

Adhesion at Toner/Paper Interface in Electrophotographic Printing

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Abstract: In all printing processes, the quality of ink adhesion is of primary importance to ensure the legibility and permanence of the transmitted information. However, contrary to the other processes, which use a fluid ink penetrating the support, electrophotography consists in depositing a fine layer of powder containing pigments and to fuse it onto the paper surface. The mechanisms involved in obtaining good adhesion at the toner/paper interface have thermal, rheological and physico-chemical origins.

In this paper, the three main mechanisms of adhesion are reviewed: mechanical anchoring, adsorption and diffusion. Experimental modifications of paper roughness, surface energy and diffusion potential are described and analysed in order to determine which parameter is prevalent to achieve good toner adhesion.

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Introduction

Toner fusing is the last step in electrophotographic printing and is critical in achieving good print quality. The most common fixing method is hot roll fusing, where heat and pressure between two rolls bond toner to the paper. Many authors focused on the influence of toner properties on the toner adhesion to substrates, but only little interest was devoted to the influence of paper properties on toner adhesion. Apel *et al*⁽¹⁾ found that the fixing quality tends to be reduced as roughness increases, but the deviation in toner adhesion measurements were high. Sanders⁽²⁾ studied the influence of the main additives used in the paper composition and found that toner fixing was improved by using a styrene-maleic anhydride (SMA) copolymer as the surface sizing agent and attributed it to an affinity of SMA with the polystyrene contained in the toner particles. Other authors reached the same conclusions with various types of polymers, such as styrene-acrylic copolymers (Barker *et al*⁽³⁾), styrene-acrylic emulsions (Tsai *et al*⁽⁴⁾) or encapsulated acrylate-methacrylate copolymers (Hemel *et al*⁽⁵⁾).

From a theoretical point of view, the concept of adhesion includes thermodynamic, chemical and mechanical aspects, which cannot be treated separately.

Thermodynamic adhesion refers to an equilibrium of interaction forces between two phases in contact, but this definition considers adhesion rupture to be a reversible process, which is seldom the case. Phase separation is generally accompanied by the dissipation of considerable viscoelastic energy. In addition, the mechanical resistance of the interface depends to a large extent on the quality of the contact between the two phases, with contact imperfections at the interface being the source of a stress-concentration phenomenon.

Chemical adhesion results from the formation of chemical bonds at the interface. It increases adhesion, even in the case of a clear interface without interdiffusion, prevents slip and increases the rupture energy by increasing the level of the interactions (order of magnitude of approx. 100 kJ/mol, instead of 1 kJ/mol for dispersive thermodynamic forces).

Mechanical adhesion is widely used to promote adhesion in the case of porous substrates such as paper, leather and fabrics. When the pores have a shape of the type shown in Figure 1, it may be necessary to break the cohesion of material A to separate it from material B.

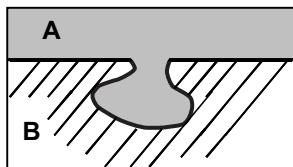


Figure 1: Schematic view of mechanical anchorage

In most cases, the mechanisms quoted above occur simultaneously. Adhesion between toner (which is a molten polymer soon to be solidified) and paper (the roughness and chemical surface composition of which can vary considerably), results from a complex intervention of these mechanisms. Our work consisted in performing various modifications of the paper surface, with the aim of achieving the most specific action on each of these three adhesion mechanisms and in analysing the impact of these modifications on toner adhesion measurements.

Experimental—Paper Modifications

Different surface treatments were applied on paper:

- **Calendering**

Two different papers were calendered at different levels, in order to obtain different surface topographies: one commercial copy paper (Paper A, surface sized with starch only) and one pilot coated paper (Paper B, slightly coated with 100 p of ground CaCO_3 and 14 p of a styrene-butadiene latex).

Calendering was performed on a laboratory calender operating at a speed of 25 m/min, including a steel roll, which could be heated and a paperboard roll. The temperature of the steel roll was either 23 or 100°C, the force applied to paper per unit width was adjusted between 28 and 95 N/m and the sheet was passed once to 5 times in the nip, in order to obtain 10 different surface smoothness levels for each paper. Bekk smoothness was determined for each paper sample.

- **Corona treatment**

Corona treatment is very often used in the manufacture of polyethylene/paper or polypropylene/paper complexes in order to improve their adhesion. It consists in exposing the surface to an electric discharge between two electrodes. The air between the two electrodes is ionised and ions, electrons and photons are created. Their action on atmospheric oxygen leads to the formation of ozone and free radicals which oxidize the surface. This contributes to increasing surface energy and to creating hydrogen bonds, and thus to improving adhesion.

Different intensities of Corona treatment were applied on one copy paper. Contact angles were measured with water, formamide and α -bromonaphthalene within three hours following the Corona treatment. The surface energy was calculated using Wu's method (Wu⁽⁶⁾).

- ***Pre-printing with different types of inks***

Many documents printed in electrophotography result from a double printing operation. The first is carried out by offset and aims at covering the paper with a uniform colour or a colour shade, or to print data which will be identical on all specimens (e.g. logos). The second is carried out by electrophotography and consists in personalizing the document to make a single specimen. In that case, the toner is deposited and melted on an inked paper and this modifies the toner/paper interactions. It seemed of interest to determine the impact of the various types of inks, which can be used for the pre-printing step, on toner adhesion.

The same 100% chemical pulp paper, 80 g/m², highly sized, was pre-printed on industrial machines. Four types of inks were used: two conventional offset inks (a mineral ink and a vegetable ink), one UV offset ink and one water-based flexographic ink. The printed pattern consisted of a 20 cm \times 29 cm uniform screen centred on an A4 format. 3 ink coverages were applied, respectively at 10, 30 and 100%.

Experimental—Determination of Toner Adhesion

A recent European standard deals with the determination of toner adhesion (EN 12283: "Paper—Copy paper—Determination of toner adhesion"). This standard is based on the submission of a solid area to the IGT picking test at constant speed with a medium viscosity oil. The test was adapted to our study by using accelerating picking speed in order to be able to quantify high toner adhesions. Toner adhesion was therefore expressed as a speed: the higher the speed, the better the toner adhesion.

Results and Discussion: Influence of Paper Roughness

The two series of calendered papers were printed on an office laser printer. The results of the pull-off speed necessary to detach toner particles as a function of Bekk smoothness are presented in Figure 2.

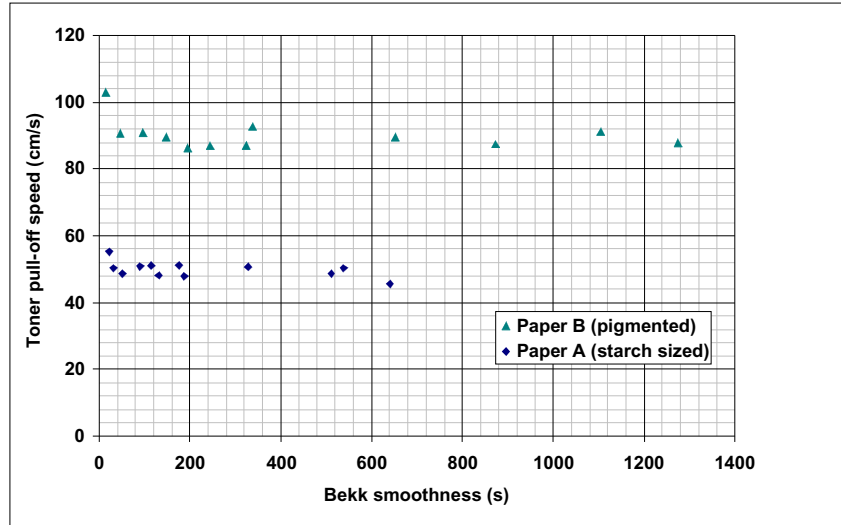


Figure 2: Toner pull-off speed as a function of Bekk smoothness

With regard to paper A, a slight tendency toward a reduction in toner adhesion was observed when the paper smoothness was increased. The loss of adhesion was about 18% when the Bekk smoothness value went from 22 to 640 s.

With regard to paper B, the toner adhesion had higher values than those obtained with paper A. A significant reduction in adhesion was observed between papers having Bekk smoothness of 16 and 47 s, respectively, followed by stabilization of the toner pull-off speed around a value of 90 cm/s.

Adhesion is supposed to be proportional to the contact area, which is lower when the paper is smoother. In our experiments, the measured reduction in toner adhesion after calendering was lower than the reduction in the developed surface area. This may be explained by the fact that wetting was better when the paper was smoother and thus compensated the reduction in contact area. Indeed, in the case of rough papers, the wetting of the paper surface by the molten toner may not have been complete and the surface irregularities could lead to a reduction in the contact area between toner and paper, as shown in Figure 3 (Van der Leeden *et al*⁽⁷⁾).

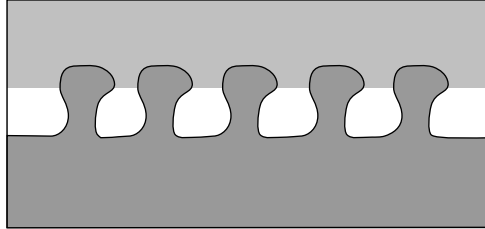


Figure 3: Reduction in contact area between the toner and a rough paper due to insufficient surface wetting

Results and Discussion: Influence of Paper Surface Energy

The paper samples submitted to the Corona treatment were printed on an office printer ten minutes after the treatment. The same samples were printed one day later and five days later, in order to evaluate the permanence of the Corona treatment effects on adhesion.

The results obtained in terms of toner pull-off speed are presented in Figure 4 as a function of the Corona current intensity and the time elapsed between treatment and printing.

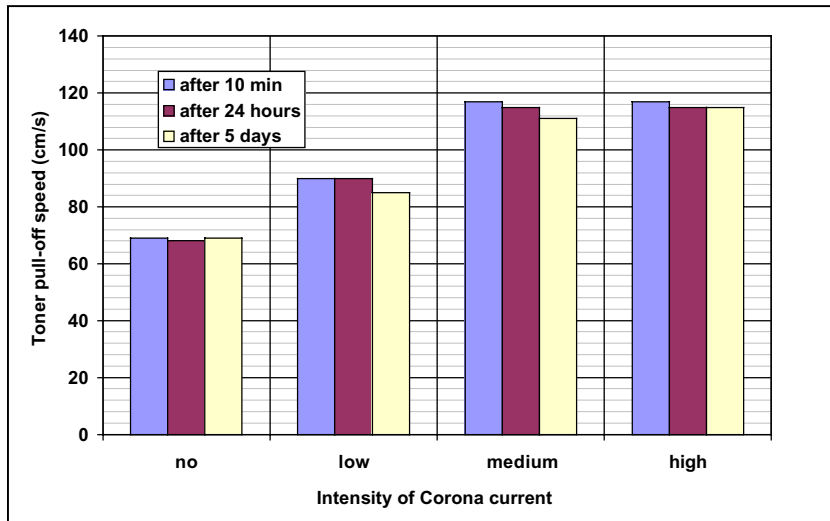


Figure 4: Toner adhesion as a function of Corona current intensity and time elapsed between treatment and printing.

Clearly, the corona treatment had a positive effect on the toner adhesion.

A threshold intensity had to be overcome for the discharge to occur between the two electrodes. As soon as this minimum intensity was applied, the effect became appreciable on the toner adhesion. Above this value, the higher the current intensity, the higher the toner adhesion, until the latter reached a constant maximum value. In these experiments, the results were almost identical for the papers treated with a medium or a high intensity current, and the improvement in toner adhesion attained about 65%.

The effect of Corona treatment was almost unchanged for 24h, but decreased slightly after five days for the papers treated with a current of low and medium intensity (loss in toner adhesion of approximately 5%). For the paper treated with a high intensity current, the improvement in toner adhesion remained unchanged even five days after the treatment.

The theoretical work of adhesion between toner and treated papers was calculated according to Wu's expression:

$$W_a = W_a^d + W_a^p = 4 \frac{\gamma_T^d \gamma_P^d}{\gamma_T^d + \gamma_P^d} + 4 \frac{\gamma_T^p \gamma_P^p}{\gamma_T^p + \gamma_P^p}$$

where γ_T^d , γ_P^d , γ_T^p and γ_P^p are respectively the dispersive and polar components of toner and paper surface energies determined by Wu's method.

γ_T^d and γ_T^p were determined by measuring contact angles of different liquids on toner flat pellets and the values obtained were respectively 32.4 and 2.0 mJ/m².

γ_P^d and γ_P^p were determined through contact angles measurements of different liquids on Corona treated papers. The values obtained are given in Table 1, as well as the value of the theoretical work of adhesion W_a (mJ/m²).

Corona Intensity	Surface energy (mJ/m ²)			Work of adhesion
	γ_P^p	γ_P^d	γ_P^{total}	
no	23,8	0,0	23,8	54,9
low	35,4	0,0	35,4	67,7
medium	43,3	4,7	48,0	79,7
high	43,3	5,9	49,2	80,1

Table 1: Surface energy and work of adhesion of papers submitted to Corona treatment

If the toner adhesion measured 10 minutes after the Corona treatment was plotted as a function of the thermodynamic work of adhesion, the curve in Figure 5 was obtained.

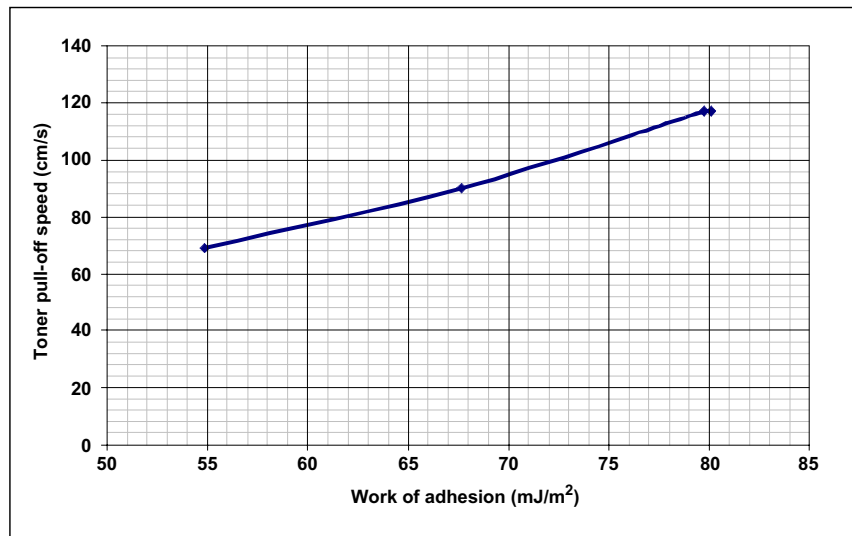


Figure 5: Toner adhesion measured on printed papers 10 minutes after the Corona treatment as a function of the thermodynamic work of adhesion

A very good correlation was observed between the toner adhesion evaluated with the pull-off test and the thermodynamic work of adhesion calculated from measurements of surface energy. It appears therefore that for this Corona-treated paper, the adsorption adhesion mechanism is predominant.

Results and Discussion: Influence of Pre-Printing Inks

The blank paper and all the pre-printed samples were printed on a high-speed printer that is particularly adapted to the personalization of pre-printed documents. The results in terms of toner pull-off speed are presented in Figure 6.

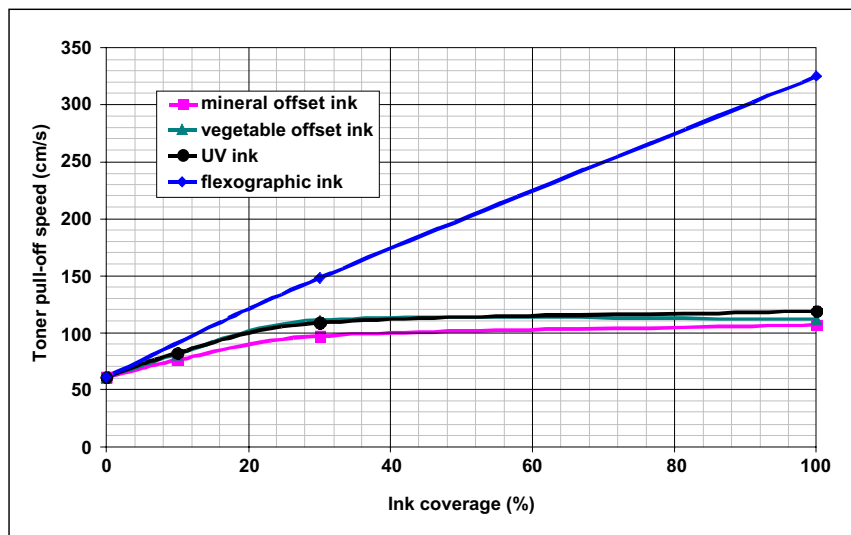


Figure 6: Toner adhesion on pre-printed papers

With all types of inks, an improvement in toner adhesion was observed when the ink coverage was increased. This improvement was essentially the same with the three offset inks, with a regular growth between 0 and 30% of ink coverage and then a more modest increase between 30 and 100%. For the paper pre-printed in flexography, the increase in toner adhesion was very high and linear between 0 and 100% of ink coverage. The extent of toner adhesion on the blank paper was multiplied by 5 when the paper was printed with an ink coverage of 100%.

The possibility for the toner molecules to diffuse into the polymer of the ink varnish seems to be the cause of the significant improvement in toner adhesion. The fact that the adhesion was much higher on the paper covered with flexographic ink, compared to the offset ink counterparts, may be attributed to the presence of waxes at the surface of offset inks, acting as a weak cohesion layer. Although they represent only a small proportion in the ink (approximately 4% in weight), these waxes are known to migrate to the paper surface and consequently to degrade toner adhesion.

Conclusion

It has been possible to take into account the three main adhesion mechanisms encountered at the toner/paper interface, namely mechanical anchoring, adsorption and diffusion. While it was not always possible to dissociate these

mechanisms, the following results were however relevant to the understanding of the complex phenomena:

The modification of the paper roughness, within the typical range related to papers used in electrophotographic printing, resulted only in a minor modification of the extent of toner adhesion, corresponding basically to the modification in the contact area between toner and paper. Specific anchoring sites were not involved, even on high roughness surfaces. On the contrary, they became more difficult to wet by the toner. The small influence of roughness on the toner adhesion means that its effects could be ignored in the analysis of the other mechanisms.

The paper surface energy was modified by Corona treatment. An increase in toner adhesion, proportional to that of the thermodynamic work of adhesion, was observed, highlighting the importance of the adsorption mechanism in the adhesion between toner and paper.

The modifications introduced by pre-printing had an effect on both the surface energy and the capacity of toner macromolecules to diffuse into the ink polymeric medium. Both these aspects played a favourable role and toner adhesion was therefore clearly strengthened. A water-based flexographic ink, which is not currently used for pre-printing applications, seemed particularly suited in this context, thanks to both its high surface energy and good film-forming aptitude, as well as because of the absence of waxes in its composition.

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