Printability

OFFSET INK TACK AND RHEOLOGY CORRELATION--1: INK RHEOLOGY AS A FUNCTION OF CONCENTRATION

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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 1, and comparison with the SeGan Ink Surface Interaction Tester (ISIT) in part 2. 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 .

Application: Controlling the dynamics of a preferred network absorption pathway in relation to the total pore volume is a major factor in controlling the press runnability of coated paper in relation to the development of tack.

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

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 surface of the paper coating. 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 that 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 conditions 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 3-D 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 (a software program of the Environmental and Fluids Modelling Group, University of Plymouth, PL4 8AA, UK), 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 (ISIT; a product name of SeGan Ltd., Perrose, Lostwithiel, Cornwall PL22 0JJ, England) 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.

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 nonporous medium, e.g. a cured latex film, the latter is molecular and applies mainly to molecular mixing or exclusion. The consequence is an up-concentration 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 (4, 7). 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 we used a StressTech (a product name of ReoLogica Instruments AB, Lund, Sweden) controlled stress rheometer with a plate-plate geometry (UP40). 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 (a product name of K+E Inks, Stuttgart, Germany) 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 $\eta^*(t)$.

The ink and the oil were mixed thoroughly first by hand using a spatula, then under ultrasonic for 5 min 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.

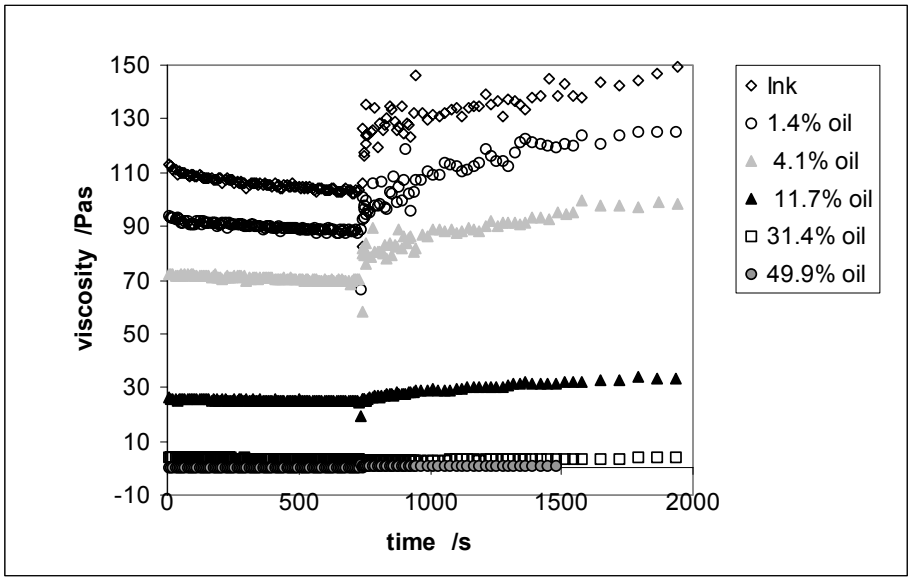

Fig. 1 Overview of shear viscosity at 30 s^{-1} and subsequent relaxation monitored by stress oscillation in the linear visco-elastic (LVE) regime as a complex viscosity, η^*.

Figure 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:

$$\eta^*(t) = \left(\eta^*(\infty) - \eta^*(0)\right) \cdot \left(1 - e^{-t/\tau_0}\right) + \eta^*(0) \qquad (1)$$

where $\tau 0$ represents the characteristic relaxation time. Eq. 1 was entered into TableCurve 2D (a product name of SPSS Inc.), which fits $\tau 0$, $\eta^*(0)$ and $\eta^*(\infty)$ to achieve the smallest residue r2. (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, **Fig. 2** shows the blend containing 11.7 w/w% oil, with a $\tau 0 \sim 500$ s.

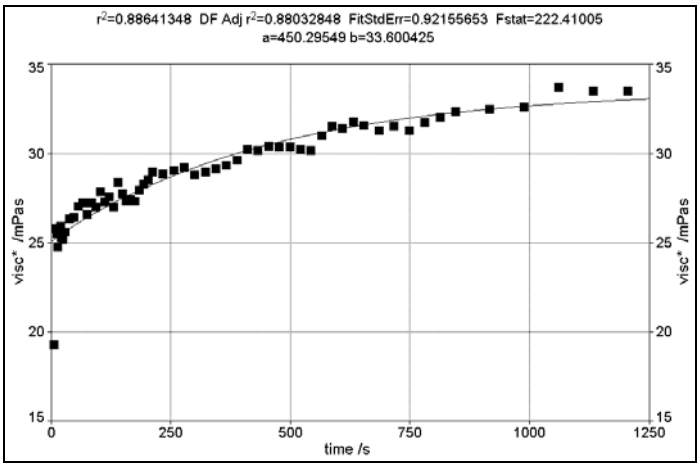

Fig. 3 Ink structure recovery regime fitted with Eq.1

The viscosity data for η∗(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,

$$\ln \eta^* = a + b\Delta\phi_{\text{oil}} \qquad (2)$$

where a and b are fitting parameters and Δϕoil is the added oil content in w/w% with respect to the sum of the undiluted ink plus the added oil. **Figure 3** shows the resulting curve, with the parameters a and b shown, which are used later to compare with the ISIT findings.

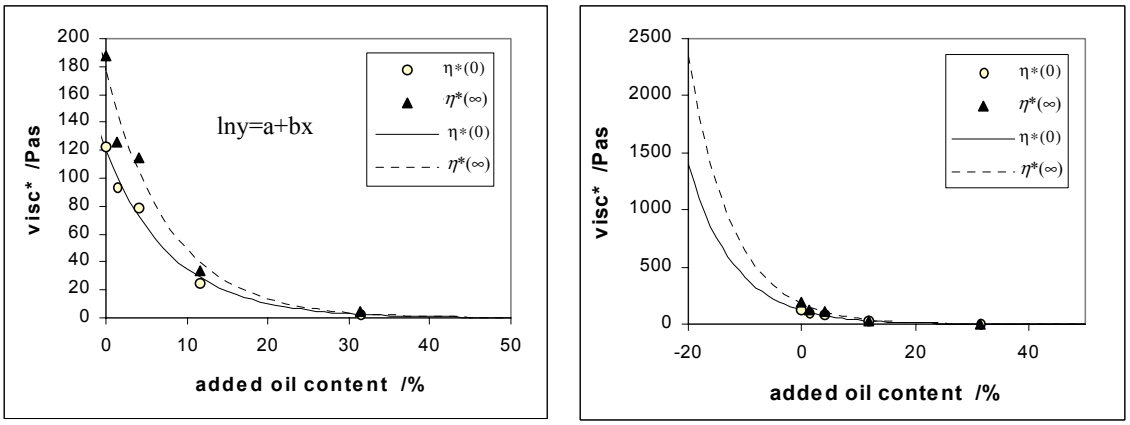

Fig. 5 Comparison of η∗(0) and η∗(∞) as a function of added oil content of the ink $\Delta\phi_{oil}$ (w/w%) - the extrapolation of η∗(0) (a=4.78, b= -0.122) , on the right, to reduced oil content, is used as the basis for the viscosity comparison with ink tack measurement in part 2 of this paper.

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 η∗(0) and η∗(∞). 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.

The methodology we go on to show in part 2 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.

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