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INK RELEASE FROM PRINTED SURFACES – NEW METHODOLOGY AND INITIAL INSIGHTS TO THE TRUE MECHANISMS BEHIND INK DETACHMENT

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ABSTRACT

The aim of this study was to develop and test a new equipment for evaluating the mechanism behind ink detachment from printed model surfaces. The equipment developed for this purpose consisted of an impinging jet cell, a printed model cellulose surface and a microscope equipped with a CCD camera for image collection. By applying image analysis to images of the printed surfaces at different time intervals, during the detachment studies, it was possible to quantify the ink detachment from the surface. Mechanistic studies of offset ink and flexographic ink detachment were also performed with the new equipment. Results show that the flexographic inks seem to be removed by a washing process in which the printed image is gradually removed from the surface. For the offset print the results are quite different. In order to remove the printed offset ink it is necessary to have a certain hydrodynamic shear in combination with a swelling of the cellulose surface. This swelling seems to create a relative movement between the ink and the cellulose surface. In solutions with higher ionic strength no offset ink is removed.

These results are in line with earlier assumptions about the deinking mechanisms but in the present work these processes are actually shown for the first time.

INTRODUCTION

Recycled papers are today a very important raw material resource for the production of many different paper grades from containerboard and hygiene papers to high quality printing papers such as SC grades. For hygiene papers and printing papers ink is one of the major contaminants and the quality of the secondary pulp is determined largely by the extent of ink removal. Today flotation deinking is used with rather large success in Western Europe whereas wash deinking is more common in North America. This difference has been dictated by more common use of flexographic printing of newsprint in North America. However, despite the common use of these processes there is still no fundamental understanding of the true mechanism responsible for the ink detachment from the fibre surface. A better knowledge of this would enable a faster development of new chemicals for deinking and, furthermore, this knowledge could initiate the development of new deinking processes. The aim of the present work was hence to bridge this gap in our knowledge.

A deinking process can be divided into three processes: a) ink detachment from the fibres; b) ink agglomeration or ink dispersion and c) removal of ink by air flotation or washing.

In an effort to reach the most efficient deinking system, it is important to study, in detail, each part of every process to find the critical factors in every step. Studies of the deinking process can be a real challenge due to the mixture of different fibres, additives and seasonal variations that represent the raw material of secondary fibres. It is therefore important to find a reliable model system that represents each part process in a deinking process. A model system in this respect is defined as a well-controlled system without any unwanted or unknown variations. Some research groups have developed and used model systems for ink detachment studies. Rao et al. investigated how mechanical and chemical factors affect the ink detachment from printed model papers [1]. Borchardt et al. used a model system based on ^{1}H-NMR imaging where the ink detachment was followed *in situ* [2]. Summaries of the knowledge of the deinking process [3] and deinking fundamentals [4] have been given earlier and will not be given here. In this paper we report about a new methodology for studies of ink detachment from model surfaces. The

equipment mainly consists of three different components: a) an impinging jet set-up for treatment of model surfaces; b) printed model surfaces and c) microscopic detection of ink release with the aid of image analysis of collected images from a CCD camera attached to a microsope. Part b) and part c) are new developments and will be described more in detail later in this paper whereas the impinging jet technique is an already existing technique. The history of using an impinging jet methodology for deposition studies goes back to 1983 when van de Ven reported this new technique [5]. The main advantage was that it made it possible to study deposition directly and at stagnation point flow. Van de Ven and co-workers also showed how the impinging jet technique could be used to study deposition of latex particles [6], fines and fillers [7] at the air/water interface. This was found to be a representative model system for the flotation process.

Corak et al. have also reported about deposition and detachment studies using the impinging jet methodology [8]. In their work the deposition of latex particles, as a model for pitch, on special treated polyethylene films was studied. Detachment of the deposited latex particles gave, however, no satisfactory results. The amount of detached particles was very low and no significant differences between different polymer treatments of the surface could be established. Van de Ven [7] also showed that outside the stagnation point, where pure diffusion will prevail, there is an increased hydrodynamic shear. This means that studying the ink detachment with an impinging jet set-up will allow for studies on both diffusion and shear controlled ink release.

EXPERIMENTAL

Impinging jet cell

Construction drawings of the jet cell was kindly supplied by Robert Pelton, McMaster University, Hamilton, Canada, and a schematic representation of the new set-up is shown in Figure 1.

A schematic drawing of the impinging jet cell is also shown in the inset in Figure 1. A fluid, in this case an aqueous solution, flows up the centre tube of the cell and hits the printed cellulose surface and then runs down the cell and exits through the outer tube. The syringe pump (SCA Research, Sundsvall, Sweden) gives a pulsation free flow of water with a well-controlled rate. The printed surface is observed through a microscope (BX30M, Olympus) and with a CCD-camera (ICD-46E, Ikegami). Images are collected (program prepared at SCA Research, Sundsvall, based on Visual Basic) during the trial and are subsequently analysed manually or by automatic image analysis (prepared at SCA Research, Sundsvall, based on Matlab). The fluid hitting

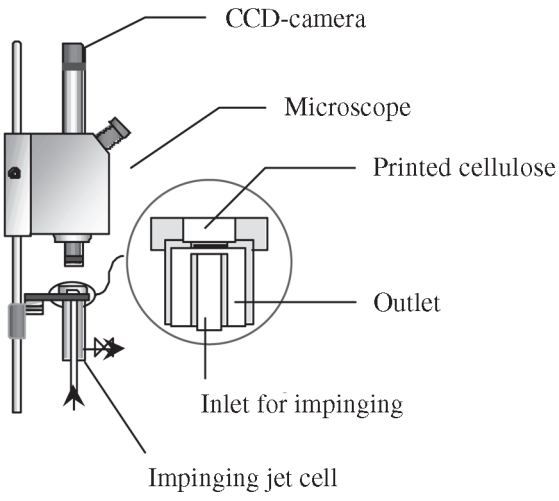

Figure 1 Schematic description of the impinging jet equipment.

the surface results in a stagnation point flow in the impingement area. In this point the shear rate is zero but increases linearly with radial distance from the stagnation point [9]. The internal radius of the centre tube was 1.0 mm and the distance between the centre tube and the printed surface was 1.5 mm.

Model surfaces

A glass surface, precoated with a cationic polymer, was covered with cellulose by the following spin coating technique [10]: A cleaned round glass slide (diameter = 19 mm and thickness = 1.2mm) was treated with polyvinylamin-HCl solution (11% solids content and diluted to 0.1 g/l before use (BASF AG, Ludwigshafen, Germany)) for 30 minutes. The glass was rinsed with water and dried in an oven at 50°C for 15 minutes. Cellulose (0.5 g., dissolving pulp, Modo Paper, Domsjö, Sweden) was torn into small pieces and placed in an Erlenmeyer flask. NMMO (50%, 25 g., N-Methylmorpholine N-oxide, Aldrich) was added and the suspension was heated to 115°C, just enough to dissolve the cellulose. The clear yellow solution was diluted with DMSO (25 g, Dimethylsulfoxide Aldrich). The temperature was allowed to decrease

to 98°C and was maintained at this level during the preparation of the cellulose films.

The precoated glass slide was placed on the spin coater and the surface was covered with cellulose solution. At high rpm (revolutions per minute) a thin transparent film of cellulose was created on the slide. The cellulose surface was placed in water for 4 hours. During this time the water was changed once. The surfaces were dried and stored in a desiccator before use. ESCA analysis of the prepared surfaces showed no sign of impurities on the cellulose surface [10].

By changing the spincoated material or by chemical treatment of the cellulose surface, the model surface was very easily modified. Hydrophobic surfaces were easily prepared from cellulose surfaces, which were treated with AKD dissolved in toluene (0.5 g/l) at room temperature for 15 minutes [11]. The surfaces were rinsed with toluene and cured at 105°C for 30 minutes.

The glass slide was also covered with cellulose acetate, using the same technique as described in literature [11]. In order to test a high energy surface which would be inert to electrolyte solutions the glass slides were covered with gold by using a sputtering technique.

A screen pattern was then printed on the cellulose surface with two different printing techniques.

Images of flexographic ink (82 Aquajet black, A/S Torda Fabrikker, Lierstranda, Norway) were printed with IGT Printability Tester F1, IGT, Amsterdam, The Netherlands. Offset images were printed with a Prüfbau multipurpose printability tester, Prüfbau, München, Germany, using offset ink (DDPFF offset standard, Lorilleux, Denmark).

Detachment

The printed images were exposed to light at room temperature for three days before use. To prevent fast ageing of the prints, they were thereafter placed in black bags filled with nitrogen and stored in a refrigerator before use. In this way it was possible to keep the prints for weeks without any changes in physical properties of the printed ink due to ageing.

The printed surface was placed in the impinging jet cell and impinged with water solutions at room temperature. During all trials, the volumetric flow rate was kept at 1 ml/s, which corresponds to a velocity of 0.3 cm/s. Images of the ink release were collected every second and analysed manually or by automatic image analysis.

The water solution was treated with different additives: sodium silicate, sodium chloride, sodium hydroxide and Bimex 400, a non-ionic surfactant

(BIM Kemi, Stenkullen, Sweden). Sodium silicate (Na_2SiO_3 x 5 H_2O), sodium chloride and sodium hydroxide were all purchased from Kebo AB. All solutions were prepared with freshly distilled and deionized water.

Two different types of experiments were conducted with the impinging jet technique. In one set of experiments the cellulose surfaces were mounted in a non liquid-filled cell and then exposed to the different solutions tested in the experiments. In another set of experiments the surfaces were mounted in a liquid-filled cell and then exposed to the different test liquids. This means that the cellulose surfaces were allowed to swell to their equilibrium swelling. The degree of swelling was roughly evaluated with an Atomic Force Microscope (AFM) Nanoscope III from Digital Instruments, USA, from measurements of dry and wet model surfaces.

Work of adhesion and surface properties

An attempt was also made to investigate how the work of adhesion between the ink and the model surface could be linked to ink removal. In order to do this the following approach was used.

The total energy change connected with the separation of cellulose and offset ink in water (W_{cow}) can be estimated with the following equations:

$$W_{cow} = W_{co} + W_{ww} - W_{cw} - W_{ow} = \gamma_{cw} + \gamma_{ow} - \gamma_{co} \quad (1)$$

W_{cow} = Total energy change when separating cellulose and offset ink in water
W_{co} = Work of adhesion between cellulose and offset ink
W_{cw} = Work of adhesion between cellulose and water
W_{ow} = Work of adhesion between water and offset ink
W_{ww} = Work of cohesion for water
γ_{co} = interfacial energy of cellulose and offset
γ_{cw} = interfacial energy of cellulose and water
γ_{ow} = interfacial energy of offset and water

If W_{cow} is larger than 0 the ink release is not spontaneous if the work of adhesion and cohesion are the only determining factors for ink removal. Knowledge of the different interaction parameters to check if this holds true would therefore be essential.

The interfacial energies can then be determined from contact angle measurements using Young's equation and the Lifshitz van der Waals/acid-base approach. [12] These equations are given below

Young's equation

$$\gamma_{sw} = \gamma_s - \gamma_w \cos \Theta_{sw} \quad (2)$$

γ_s = surface energy of solid (cellulose or offset)
γ_w = surface energy of water
Θ_{sw} = contact angle between solid and liquid

The following equation is used in the Lifshitz van der Waals/acid-base method to estimate the acid base properties of the different materials involved in the release process

$$\gamma_s = \gamma_s^{LW} + 2\,(\gamma_s^- \cdot \gamma_s^+)\,½ \quad (3)$$

γ_s^{LW} = Lifshitz van der Waals component of the surface energy
γ_s^- = Lewis base component
γ_s^+ = Lewis acid component

The interfacial energy between two materials (1 and 2) can then be calculated with the following equation

$$\gamma_{12} = \gamma_1 + \gamma_2 - W_{12} =$$
$$((\gamma_1^{LW})^{0.5} - (\gamma_2^{LW})^{0.5})^2 + 2\cdot((\gamma_1^+ \cdot \gamma_1^-)^{0.5} + (\gamma_2^- \cdot \gamma_2^+)^{0.5} - (\gamma_1^+ \cdot \gamma_2^-)^{0.5} - (\gamma_1^- \cdot \gamma_2^+)^{0.5}) \quad (4)$$

The total surface energy is hence separated into three components, Lifhitz van der Waals contribution, and an acid and a base contribution. These are calculated from contact angle measurements with three reference liquids with known surface properties.

Contact angle measurements were performed with a Dynamic Absorption Tester, Fibro DAT 1121/1122. The contact angles were measured in advancing mode.

RESULTS

Characterisation of model surfaces

The surfaces were characterised by contact angle measurements (Table 1). The achieved results from contact angle measurements were comparable with values from earlier investigations [13].

Table 1 Contact angle of water on model surfaces.

Surface	Contact angle (°)
Cellulose	24
AKD-cellulose	61.5
Cellulose acetate	56
Offset	104

Detachment of flexographic ink and of offset ink

Flexographic and offset prints were both detached when exposed to alkaline water solution (pH 11.5) in the impinging jet cell. However, images collected during the experiments showed two completely different mechanisms (Figures 2 and 3).

Flexographic ink seems to be detached by a dissolution mechanism. If the print was old (more than a week in room temperature), the ink layer closest to the cellulose surface was not detached. Detachment of flexographic ink was also quantified by determination of the reduction of the remaining ink area as a function of time and the results from this are shown in Figure 4.

The results in Figure 4 were calculated as the remaining amount of ink after converting the initially collected images to binary images.

Offset ink was released when the liquid front reached the dry print, in the zone with higher shear rate. No release was observed in the zone near the stagnation point. This resulted in a circle, where the print was released, on the printed cellulose surface (Figure 5).

Because of the different mechanisms of offset ink and flexographic ink detachment, the image analysis program could not be used directly to analyse

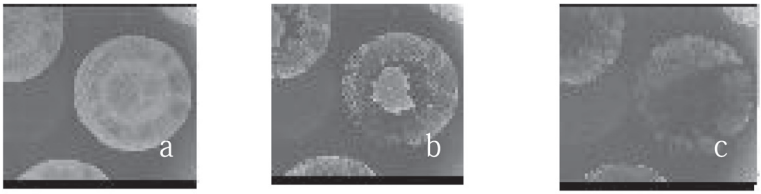

Figure 2 Three images collected during ink detachment of flexographic ink on cellulose surface. a) 1 second, b) 11 seconds and c) 13 seconds exposure of basic water solution (pH 11.5). These measurements were collected from experiments with an initially dry cell.

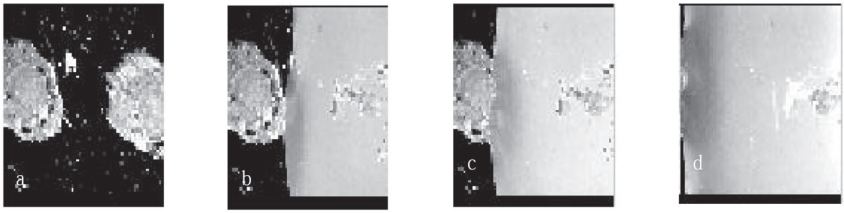

Figure 3 Offset ink detachment from cellulose surface. Images were collected during the experiment. a) Dry cellulose surface with two printed offset dots. b-d) Water (with a brighter shade) is gradually covering the cellulose surface. The print is released when the water reaches the dry print. These measurements were collected from experiments with an initially dry cell.

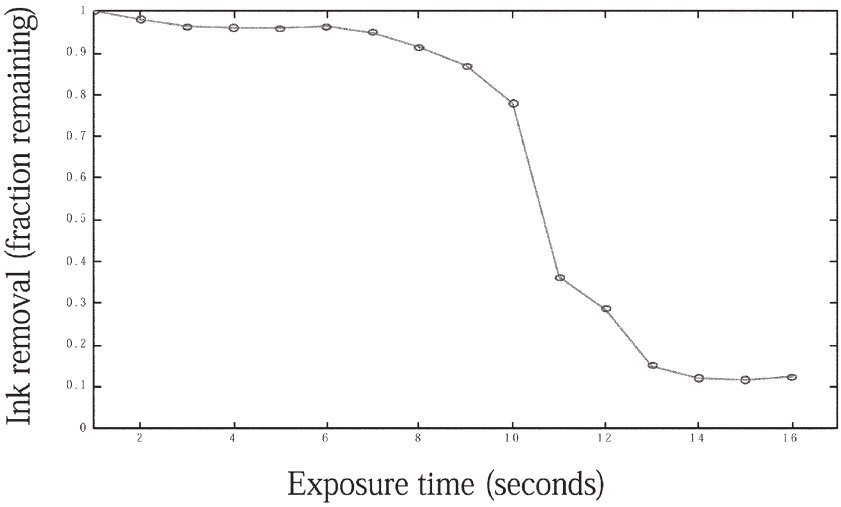

Figure 4 Flexographic ink removal from cellulose surfaces as determined from binary images.

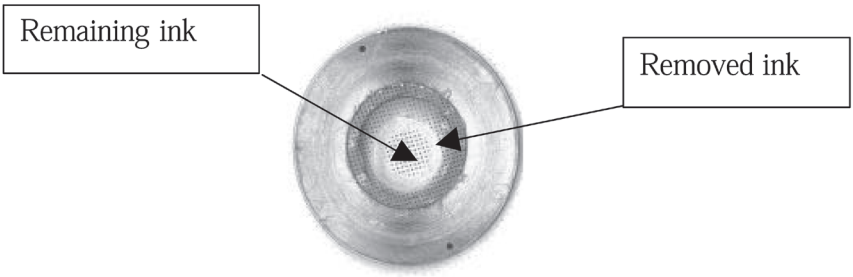

Figure 5 Offset ink removal from the model cellulose surface.

the offset images. Instead, visual analysis based on removed ink or not removed ink was used for the evaluation of offset ink removal.

Detachment of offset ink – influence of different additives

Water solutions of non-ionic surfactants and of silicate at different pH levels were impinged on offset printed cellulose surfaces.

Both for the silicate solutions and surfactant solutions the ink detachment became more efficient when the pH was increased (Table 2). A decrease of ink

Table 2 Summary of results from experiments with removal of offset ink from cellulose with different additives and change of pH. All experiments were conducted with a non liquid-filled cell.

Additives	Concentration	pH[b]	Removed ink
Bimex 400[a]	0.01 g/l	10	No
Bimex 400[a]	0.01	11	No
Bimex 400[a]	0.01	12	Yes
Bimex 400[a]	0.1	10	No
Bimex 400[a]	0.1	11	No
Bimex 400[a]	0.1	12	Yes
Sodium silicate	1.5 %	7.5[c]	No
Sodium silicate	1.5	10[c]	Some
Sodium silicate	1.5	13	Yes
Sodium chloride	1 M	12	No
No additives		12	Yes

[a]Non-ionic surfactant, BIM Kemi. [b]pH was adjusted with NaOH. [c]pH was adjusted with HCl.

removal was also observed when sodium chloride was added to alkaline water solution.

Again, as in the initial experiments, the ink was readily removed from the area with high shear rate. This phenomenon was further investigated when the dry printed cellulose surface was exposed to alkaline water solution. No release of offset ink could be detected in the stagnation point or when the surface was pre-wetted, which was done by filling the outer tube with the water solution, before starting the experiment.

Surface variation

In order to clarify the importance of surface energy, different types of surface treatments were investigated. The printed surfaces where impinged with alkaline water solution (pH 12).

When printing offset ink directly onto a gold surface (Table 3) a significant decrease in ink detachment from the surface was detected. The same result was found for cellulose acetate and AKD sized cellulose.

Table 3 Offset ink removal with alkaline water solution (pH12).

Surface	Removed ink
cellulose	Yes
AKD-cellulose	No
cellulose acetate	No
gold	No

Surface energies

Surface properties were calculated from the contact angle measurements summarised in (Table 1) and from contact angle measurements with diiodomethane and ethyleneglycol in order to clarify if there should be a spontaneous release of the ink when the printed surface was exposed to water or not. The results from these measurements and the application of equations 2 and 3 resulted in the data summarised in Table 4. By using equation 4 the following interfacial energies were calculated

γ_{co} = – 1.25 mN/m
γ_{cw} = – 21.5 mN/m
γ_{ow} = 7.89 mN/m

Table 4 Surface energy (mJ/m^2) of solid surfaces.

solid	γtot	γ^{LW}	γ^+	γ^-
cellulose	45	42,3	0,031	57,7
offset	30,8	25,1	0,46	17,22
cellulose-AKD	38,3	37,6	0,005	24,1

Together with equation [1] this will result in a W_{cow} of –12.4 mN/m indicating a spontaneous ink release from the surface when the printed surface was immersed in water. By doing the same calculation with the AKD treated cellulose a value of +11.2 mN/m was achieved indicating no spontaneous release of the offset ink from the AKD-treated cellulose surface when this surface was immersed in water. This is in accordance with the measurements shown in Table 3 above and the use of these calculations will be further discussed under Discussion.

The occurrence of negative values of the interfacial tension is hard to explain with standard thermodynamic arguments. However, with the application of the acid/base approach, i.e., Equations 3 and 4, it is quite possible to reach negative values and Good [16] and van Oss [17] have also discussed the phenomenon. From the equations it might be found that this situation occurs when the work of adhesion is larger than the cohesion of the interacting phases. Van Oss [17] also claims that a negative value of the interfacial tension in most cases is a sign of a non equilibrium situation where the phases slowly will dissolve in each other but that there also exists cases where the negative value is permanent. This will also be handled further under Discussion.

DISCUSSION

The aim of this study was to evaluate ink detachment studies with the impinging jet method and to investigate the mechanism of ink detachment.

Flexographic ink and offset ink on cellulose were readily detached with alkaline water solution, but by completely different mechanisms. This was readily investigated by the collected images during the ink release. Flexographic ink, which often consists of alkali water-soluble resins, was gradually detached due to interaction between the liquid and the ink/cellulose surface. One important factor that strongly influences the ageing of flexographic prints seems to be the exposure of the print towards oxygen. This result could be established in an ageing study where flexographic prints on cellulose surfaces were stored under different conditions.

When the prints were stored in black bags, at room temperature but in different atmospheres, air and nitrogen, differences in ink detachment were observed after two days' storage. Prints stored under nitrogen were completely detached with an alkali solution (10 mM NaOH) while the prints stored in air were more difficult to remove. A thin layer of ink, closest to the surface, was not detached and the amount remaining on the surface was about 20% of the initial ink as shown in Figure 4. The influence on exposure towards UV light from standard flourescent tubes was also studied. In these experiments the printed surfaces were stored both in dark plastic bags (reference) and in transparent plastic bags in UV light in a ventilation hood. No remarkable differences were observed between the two prints when stored under nitrogen, at room temperature, both under light and in darkness, e.g., in black plastic bags. After four days in air the ink was difficult to detach from both of the surfaces. After seven days, the printed surfaces stored under the UV light were not detached at all while the surfaces stored in a black bag detached to some extent, leaving a layer of insoluble ink on the cellulose surface. The temperature seems to have the least effect on ink ageing, at least under the conditions used in the present experiments. When the prints were stored in darkness, under nitrogen but at different temperatures, room temperature and in a refrigerator, there were no detectable differences in detachment of ink. After one week the ink was easily detached without leaving any layer of ink on the surfaces. After two weeks, most of the ink was detached. However, a thin layer of ink was left on both types of cellulose surfaces, i.e., stored under different conditions. An exact determination of the amount of ink remaining on the surface after detachment was not possible with the image analysis program available at the time of the experiments, only the change in the grey-values. These have been given in rather qualitative terms in this discussion but the equipment is just being rebuilt to enable a detection of exact amount of ink remaining on the surface at different time intervals. No doubt the discussion above shows the potential of the experimental procedure.

It has been suggested that the difficulties to remove ink from aged paper are due to oxidation of hydroxyl-groups to carboxylic acids both in the fibres and in the ink. Effective hydrogen bonds can then be formed between the ink and the cellulose making the detachment more difficult. [18] It is also possible that an oxidation polymerisation of the ink resin is the reason for ageing of ink. However, this has not been studied in detail. Inks used for offset prints contain binders dissolved in mineral or vegetable oils, which do not dissolve in alkaline water solutions once they are dried. These inks were not gradually removed from the surfaces. As shown in Figure 3 the ink was removed when the water reached the printed dots. Further, the detachment occurred in the

zone with a higher shear rate. No release was observed in the area close to the stagnation point. Shearing hence seems to be one of the critical factors for efficient ink release.

Typical additives used in the deinking process [14] gave no effect on the offset ink release. Only when the pH was increased to pH 11–12 was ink detached from the cellulose surface (Table 2). In this system, high pH, i.e., cellulose surface swelling seems to be a critical factor for good ink detachment. The importance of the surface swelling was also indicated by the results from the experiments with increasing NaCl concentrations. A clear decrease of ink removal was observed when sodium chloride was added to the alkaline water solutions. This indicates that the surface swelling is essential for ink removal since it is well known that swelling of cellulose gels is reduced when the electrolyte concentration is increased [15]. The swelling of the model surfaces used in the present investigation was also determined with the AFM technique mentioned in the experimental section. When the model surfaces were exposed to deionised water they swelled more than 100%. Further swelling measurements of model surfaces in different liquids are underway but are not available at present. It should also be mentioned that detachment studies of offset ink on gold surfaces also supported the importance of surface swelling since no ink was released from the gold surface. Shearing in combination with surface swelling will give rise to a relative motion between the surface and the ink and obviously this process is necessary to get offset ink removal. In the stagnation point, where no ink detachment occurred, there is no relative motion between liquid and surface.

The hypothesis of a combination of shearing and surface swelling, i.e., relative motion between ink and surface was also tested in the experiments with a dry surface and a pre-wetted surface. When swelling of the surface occurs before shearing from the water jet no ink-release is observed, probably due to the lack of relative motion between the ink and the surface as schematically depicted in Figure 6. No ink removal was detected when the pre-wetted surface was exposed to alkaline water solutions.

The decrease of removed ink from AKD sized cellulose and cellulose surfaces can be an effect of delayed swelling of the surface. Due to the hydrophobic surface the wetting is retarded and hence also the swelling. Another explanation could be that ink, due to molecular similarities with AKD, could penetrate down the AKD layer and form a strong link between cellulose and ink that can protect the ink from detachment. Further investigations are needed to critically test the suggested mechanisms. In these experiments it is also necessary to use model inks with exactly known chemical components.

A procedure to determine the influence of interfacial energies between offset and cellulose and the interaction between these components and water

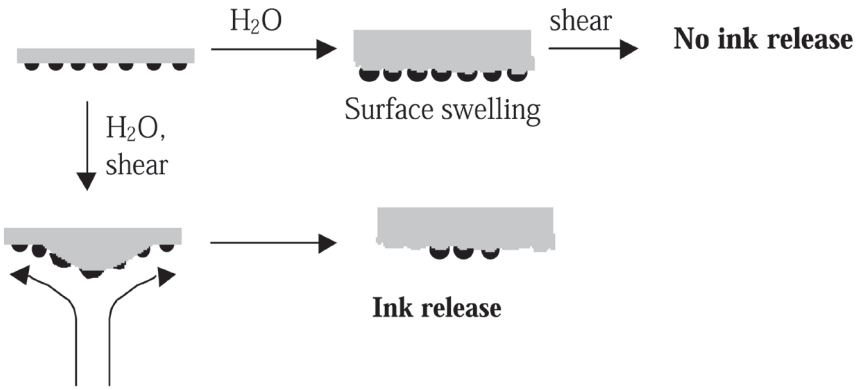

Figure 6 Schematic representation of ink removal of offset print from a cellulose surface. No ink was removed when the surface was pre-wetted but a combination of surface swelling and shearing was sufficient to remove the ink.

to predict the limits for ink release was also used. As mentioned under results the calculation predicted that the ink should be released when offset printed surfaces were placed in water in accordance with experimental results. There is however one uncertainty with these calculations and that is the negative interfacial energies found for cellulose/water and ink/cellulose interactions. These negative values are quite possible to achieve with the van Oss/Good approach [12] but from more classical thermodynamic arguments they are not easy to explain. As was mentioned earlier, Good [16] and van Oss [17] both summarise that these negative values are achieved when the interfacial interaction is larger than the cohesive properties of the respective interacting phases. It is then logical to assume, as done by van Oss [17], that his situation is a quasistatic equilibrium that eventually will lead to a mixing of the interacting phases but there are experimental values showing that the negative values may persist over time [17]. When examining the calculated values in Table 4 it is also interesting to note the high values for the base properties of cellulose. These values are much higher than the values shown by van Oss [19] but the contact angle of water on cellulose is also much lower in the present work than the values shown by van Oss [19]. Since values around 20–25° are more reasonable [10] it is strongly believed that the values presented in the present report are not due to poor characterisation of contact angles on cellulose. When using the same methodology for characterising the interaction between AKD treated surfaces and offset ink the calculations

predicted no spontaneous release of the offset ink when the surfaces were placed in water which is also in accordance with experimental results. In practice it is however often found that AKD-sized paper is easier to deink than unsized paper. One explanation to this difference could be that for sized papers a very hydrophobic surface could be achieved despite a poor surface coverage of the AKD. It has for example been shown by Ström [20] that a surface coverage of AKD of 15% is enough to make a wood fibre appear totally hydrophobic, i.e., fully covered from contact angle measurements. This in turn means that when a surface is printed with offset ink about 85% of the interaction will be between cellulose and ink and only 15% between AKD and ink. In order to avoid this situation the surfaces in the present investigation were treated with AKD dissolved in toluene but no quantitative measurements were conducted to determine the exact surface coverage of AKD on the model surfaces. Atomic Force Microscopy images of the surface indicated a complete coverage but a chemical characterisation of the elements on the surface would also be very useful. No doubt, more experiments are needed to elucidate the influence of interfacial interactions but it is obvious that the experimental procedure presented in the present report gives a fast and simple alternative to determine these interactions. This type of work is currently underway in our laboratories. There is no doubt though that the interfacial energies are important for the ink release. Rao and Stenius [1], for example, found that when the surface energy of the water was decreased the ink came off the printed surface in larger pieces compared with the situation without addition of surfactant.

In order to determine the validity of Equation 1 it is suggested for future work the direct work of adhesion between the ink/cellulose, ink/water and cellulose/water should be determined with the methodology outlined by Chaudhury [21] and as applied to cellulose by Rundlöf et al [22]. This way of evaluating the importance of the adhesion between ink and cellulose is currently underway in our laboratory.

CONCLUSIONS

The present paper has shown that a new equipment consisting of an impinging jet cell, a printed model cellulose surface and a microscope equipped with a CCD camera for image collection is a useful tool for studying the mechanism behind ink removal from model surfaces. By applying image analysis to images of the printed surface at different time intervals, during the detachment studies, it is possible to quantify the ink detachment from the surface. The technique can be used to determine the influence of

different fundamental parameters on the ink detachment process and the present work is only an initial example of how the technique may be used. By making clear-cut experiments on different types of model surfaces and with model chemicals it is believed that new deinking chemicals can be efficiently developed and that ideas behind new deinking processes may be initiated. Experiments with a) porous surfaces to clarify the importance of penetration of ink into surface pores; b) pure surfaces of hemicellulose and lignin to clarify the importance of the chemistry of the fibre surface are underway. Furthermore, the model surfaces can be used to study ink re-deposition by exposing "clean" surfaces to dispersions of ink with the impinging jet technique. The technique has also shown both repeatable and reproducible results which is very interesting for deinking studies since deinking studies with collected papers are known to give annoyingly large scatter in the data.

The differences in mechanisms for flexographic ink detachment and offset ink detachment were furthermore established with the equipment. Flexographic ink is gradually removed in alkaline water solutions. In the experiments regarding removal of offset ink it was found that ink was only removed in the zone where there was a relative motion between ink and the cellulose surface. The experiments all showed that there was no ink removal in the stagnation point. The critical factors for ink release seem be a combination of surface swelling and shearing. Even though these might be rather expected results the present experiments are the first to directly show that this is actually happening. It is also the firm belief of the authors that the equipment will have many useful applications in the studies of the part processes of the deinking process.

Attempts to use interfacial energies to predict ink release show some promise but more experiments are needed to clarify the applicability of the van Oss/Good approach to ink release from the model surfaces used in the present investigation.

The present investigation is also the first study where the ink detachment from cellulose surfaces has been directly determined.

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Transcription of Discussion

INK RELEASE FROM PRINTED SURFACES – NEW METHODOLOGY AND INITIAL INSIGHTS TO THE TRUE MECHANISMS BEHIND INK DETACHMENT

Ulrika Andreasson[1] *and Lars Wågberg*[2]

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[2]Mid-Sweden University

At the time of the presentation of the paper the author realised that there was an error in this paper. Due to an error in the calculations pages 349–350 and 352–355 should be amended. Corrections are printed here.

(Pages 349–350)

Surface energies

Surface properties were calculated from the contact angle measurements summarised in (Table 1) and from contact angle measurements with di-iodomethane and ethylene glycol in order to clarify if there should be a spontaneous release of the ink when the printed surface was exposed to water or not. The results from these measurements and the application of Equations 2 and 3 resulted in the data summarised in Table 4. By using equation 4 the following interfacial energies were calculated

$$\gamma_{co} = -2.99 \text{ mN/m}$$

$$\gamma_{cw} = -20.4 \text{ mN/m}$$

$$\gamma_{ow} = 31.1 \text{ mN/m}$$

Together with Equation 1 this will result in a W_{cow} of 13.5 mN/m indicating no spontaneous ink release from the surface when the printed surface was

Table 4 Surface energy (mJ/m^2) of solid surfaces.

solid	γtot	γ^{LW}	γ^+	γ^-
cellulose	46.0	42.3	0.060	56.7
offset	27.1	25.1	0.46	2.28
cellulose-AKD	38.3	37.6	0.005	24.1

immersed in water. By doing the same calculation with the AKD treated cellulose a value of +36.9 mN/m was achieved indicating no spontaneous release of the offset ink from the AKD-treated cellulose surface when this surface was immersed in water. This is partly in accordance with the measurements shown in Table 3 above and the use of these calculations will be further discussed under Discussion.

The occurrence of negative values of the interfacial tension is hard to explain with standard thermodynamic arguments. However, with the application of the acid/base approach, i.e. Equations 3 and 4, it is quite possible to reach negative values and Good [16] and van Oss [17] have also discussed the phenomenon. From the equations it might be found that this situation occurs when the work of adhesion is larger than the cohesion of the interacting phases. Van Oss [17] also claims that a negative value of the interfacial tension in most cases is a sign of a non-equilibrium situation where the phases slowly will dissolve in each other but that there also exists cases where the negative value is permanent. This will also be handled further under Discussion.

(Pages 352–355)

The decrease of removed ink from AKD sized cellulose and cellulose surfaces can be an effect of delayed swelling of the surface. Due to the hydrophobic surface the wetting is retarded and hence also the swelling. Another explanation could be that ink, due to molecular similarities with AKD, could penetrate down the AKD layer and form a strong link between cellulose and ink that can protect the ink from detachment. Further investigations are needed to critically test the suggested mechanisms. In these experiments it is also necessary to use model inks with exactly known chemical components.

A procedure to determine the influence of interfacial energies between offset and cellulose and the interaction between these components and water to predict the limits for ink release was also used. As mentioned under results the calculation predicted that the ink should not be released when offset printed surfaces were placed in water, which is not in accordance with

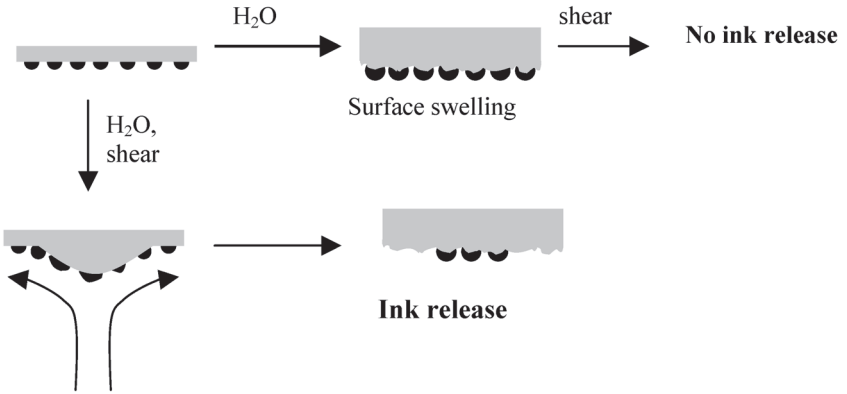

Figure 6 Schematic representation of ink removal of offset print from a cellulose surface. No ink was removed when the surface was pre-wetted but a combination of surface swelling and shearing was sufficient to remove the ink.

experimental results. There is however one uncertainty with these calculations and that is the negative interfacial energies found for cellulose/water and ink/cellulose interactions. These negative values are quite possible to achieve with the van Oss/Good approach [12] but from more classical thermodynamic arguments they are a not easy to explain. As was mentioned earlier, Good [16] and van Oss [17] both summarise that these negative values are achieved when the interfacial interaction is larger than the cohesive properties of the respective interacting phases. It is then logical to assume, as done by van Oss [17], that his situation is a quasistatic equilibrium that eventually will lead to a mixing of the interacting phases but there are experimental values showing that the negative values may persist over time [17]. When examining the calculated values in Table 4 it is also interesting to note the high values for the base properties of cellulose. These values are much higher than the values shown by van Oss [19] but the contact angle of water on cellulose is also much lower in the present work than the values shown by van Oss [19]. Since values around 20–25° are more reasonable [10] it is strongly believed that the values presented in the present report are not due to poor characterisation of contact angles on cellulose. When using the same methodology for characterising the interaction between AKD treated surfaces and offset ink the calculations predicted no spontaneous release of the offset ink when the surfaces were placed in water, which is in accordance with experimental results. In practice it is however often found that AKD-sized paper is easier to deink than

unsized paper. One explanation to this difference could be that for sized papers a very hydrophobic surface could be achieved despite a poor surface coverage of the AKD. It has for example, been shown by Ström [20] that a surface coverage of AKD of 15% is enough to make a wood fibre appear totally hydrophobic, i.e fully covered from contact angle measurements. This in turn means that when a surface is printed with offset ink about 85% of the interaction will be between cellulose and ink and only 15% between AKD and ink. In order to avoid this situation the surfaces in the present investigation were treated with AKD dissolved in toluene but no quantitative measurements were conducted to determine the exact surface coverage of AKD on the model surfaces. Atomic Force Microscopy images of the surface indicated a complete coverage but a chemical characterisation of the elements on the surface would also be very useful. No doubt, more experiments are needed to elucidate the influence of interfacial interactions but it is obvious that the experimental procedure presented in the present report gives a fast and simple alternative to determine these interactions. This type of work is currently underway in our laboratories. There is no doubt though that the interfacial energies are important for the ink release. Rao and Stenius [1], for example, found that when the surface energy of the water was decreased the ink came off the printed surface in larger pieces compared with the situation without addition of surfactant.

In order to determine the validity of Equation 1 it is suggested for future work the direct work of adhesion between the ink/cellulose, ink/water and cellulose/water should be determined with the methodology outlined by Chaudhury [21] and as applied to cellulose by Rundlöf et al [22]. This way of evaluating the importance of the adhesion between ink and cellulose is currently underway in our laboratory.

CONCLUSIONS

The present paper has shown that a new equipment consisting of an impinging jet cell, a printed model cellulose surface and a microscope equipped with a CCD camera for image collection is a useful tool for studying the mechanism behind ink removal from model surfaces. By applying image analysis to images of the printed surface at different time intervals, during the detachment studies, it is possible to quantify the ink detachment from the surface. The technique can be used to determine the influence of different fundamental parameters on the ink detachment process and the present work is only an initial example of how the technique may be used. By making clearcut experiments on different types of model surfaces and with model chemicals it is believed that new deinking chemicals can be efficiently

developed and that ideas behind new deinking processes may be initiated. Experiments with a) porous surfaces to clarify the importance of penetration of ink into surface pores; b) pure surfaces of hemicellulose and lignin to clarify the importance of the chemistry of the fibre surface are underway. Futhermore, the model surfaces can be used to study ink re-deposition by exposing "clean" surfaces to dispersions of ink with the impinging jet technique. The technique has also shown both repeatable and reproducible results which is very interesting for deinking studies since deinking studies with collected papers are known to give annoyingly large scatter in the data.

Dick Kerekes University of British Columbia

I have a comment and a question concerning the forces from the impinging jet in concentric zones where you saw a removal of ink. This is a high shear zone. You can calculate from the centre point radially outward, so you might be able to get by with this apparatus from information in the fluid mechanics literature, estimating the shear radially outward. You can pick out where it removed ink and where it didn't and know what the shear is. You may not have to build another apparatus.

The other point may be more important. I was always under the impression that a lot of the forces for ink removal come from fibre-fibre rubbing; that is, friction between fibres, and this is a mechanical force. How does this compare to the fluid forces you are using?

Lars Wågberg

The first comment is naturally correct. Bob Pelton made CFD calculations on this kind of geometry but we haven't repeated that. We felt that if we built it with a tangential flow, the results would be easier to interpret, but thanks for your comment.

To the other comment, regarding the shearing of fibres against each other, that's true, but its very hard to quantify the influence of that compared to the influence of the chemicals that we're seeing here. So our approach has been to check this first and then do real studies on fibres. See if there is a correlation, maybe there isn't. Also we can use mechanical action on these surfaces, and we are planning to do so.

Discussion

Patrick Gane Omya AG

Your picture (Figure 3 Page 347) that showed the fact that you probably needed a liquid-air-solid interface, would suggest to me, and I'd appreciate your comment, that the problem of adhesion there is not so much the standard adhesion between two defined surfaces, but actually the separation of two planes within a fluid and if you have the air interface, that breaks down that fluid junction between those two planes. Is that a picture that you have?

Lars Wågberg

The picture I have is from an idea that I got at a conference. Prof. D. Wasan was listening to popping of bubbles in orange juice at breakfast and he wondered if this popping was due to the breakage of the lamella at the air-water interface. So he went back into the lab and he added small particles to the three phase contact line (air/liquid/solid) and found that the tiny colloids concentrated at the three phase line, and by doing so they created a huge osmotic pressure that could actually lift contaminants from the solid surface. This was one of the ideas behind the sodium silicate experiment. We wanted to have small, precipitated particles of sodium silicate, which we would get at the lower pH to ease the removal of the ink. But we didn't see any effect of it, but regardless of that, I do agree with you on the view that you have of this interface and a lot of other things can happen at three phase contact time.

Patrick Gane

If the chairman will allow me to make one comment on the flexographic ink. In some studies that we did recently we found that the flexographic inks as dried on the surface are very highly loaded with polymer and I think that your question of, 'is it possible to get hold of raw materials for ink?', it would be interesting to see what sort of networks these polymers build under UV, because it looks to me as if you are making a transition from an attrition state of de-inking on fresh flexographic ink to the offset situation where the ink has formed a solidified object which then has to be removed as a lamella.

Lars Wågberg

Yes, that is exactly the kind of work that we are planning to do, to go into the details a bit more about ink curing on the solid surface.

Chad Bennington University of British Columbia and Paprican

We have been studying the effect of shear stress on ink removal. One fact that might influence the design of your next apparatus is that when quantifying the amount of ink removed as a function of shear stress, we find that for some inks the wet tensile strength of the sheet must be exceeded before significant ink is removed. We apply the sheer stress using a fibre suspension to create friction between the fibres and an ink film printed on a sheet of paper. When you add chemicals to the suspension it affects the ease with which the ink is removed.

Lars Wågberg

That is another thing that links to something that I mentioned in my talk. We are planning to do an experiment where we swell the ink and not the cellulose to see if it is relative motion that is an important factor.

Jean-Claude Roux EFPG

It is more of a comment, after what Chad Bennington said, in the work of Benjamin Fabry we found that the shear factor was an increasing function of ink detachment/release for this kind of material. So I understand when you say that the offset ink release is influenced by surface swelling and shear, of course the average shear stress can be some image of this effect.

John Roberts Department of Paper Science, UMIST

What do you think are the deficiencies in using a regenerated cellulose. It is regenerated from N-Methylmorpholine N-Oxide, so not only has it lost its morphology but it is also in a different crystallographic form, do you feel that it is a reasonably good model for paper surface?

Lars Wågberg

That is a usual comment that we get, i.e. what crystallographic form have we got on the regenerated cellulose and we are working really hard to find this out. I think Susanna Gimmars who was working on this says that it is semi crystalline Cellulose-I but to be honest we don't know exactly the crystallographic form. We do know that it is pure cellulose and we know that from contact angle measurement. We also know that the surface swells as wood fibre does with changing salt concentrations and with pH. When it comes to the morphology, we are going to use cellulose acetate, because then we can

use cellulose membranes which we de-acetylate and also get the influence of the porous structure. Naturally, when you work with a model surface, it is only a model and you have to work also with the fibres, but so many other people have worked with fibres and what it boils down to is where the ink sits also from a molecular point of view. The Norwegian group of Prof. Helle have worked very hard on the image analysis and scanning electron microscopy to see where the ink sits in the paper structure and I think that's one very good approach. On the other hand if you re-slush fibres in water, filter them off and measure ERIC values or k-values you are totally in the dark when it comes to a molecular understanding of ink release. A combination of model studies and studies with fibres is the best and we are naturally going to do this.