibition from the initially viscosifying ink layer into the paper. Instead of plotting the force values at the relative coarse time steps shown in Fig. 1, we analyzed the force-time integral, as suggested intuitively by Gane, Seyler and Swan [7], of the single pull-off curves illustrated in Fig. 3, within the tack rise region, given by,

$$h_{\mathrm{p}} = \frac{\int F\mathrm{d}\,t}{A_{\mathrm{F}}} \tag{1}$$

where A_{F} is the footprint area formed by the contact of the tack wheel with the paper surface (Fig 4). The obtained expression has the units of viscosity, a "process" viscosity, h_{p}, and is plotted in Fig. 2.

---

[2] Ikonofix is a product name of Zanders Feinpapiere AG, D51439 Bergisch Gladbach, Deutschland

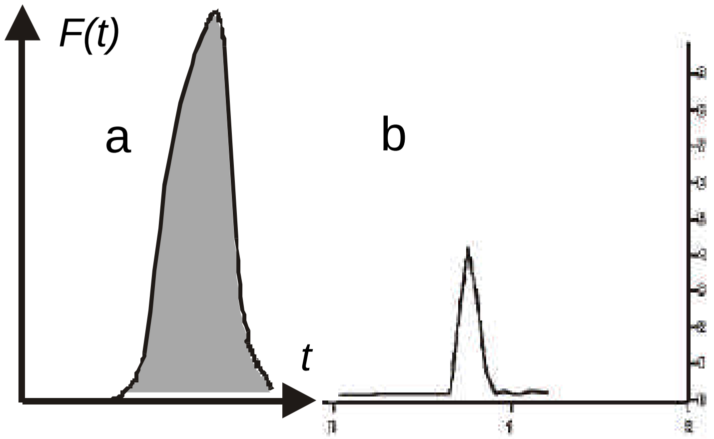

Fig. 3 *a) schematic pull-off curve with integrated area,   b) typical pull-off curve asseen in the tack rise region of Fig. 1*

Some relevant data for the physical characterization of our tack experiments are given in Table 1 and a schematic sketch is given in Fig. 4.

	Symbol	Value	Unit
Ink density	r_{i}	1.01 x10^{3}	kgm^{-3}
Printed area	A_{p}	46.62 x10^{-4}	m^{2}
Pull-off or footprint area	A_{F}	5*17 (x*y) x10^{-6}	m^{2}
Mass of ink component *i*	m_i		kg
Ink layer thickness	L_0	0.99 x10^{-6} (n=37, ± 0.12)	m

Table 1 *Symbols, abbreviations and values used in the relevant calculations, n is the number of measurements*

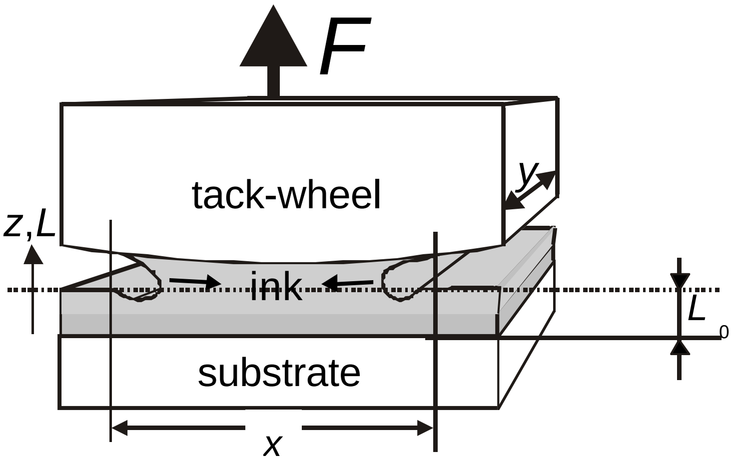

Fig. 4 *Schematic view of tack set-up under the assumed formation of an extensional force.*

Applying an extensional model

The static pull-off mode of the ISIT provides a close approximation to a constant acceleration extensional regime. Going back to Fig. 2 and Fig. 4, and Eq. 1, we now consider an uniaxial extensional term as, for example, given by the Hencky strain expression (Macosko [8]) in which the extension to a dimension of L occurs from a start dimension of L_0:

$$e = \ln(L/L_0) \tag{2}$$

such that the uniaxial extensional viscosity, h_u, can be expressed via the stress tensor, T_{ij},

$$h_\mathrm{u} = (T_{zz} - T_{yy})/\dot{e} \quad = \quad F(t)e^{\dot{e}t}/\left(A_\mathrm{F}\dot{e}\right) \tag{3}$$

where e is the Hencky strain. To remove the unknown rate of change of strain, we integrate Eq. 3 with respect to time over the complete single pull-off curve using $F(t)$ as the measured separating force to obtain a process extensional viscosity, h_pu .

$$\frac{\int_0^\infty F(t)\mathrm{d}t}{A_F} = \int_0^\infty h_\mathrm{pu}\,\dot{e}\,e^{-\dot{e}t}\mathrm{d}t = \left[-h_\mathrm{pu}e^{-\dot{e}t}\right]_0^\infty = h_\mathrm{pu} \tag{4}$$

The ISIT software provides directly the force-time integrals, so we can obtain h_pu directly, confirming the intuitively proposed Eq. (1). We can now match the values with the extrapolated, independently-determined, $h^*(0)$ from the relaxation measurements using a scaling via the Trouton ratio,

$$h_\mathrm{pu}(t) = 3h_1(t) \tag{5}$$

which relates the extensional viscosity to the shear viscosity and normalizing $h_1(0)$ with $h^*(0)$ by a simple scaling factor, k.

The assumptions implicit in the integration made in Eq. (4) are that the effect of changing L_0 is ignored and that L is large when T represents the end of the pull-off, i.e. that $\mathrm{d}e/\mathrm{d}t$ is large as the tack wheel finally extends the ink to fracture point. This allows the boundary of the integral in t to be considered as $t \sim \infty$. If this were not the case then Eq. 4 would become,

$$\frac{\int_0^T F(t)\mathrm{d}t}{A_\mathrm{F}} = \int_0^T h_\mathrm{pu}\,\dot{e}\,e^{-\dot{e}t}\mathrm{d}t = \left[-h_{pu}e^{-\dot{e}t}\right]_0^T = h_{pu}\left(1 - e^{-\dot{e}T}\right) \tag{6}$$

Practically, L_0 is related to the wet or effectively mobile layer. However, the extension of the film is so great, leading in fact to a final fracture of the film, that the ratio L/L_0 is always assumed large over the extent of the pull-off action such that we consider conditions of strong flow only. For thicker layers and slower separation times the change to weak flow might be a complicating factor. However, if we stay in one regime, the scaling factor k can be expected to make a good compensation for this assumption. Development of the instrument to obtain position-sensitive data during the pull-off would allow evaluation of e and $\mathrm{d}e/\mathrm{d}t$. Meanwhile, the information is already present in terms of the value of the experimental separation time, T_S, such that the scaling factor, k, could be related to already known parameters by the expression:

$$k = \left(1 - e^{-\dot{e}T_\mathrm{S}}\right) \tag{7}$$

to obtain an estimate for $\mathrm{d}e/\mathrm{d}t \sim 0.6\ \mathrm{s}^{-1}$, for a pull-off time of $T_\mathrm{S} \sim 0.2$ s and $k \sim 0.11$ (Table 2). This is a subject for further direct confirmation.

Data point	Time /s	Pull-off integral ∫Fdt /Ns	Solution for h_{pu} /Pas	Solution for h_{pu} normalized † to h*(0) /Pas
1	1.8	0.28	1098.04	122.65
2	4.1	0.3	1176.47	131.41
3	7	0.42	1647.06	183.97
4	9.7	0.49	1921.57	214.63
5	12.3	0.49	1921.57	214.63
6	13.7	0.5	1960.78	219.01
7	14.9	0.52	2039.22	227.78
8	17.5	0.6	2352.94	262.82
9	18.5	0.64	2509.80	280.34
10	19.5	0.67	2627.45	293.48
11	20.2	0.66	2588.24	289.10
12	24.9	0.75	2941.18	328.52

Table 2 *Values obtained from the extensional viscous model, † normalizing constant k=0.1117.*

THE INK RHEOLOGY AS IT SETS – obtaining the solids content as a function of time on paper

Combining Eq. 2 from part I of this paper with Eq. 4 and Eq. 5 in this part II we obtain an approximation for the change in oil content in our system as a function of the tack force-time integrals and the footprint area,

$$\Delta f_{\mathrm{oil}} \approx \frac{\ln\left(\dfrac{\int F(t)\mathrm{d}t}{3A_{\mathrm{F}}}k\right)-a}{b} \qquad (8)$$

where k is the scaling factor used in Table 2, a and b are the fitting parameters from the fit of h*(0) as a function of oil dilution given in Fig. 3 of part I of this paper.

The values are plotted in Fig. 5 for the tack data of Fig. 2 showing the time dependent decrease in oil content of the ink. Recent work by Rousu and co-workers [9,10] has shown the initial preferential absorption of mineral oils, while the removal of linseed oil is more retarded. Not knowing the formulation of our ink at time t and hence the total oil makeup, we assume that at the time of 30 s, which is on the tack force plateau, the largest amount of oil removed from the setting ink is mineral-based.

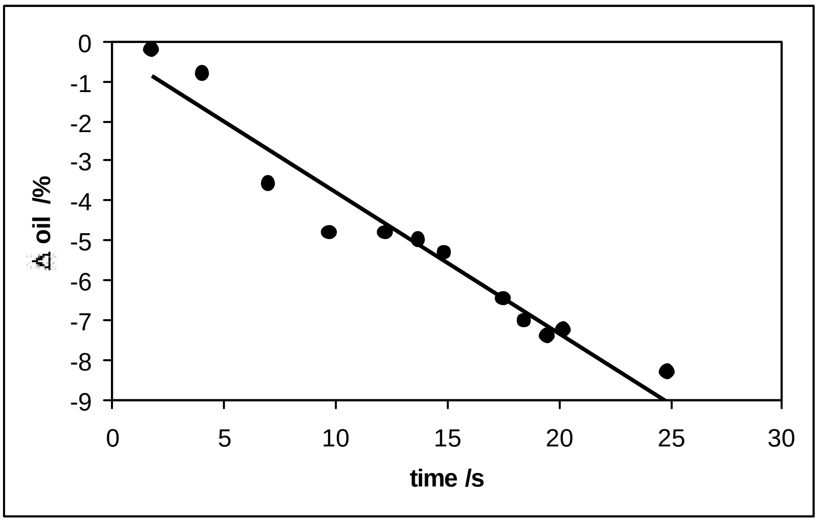

Fig. 5 *The proposed differential oil content of the ink from Eq. 8 as a function of time in contact with the paper surface*

The fraction of oil content being absorbed by the paper is decreasing linearly with time over the timescale of tack increase (Fig. 4). If we assume the following linearity,

$$\Delta f_{\text{oil}}(t) = f_{\text{oil}}(t) - f_{\text{oil}}(0) = -ct \tag{9}$$

where $$1/f_{\text{oil}}(t) = \frac{m_{\text{oil}}(t) + m_{\text{solid}}}{m_{\text{oil}}(t)} = 1 + \frac{m_{\text{solid}}}{m_{\text{oil}}(t)} \tag{10}$$

such that, rearranging, we have the mass of oil in the ink as a function of time, $m_{\text{oil}}(t)$, in terms of the unchanging mass of solids, m_{solid}, and the original mass fraction of oil, $f_{\text{oil}}(0)$ in the ink, respectively.

$$m_{\text{oil}}(t) = \frac{m_{\text{solid}}}{1/f_{\text{oil}}(t) - 1} = \frac{m_{\text{solid}} f_{\text{oil}}(t)}{1 - f_{\text{oil}}(t)} = \frac{m_{solid}\left(f_{\text{oil}}(0) - ct\right)}{1 - \left(f_{\text{oil}}(0) - ct\right)} \tag{11}$$

This is an interesting finding, in that absorption of free fluid over such timescales would normally be expected to follow a $\surd t$ relationship.

To obtain the rate of mass loss of oil, we can differentiate, to obtain,

$$\frac{\mathrm{d}m_{\text{oil}}(t)}{\mathrm{d}t} = \frac{-cm_{\text{solid}}}{\left[(1 - f_{\text{oil}}(0)) + ct\right]^2} \propto -1/t^2 \tag{12}$$

to find that this rate falls off as $\sim t^{-2}$.

In this case, the existence of a resistive factor forming as the ink becomes more viscous is the likely explanation. This will need to be tested independently and is the subject of future work.

CONCLUSIONS

The balance between the interface adhesive and internal cohesive aspects of a fluid layer in contact with surfaces of differing surface energy and roughness has been illustrated using an offset ink and a variety of substrates. It was found that for a non-absorbent smooth surface, the cohesion of the mobile ink film plays the dominant role in respect to the force required to separate a second contacting surface. This was likened to the situation that might occur between two parallel plates in the case where the basal area of one surface is much larger than the other, such that the ink film can be considered infinite and continuous. This, we conclude, differs in the case of a rough or a porous, permeable surface which would allow the influx of air and rupture at surface discontinuities, in which case the separation force is dominated by viscous, cavitational and, if rapid, inertial forces. Furthermore adhesive forces are important when separation occurs at the boundary layer.

We have shown that it is possible to use tack measurements based on the pull-off technique, as used by the ISIT tester, to determine a model for the viscosity and solids content of an offset ink as the ink begins to set on a paper surface. Under these conditions, the separation force is related predominantly to the viscous properties of the cohesive ink layer. This technique is shown to maintain the cohesion between the wet mobile ink layer and the immobilizing ink-paper interface. Therefore, the concept of a distinct mobile layer existing above that of a delineated forming filtercake is precluded. The continuity between the mobile ink and the concentrating interface is thus maintained and the increase in measured tack is related to the fluid loss and viscosity increase as defined through a uniaxial, extensional viscosity model.

The method developed for correlating the viscosity of an ink, as a function of solids content, with the ISIT pull-off force-time integral provides a potential universal tool for workers to study the solids and viscosity properties of a wide variety of polymer and particulate suspensions as they interact with the surface of a substrate. It permits the progressive change in fluid properties, for example, through evaporation, absorption, catalysis or external curing, to be monitored in situ.

REFERENCES

1. Gane, P. A. C., Schoelkopf, J., Spielmann, D. C., Matthews, G. P., and Ridgway, C. J., "*Fluid transport into porous coating structures: some novel findings*", Tappi Journal, 83(5), 2000, p77-78

2. Schoelkopf, J., Gane, P. A. C., Ridgway, C. J., and Matthews, G. P., "*Influence of inertia on liquid absorption into paper coating structures*", Paper and Coating Chemistry Symposium, Stockholm, Sweden 2000, p80

3. Schoelkopf, J., Ridgway, C. J., Gane, P. A. C., Matthews, G. P., and Spielmann, D. C., "*Measurement and Network Modeling of Liquid Permeation into Compacted Mineral Blocks*", Journal of Colloid and Interface Science, 227, 2000, p119-131

4. Schoelkopf, J., Gane, P. A. C., Ridgway, C. J., and Matthews, G. P., "*Practical observation of deviation from Lucas-Washburn scaling in porous media*", Colloids and Surfaces A: Physicochemical and Engineering Aspects, 206(1-3), 2002, p445-454

5. Ridgway, C. J., Schoelkopf, J., and Gane, P. A. C., " *A new method for measuring the liquid permeability of coated and uncoated papers and boards*", Nordic Pulp and Paper Research Journal, 2002, accepted for publication

6. Schoelkopf, J., Gane, P. A. C., Ridgway, C. J., Spielmann, D. C., and Matthews, G. P., "*Rate of vehicle removal from offset inks: a gravimetric determination of the imbibition behaviour of pigmented coating structures*", Tappi 2001 Advanced Coating Fundamentals Symposium Proceedings, San Diego, Tappi, Atlanta, 2001, p1-18

7. Gane, P. A. C., Seyler, E. N., and Swan, A., "*Some novel aspects of ink/paper interactions in offset printing*", International Printing and Graphic Arts Conference, Halifax, Nova Scotia, Tappi Press, Atlanta, 1994, p209-228

8. Macosko, C. W., "*Viscous Liquids*", Rheology: Principles, measurements and applications, VCH Publishers, New York, 1994, p425-474

9. Rousu, S. M., Gane, P. A. C., Spielmann, D. C., and Eklund, D., "*Separation of off-set ink components during absorption into pigment coating structures*", Nordic Pulp and Paper Research Journal, 15(5), 2001, p527-535

10. Rousu, S. M., Gane, P. A. C., and Eklund, D. E., "*Influence of coating pigment chemistry and morphology on the chromatographic separation of offset ink constituents*", Twelfth Fundamental Research Symposium, Oxford 2001, p1115-1148