EFFECT OF FLUORINE RESIN DISTRIBUTION THROUGH THE PAPER THICKNESS ON THE PAPER'S PROPERTIES

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ABSTRACT

The main aim of this study consists on the establishing of links between the oleo phobic character of two papers and their printability. Thus, two commercial oil proof treated samples were carefully characterised in terms of physical properties, wettability, grease proof performances, resin distribution and printability tests. These tests showed that the concentration of fluorine atoms through paper thickness as well as their homogeneity of distribution induced changes in physico-chemical properties which, in turn, influenced the paper printability.

INTRODUCTION

Last decades, the paper consumption was constantly increasing reaching about 200 kg per year and per capita, in Western Europe. Greaseproof papers followed this tendency, namely because of increasing fibre-based food packaging materials. These papers are treated by fluorine-based resins, because they should possess oil repellence properties. In general, this treatment concerns the bulk of paper *via* the wet-end part of papermaking (addition of the above mentioned resin into the fibre suspension) and the surface treatment (surface sizing thanks to size-press).

Fluorine-based wet-end additives are known to have a low surface energy and poor wettability which increase substantially the oil-resistance of treated materials. This family of product offers the lowest values of the dispersive component of the surface energy. Moreover, they do not possess any polar contribution. Indeed, one can refers to the surface energy of poly(tetrafluoroetane), the so-called Teflon, which have a surface energy lower than 18 mJ/m^2 (1). The general structure of these resins is very similar to that of some surfactants, i.e. a non-polar long aliphatic perfluorated chains and a polar part consisting, for example, on phosphoric units allowing the interaction with polar surface of cellulosic fibres (2).

The greaseproof and surface properties of paper depend strongly on the efficiency of both wet end part of paper machine as well as that of sizing operation. The present investigation concerns the bulk and surface properties of two oil-proof papers.

EXPERIMENTAL PART

The two samples studied were commercial papers prepared by incorporating fluorine resin. The resulting papers were coated with a basic weight of about 8–10 g/m¸ (talc, clay - based coating). These two samples were characterised in terms of smoothness, contact angle, inverse gas chromatography, Scanning Electron Microscopy, grease proof test as well as their printability on flexographic press. The two samples studied will be referenced as paper A and paper B.

The smoothness was determined using a Beck apparatus following NF Q 30-012 standard. Static contact angle measurements were estimated using a home-made apparatus based on image analysis and allowing to record 200 images per second (3). The liquids used were water, formamide, diodomethane; a-bromonaphthalene, ethylene glycol and hexadecane. Their characteristics have been reported elsewhere (4).

The values of contact angle were processed according to Fowkes, Zisman and Owens-Wendt approaches. Inverse gas chromatography was carried using a Delsi 121 DFL chromatograph, equipped by a FID. The paper samples were passed through a cleaned paper tape punch machine and the obtained "confetties" were collected in order to fill the column. Stainless steel columns having an internal diameter of 4 mm and lengthening about 1 meter were used. They were previously washed and degreased with acetone and then dried at 105 °C. The injector and detector blocks were maintained at 150 °C and the chromatograms were performed at 50 °C. The measurements were carried at infinite

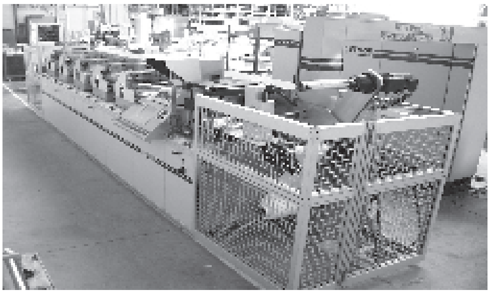

Fig. 1. *Photo of the industrial flexographic machine used in this work.*

dilution conditions which implied the injection of very small quantity of vapour probe (about 5 ml). The probes used as well as their relevant characteristics were reported previously (5). The reader can find a detailed description of IGC method and calculation procedure elsewhere (5). In this work we used the Schultz's and Gray's approaches for the calculation of the dispersive energy and that of Lara's for the acceptor and donor numbers of the solid substrate (5).

An energy dispersive x-ray analyser was also used to display atoms distribution in the thickness of paper, in particularly fluorine atoms. It is a common accessory which gives the Scanning Electron Microscope a valuable capability for elemental analysis. In this case, the electron beam in a SEM had an energy typically between 5000 and 20000 electron volts.

In order to evaluate the capacity in absorbing a given ink, we carried out a comparative test consisting on the deposition of a calibrated quantity of ink onto the paper surface, keeping it for a given time after which the excess of ink was cleaned and the optical density of the paper was measured. This semi-quantitative test gave an idea about the kinetic of ink penetration and consequently the surface porosity.

The printability tests were obtained using a flexographic industrial machine devoted to the printing of labels, as illustrated in *Fig. 1*. This machine is equipped by five printing groups and works in continuous sheet mode (roll-to-roll). The width of the roll is about 30 cm (12 inches). The speed could reach 300 meters per minute.

Tab. 1. *Inks formulations*

	Ink	Water (%)	Varnish (%)	L	c	h	h (s)
I25	GL270	11	0	79	52	128	25
I50	GL270	4	35	78	56	128	50

The inks tested were water-based and have two different viscosities, namely: 25 and 50 s, as measured by Ford cup number 4. They were formulated starting from an industrial ink (green light 270), to which a given quantity of water and varnish was added, such a way that only the viscosity of the mixture was affected. In fact, the colour compo-

Tab. 2. *Program of trials*

Trial	Paper	ink	Displacement Anilox/blanket	Displacement Blanket/paper
1	B	I50	Reference (Ref)	Ref
2			Ref	Ref minus 330µm
3			Ref minus 200µm	Ref minus 330µm
4			Ref minus 200µm	Ref
5	A	I50	Ref minus 200µm	Ref
6			reference	Ref
7			reference	Ref minus 330µm
8			Ref minus 200µm	Ref minus 330µm
9	A	I25	Ref minus 200µm	Ref minus 330µm
10			Ref minus 200µm	Ref
11			Ref	Ref
12			Ref	Ref minus 330µm
13	B	I25	Ref	Ref minus 330µm
14			Ref	Ref
15			Ref minus 200µm	Ref
16			Ref minus 200µm	Ref minus 330µm

nents were kept constant, as confirmed by spectrophotometeric measurements. These formulations were characterized and the two inks selected for experimental sets are shown in *Table 1*.

The engraved ceramic rolls had a screen ruling of 120 lines/cm. Finally, the machine speed was kept at 100 m/min. These conditions were very close to those used industrially. Different preliminary trials were performed in order to establish the optimal printing quality conditions, which were considered as the reference positions of the blanket and the anilox. Then after, different displacements between the anilox and the blanket as well as that between the blanket and the paper sheet were investigated, as summarised in *Table 2*. These displacements allowed varying the pressure between transferring units.

The printed sheets were characterised in term of optical density and marbling, as described by Armel and Wise (6, 7). For the last test, the surface of sample under investigation is about 1 mm^2.

RESULTS AND DISCUSSIONS

The smoothness of the two samples studied here was determined for both sides (coated and uncoated). The values obtained (*Table 3*) were in agreement with those used usually for paper destined for flexographic printing commonly used for packaging papers.

Tab. 3. *Main properties of paper A and B.*

	paper A		paper B	
side	coated	uncoated	coated	uncoated
thickness (mm)	96		86	
basis weight (g/m·)	94.6		91.5	
density (g/m^3)	0.98		1.06	
Bekk smoothness (s)	569	87	394	129

Nevertheless some differences were observed, namely: (i) the smoothness of coated side of paper A was the highest one, (ii) that of paper B (same side) was 30 % lower, (iii) the smoothness of uncoated side of paper A was low, i.e. 87 s, whereas paper B showed the inverse trend (48 % higher).

The contact angle measurements were conducted and the results obtained are collected in *Table 4*.

The values of the angles measured were processed following Fowkes', Owens-Wendt's and Van Oss approaches. From the data obtained, the major

Tab. 4. *Dispersive and polar components of the surface energy (mJ/m¸) of paper A and B, according to different approaches.*

Fowkes' Approach					
	g_S^D	I_{Sw}	I_{SF}	I_{SD}	
Paper A	10.9	9.8	4.2	4.2	
Paper B	31.1	44.1	14.3	9.7	
Owens-Wendt's Approach					
	g_S^D	g_S^P	g_S^T		
Paper A	11.0	0.4	11.1		
Paper B	29.3	8.6	37.9		
Van Oss' Approach					
	g_S^{LW}	g_S^+	g_S^-	g_S^{AB}	g_S^T
Paper A	10.7	0.7	0.0	0.1	10.9
Paper B	27.1	4.4	0.9	2.0	31.0

conclusion which could be deduced concerns the fact that paper A was found to possess much lower dispersive surface energy than that of B, for the three approaches used. Moreover, the interaction coefficient between water and paper A is practically five times lower than that obtained with paper B (9.8 against 44.1). The results were in agreement with those obtained with the Owens – Wendt's approach. Indeed the polar contribution of the surface energy of paper B was found 8.6 mJ/m¸ whereas that of paper A was very small (0.4 mJ/m¸). Finally the Van Oss's approach gave indications about the fact that the surface of these papers displayed a donor character. Again surface of paper B showed much higher polarity.

The IGC measurements gave results consistent with those obtained by contact angle technique ex-

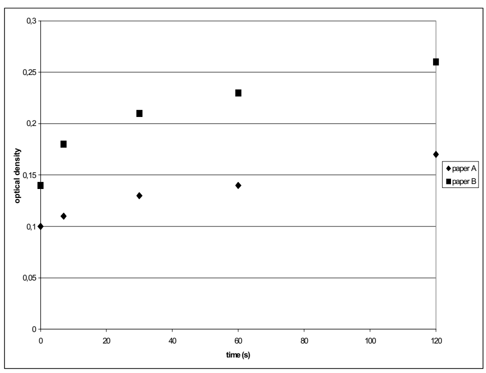

Fig. 2. *Evolution of optical density versus time.*

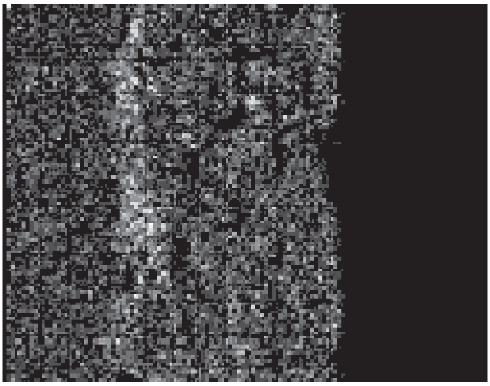

Fig. 3a. *MEB fluorine atoms distribution for paper A*

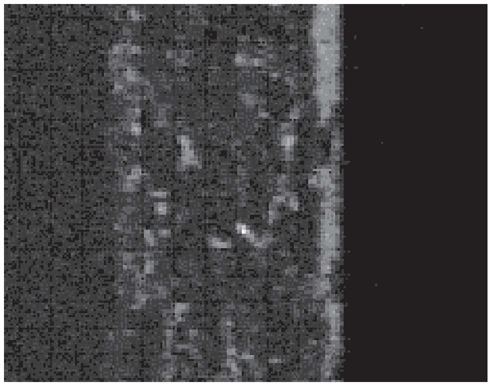

Fig. 4a. *MEB silicium atoms distribution for paper A*

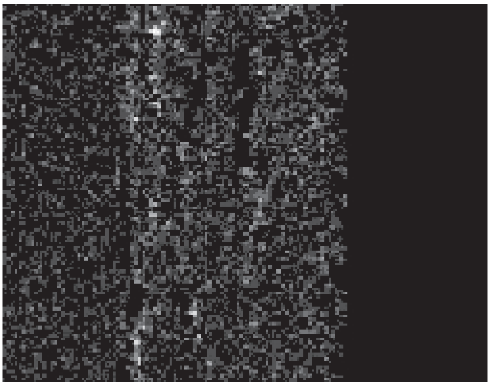

Fig. 3b. *MEB fluorine atoms distribution for paper B*

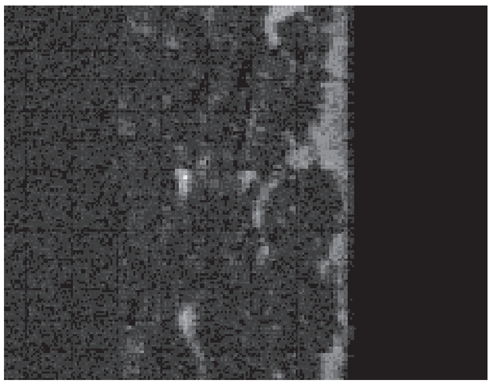

Fig. 4b. *MEB silicium atoms distribution for paper B*

cept the fact that the value of g_S^D of paper A was found relatively higher (15 instead of 10 mJ/m˛). This was attributed to the higher sensitivity of IGC techniques and to the fact that the cutting of the sample to produce confetties created new untreated surfaces.

The printability of both papers was also studied using two commonly used flexographic inks. Before testing our paper samples, the inks were characterised in terms of surface energy (the g of these two inks was about 35 mJ/m˛) and rheology. The inks studied has two major differences, namely: (i) I25 ink was found a Newtonian suspension with a viscosity value of about 52 mPa.s, whereas (ii) I50 one showed a pseudo-plastic with a slight thixotropic behaviour with a value of h around 145 mPa.s at a shear rate of 2500 s^{-1}. It is worth to remember that the viscosity of these two inks, as measured by Ford cup n° 4, was found 25 and 50 s, respectively.

The ink porometric measurements showed that paper B possessed higher ink absorption capacity to compare with paper A (*Fig. 2*).

The measurement at short time (t H” 0 s) could give additional information since it could be related to the surface smoothness (*Table 3*) rather than surface porosity. The evolution of the optical density curves showed that the gap between paper B and paper A increased from about 40 % at t H” 0 s to reach 53 % at 120 s. This indicates that the kinetic of absorption of paper B is higher than that of paper A. This data was confirmed by COBB (using water and oil) and PDA measurements.

The distribution of fluorine resin through the paper thickness was studied by Scanning Electron Microscopy, as shown in *Figs. 3*. These observations showed clearly the concentration of fluorine atoms was higher in case of paper A. Moreover, their distribution through the thickness was much more homogeneous. This explained the higher oil-repellence capacity of paper A and suggested that the migration of fluorine resins to the coated surface of paper induced a significant decrease of its wettability.

In order to ascertain the distribution of different components of coating layer, it was decided to carry out SEM analyses on Mg, Si and Al atoms. Thus, these elements are present in talc and clay used as pigments in coating colour formulations, as shown in *Figure 4* for Si atoms distribution taken as an example. This figure indicates that the coating layers of both papers seemed to be very similar, which exclude coating as a responsible for bad printability of paper A.

The flexographic tests were carried out following the experimental sets described in *Table 3*. After printing, the optical density of the printed areas was measured. *Figure 5* shows comparative data concerning the optical density of the printing areas of both papers using the two inks with different transfer conditions. From this figure, it can be seen that:

1. The optical density obtained using I25 was systematically higher than that reached with I50 because of its higher pigment content (trials # 9-16 to compare with those of # 1–8). In fact, as described before, I50 was obtained by the addition of high viscosity varnish and water to I25, which results in a dilution with respect to pigment although the viscosity increased thanks to varnish addition. Moreover, I25 is less viscous ink which decreases the residual ink quantity into engrave ceramic cells and increases its transfer from anilox to paper.
2. The optical density was found systemically higher for paper B to compare with paper A, which indicates the better printability of paper B, confirming the results obtained from ink porometric measurements (see below).
3. Then, for trials which involved printing with a reduction of the distance between blanket and paper (trials # 2, 7, 12 and 13), an increase of optical density was observed. This is attributed to the better ink transfer to paper under these printing conditions.
4. Trials # 4, 5, 10 and 15 correspond to printing with a reduction of distance between the anilox and blanket. In these experiments, the gain of optical density was ink dependent. In fact, for I50 the gain is negligible and could be attributed to its viscous character (trials # 1 and 6 to compare with those # 4 and 5), whereas for I25, a similar increase was observed as in the case of the previously described experiments, i.e. when the reduction was conducted between the blanked and the paper instead of between anilox and blanket. This allows concluding that both modifications led to the same improvement of ink transfer.
5. For trials in which the distance between anilox and blanket as well as that between blanket and paper were reduced (trials # 3, 8, 9 and 16), the results obtained were in agreement with those obtained previously. In fact, the gain was more pronounced for less viscous ink, i. e. I25.

From these data, it can be concluded that the increase of pressure between the blanket and paper is more efficient in increasing ink transfer. Nevertheless, it is worth noting that from practical point of view, it is judicious to work under minimal pressures between printing elements, in order to avoid the deformation of printing dots, which increase the printing quality, and prevent the paper under printing from mechanical stresses.

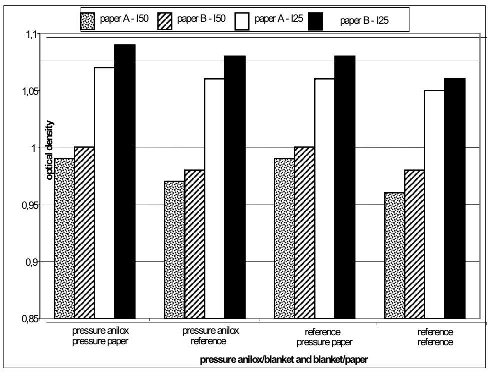

Fig. 5. *Optical density versus printing trial conditions (anilox and blanket displacement)*

The marbling index (I_M) for the paper studied showed that I25 (5) gave higher I_M values (around 22) to compare with I50 (around 11), although the fact that it gave better ink transfer, as discussed below. These papers were also characterised visually, as usually practiced industrially and the results obtained were very close to those obtained from I_M. This finding is interesting since a good correlation between a quantitative and qualitative methods was found even though the fact that I_M method analyses very small area (1 mm^2), to compare with qualitative industrial method – (global visual evaluation). It is worth noting that no significant differences were observed between paper A and paper B, in terms of I_M which was not the case for optical density measurements.

CONCLUSION

This investigation aimed at the establishing the parameters causing the difference in the printability of two commercial papers destined for food packaging, supposed to be identical and commercialised under the same reference. As shown through the overall parameters studied the physico-chemical properties as well as the fluorine atoms concentration and distribution through the thickness played a capital role in printing ability of the samples under investigation. In fact, paper A which contained more fluorine resin and more homogeneously distributed fluorine atoms, displayed lower surface energy and consequently worse printability. This is probably due to the migration of these substances and "pollution" of the coated side of the paper. Moreover, it was shown that the good ink transfer was not sufficient to ensure the printing quality even though the fact that it corroborated very well with surface smoothness and ink adsorption. Indeed, additional analyses such as marbling index gave a good idea about the homogeneity of printed zones and emphasized the fact that good ink transfer should be accompanied by good spreading of the deposited ink in order to have the best performance. This points out that in order to study seriously the ink transfer it is necessary to investigate the paper samples in terms of bulk properties (porosity, permeability, etc.) as well as in terms of physico-chemical properties (surface energy, polarity) of its surface.

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