

CHARACTERIZATION OF OIL-PROOF PAPERS CONTAINING A NEWTYPE OF FLUORO-CHEMICALS.

PART II: WATER- AND OIL-PROOF BEHAVIORS AND PRINTABILITY

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Six commercial oil-proof paper specimens, which had been manufactured with application of a new type of fluorochemical agent on their surface, were evaluated in terms of water- and oil-proof and printing properties. The new agent had been designed to comply with standards requiring six or fewer carbons in the perfluorinated alkyl chain. First, the paper samples were characterized in terms of classical properties, such as their thickness, density and ash content. The ashes were collected after the calcination of the paper samples and their contents were found to be around 15-17 wt%. The elemental analysis of these minerals indicated that they were inorganic fillers and pigments (Al- and Si-based). No traces of fluorine components were detected in this mineral part, because the fluorochemicals used in the oil-proof papers were organic-based molecules, which underwent total combustion during the calcination process. Stöckigt sizing and Cobb₆₀ tests clarified that all the paper samples had certain levels of water-proof properties both on the non-coated and on the coated sides. On the other hand, the result of the Kit test indicated that the paper samples having fluorochemicals on the non-coated surfaces had a large oil-proof barrier. The XPS of the coated surface revealed that the binder used is most probably a styrene-butadiene-like polymer and that the pigments are kaolin, calcium carbonate or a mixture of the two. On the coated surfaces of all the paper samples, oily liquids did not penetrate into the coating layers, but spread rapidly over them. The ink porosimetry test by dye-type ink was adopted for the evaluation of ink absorption of the paper samples. On the coated surfaces, all the paper samples absorbed small quantities of ink. Although further investigation is required for better understanding the ink absorption mechanisms and the retention of dye components on the coated surfaces, this study proved that water- and oil-proof effects largely influenced the behaviors of dye-type ink absorption on the paper samples.

Keywords: water-proof properties, oil-proof properties, fluorochemicals, XPS, printability

INTRODUCTION

Nowadays, paper and paperboard are very widely consumed commodities. Thus, for example, in Western Europe and North America, the consumption of such products exceeds hundreds of kg per year and per capita. In some applications, the paper grade to be used should have barrier properties against water and oil. Thus, in wrapping or packaging paper and paperboard, the substrate should display sufficient resistance against wetting or penetration of these two fluids. These properties are generally provided by adding chemical aids to the fiber suspension and/or to the surface of these substrates. Such operations could also include the

lamination of hybrid materials, such as aluminum foils or polymer films.¹

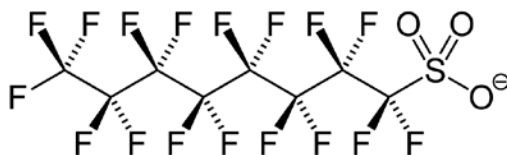
According to the wetting theory, solid surfaces with low surface energy values are able to resist to the spreading of liquids. Thus, fluorochemicals, which have extremely low surface tensions, have been widely used in such a context. Most of the fluorochemicals used have at least 8 perfluorinated carbon sequences (C₈, *i.e.* C₈F₁₇-). However, since the 1990s, the family of perfluoroalkyl chains longer than C₈ has been suspected of causing several risks in the environment and to human bodies, particularly perfluorooctanoic sulphonate

(PFOS) and perfluorooctanoic acid (PFOA).²⁻³ As a result, the use of PFOS has already been prohibited. In order to comply with the requirements imposed by the declaration of "2010/2015 PFOA Stewardship program",⁴ the use of PFOA was also eliminated from the synthesis process of fluorochemicals by 2015.

Consequently, in recent years, a new type of commercial fluorochemical products have been prepared with carbon chain lengths of 6 (C6, *i.e.* C6F13-) or shorter. For now, no risks associated

with their preparation and uses have been reported. However, the efficiency of their water- and oil-proof effects has not yet been sufficiently evaluated and discussed.

As mentioned above, traditionally, perfluorooctanoic sulphonate (PFOS) or its acid homologue (PFOA)²⁻³ was used for a long time in this context, before being prohibited and replaced by shorter molecules (six perfluorated carbon atoms maximum).



Scheme 1: Perfluorooctanoic sulphonate

These molecules can establish ionic links with the anionic sites present on the cellulose surface (glycoronic acids), through bi- and/or tri-covalent cations present in pulps or coating color formulation.

Although commercial fluorochemicals as oil-repellent reagents have been adopted since the 1960s, scientific publications about this family of materials are still very few and deal with the so-banished old-type of fluorochemicals.⁵⁻¹⁷ Recently,¹⁸ an original approach based on the use of fully sustainable and relatively inexpensive polymers, namely, cationic starch and chitosan, was proposed as a promising solution for food packaging. In our previous publication, we have drawn the most relevant conclusions of the papers available at that time.¹⁹ In the present work, we have investigated the surface properties of commercial oil-proof papers, namely, their roughness, contact angle values, surface energy and printability. In addition, the water- and oil-proof behaviors of these materials were observed. Finally, the relationships between the water- and oil-proof effects of the ensuing papers and their ink absorption features were examined.

EXPERIMENTAL

Oil-proof papers

Six commercial papers were studied. Samples #1-#5 were oil-proof papers, while sample #6 was a virgin untreated substrate. Oil-proof effects were provided to papers #1-#5 by using the new-type fluorochemicals. All the samples had a coating layer on one surface (denoted as: coated surface) intended to improve printing quality.

The other surface (called: non-coated surface) was supposed to be oil-proof treated. No further information was available about the samples, including the fabrication conditions and their formulations, but in our previous work, we succeeded to establish that sample #6 was the fluorine-free original substrate used to produce the investigated oil-proof papers. These substrates were treated by the surface coating process and the coating color used was identified in a previous work.¹⁹ The main component contained in this formulation was very similar to PFOS structure, except that the perfluorated carbon moiety contains only 6 carbon atoms.

In addition, we decided to undertake a careful but blind characterization of these papers, in order to ascertain their printability and barrier properties. Basic properties, such as basis weight, thickness and apparent density of the samples, were preliminarily measured and shown in Table 1.

The values of apparent density were calculated by dividing the basis weight by the thickness, therefore individual densities of the base paper and coating layer were not taken into consideration in this calculation. These measurements were made according to commonly used standards (ISO 536 for basis weight and ISO 534 for thickness) and were carried out 10 times for the basis weight and 40 times for the thickness on the tested samples. For each set of samples, several paper sheets (between 5 and 10) were tested in order to minimize the effect of production variability.

Calcination and elemental analysis of paper samples

Ash content (ISO 1762) was determined by calcination of a known quantity of paper sample, in a muffle furnace at 525 °C for 5 hours. After calcination, the ash residues were collected, weighed and their contents were calculated. For all the ash samples,

elemental analysis was conducted at the Centre d'Analyses CNRS at Solaize (France).

Table 1
Basis weight, thickness and apparent density of paper samples

	Basis weight (g/m^2)	Thickness (μm)	Apparent density (g/cm^3)
#1-OP	73.0 ± 0.8	72.6 ± 2.1	1.01
#2-OP	72.7 ± 0.5	66.8 ± 1.7	1.09
#3-OP	81.9 ± 0.6	76.1 ± 2.1	1.07
#4-OP	72.1 ± 0.5	65.8 ± 2.3	1.10
#5-OP	71.2 ± 1.2	64.4 ± 1.3	1.11
#6-UT	69.7 ± 0.5	60.1 ± 0.4	1.16

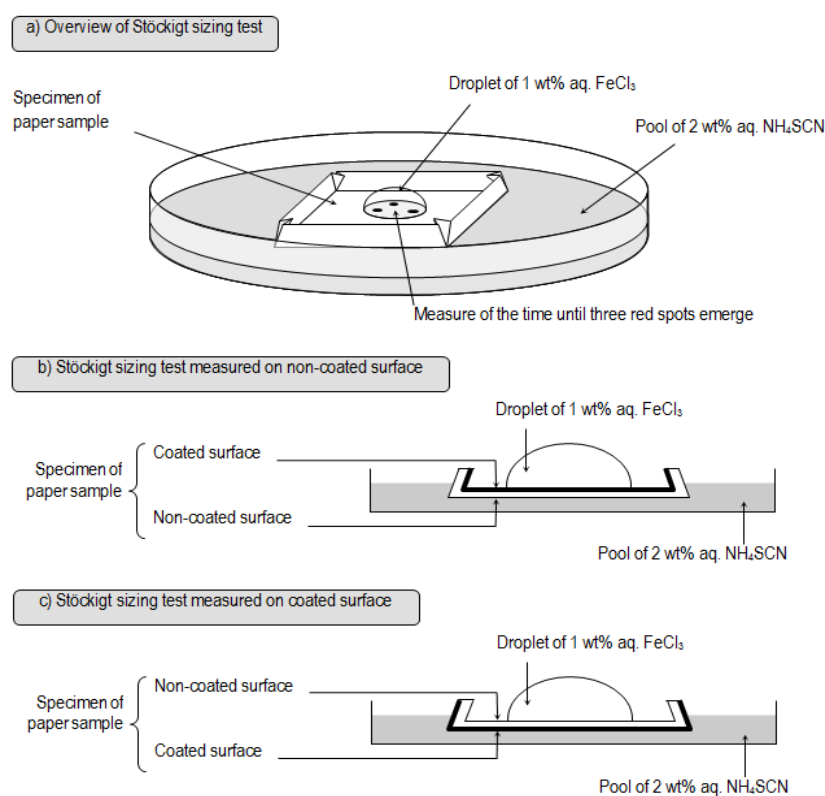


Figure 1: a) Overview of Stöckigt sizing test, b) the test measured on non-coated surface and c) that on coated surface of paper samples, respectively

Water- and oil-proofness evaluations

The Stöckigt sizing test (Japan Industrial Standard P8122) was adopted for the evaluation of water-proof properties. The principle of this test is depicted in Figure 1.

In this test, a small paper specimen was floated on a surface of 2 wt% solution of ammonium thiosulfate (NH_4SCN) and at the same time a droplet of 1 wt% solution of ferric chloride (FeCl_3) was deposited on the surface of the specimen. The time required for the appearance of three small red spots inside the droplet was measured. This lapse of time was considered as “Stöckigt sizing degree”. The longer this period of time is, the higher the water-proof efficiency. In the Stöckigt sizing test, the measured surface is that wetted by the

NH_4SCN solution. Thus, the Stöckigt sizing tests of the non-coated and the coated surfaces are illustrated in Figure 1b and 1c, respectively.

The Cobb₆₀ (ISO 535) test was also carried out for the paper samples to evaluate their water-absorption. A metal ring with a 10 cm² area was tightly set on the surface of the paper specimen, which was previously weighed. Then, 10 mL of distilled water was poured into the ring. After 45 s, the water was removed and the ring released. Then, a blotting paper was used to pull off the excess of water. The specimen was weighed after 60 s of total wetting time. The water uptake by unit area of paper specimen was considered as the index of water absorption of the paper sample.

The Kit test was conducted for the evaluation of the oil-proof effect of the paper samples, according to TAPPI T559 standard. In this test, twelve “Kit solutions” (from No. 1 to No. 12) were prepared by mixing castor oil, toluene and n-heptane in different ratios. A droplet of one Kit solution was deposited on the surface of the paper specimen and wiped after 15 s. Then, the tested area was examined in order to judge whether or not any stain of the solution was left on the surface. This process was repeated with different Kit solutions. The final “Kit number” was determined from the maximum number of Kit solutions that did not leave any stain on the paper surface. A larger Kit number indicates a stronger oil-proof effect of the substrate under investigation.

Ink absorption evaluation

Ink porosimetry tests were carried out for the evaluation of ink absorption of oil-proof papers. The adopted ink (#3809, Coates Lorilleux) was dye-based and black-colored. It was amphiphilic when properly diluted in water, ethanol, acetone, “white spirit (volatile solvent)” *etc.* This exclusive ink was applied on paper surfaces using a specific metal weight with a flat bottom of 12 mm radius and a weight of 328 g. Each time, the weight was removed after the time lapse of 0, 7, 15, 30, 60 and 120 s, respectively. The excess of ink, which had been put on the paper surfaces, was wiped out immediately. Then, the color density of black left within the ink-transferred area was measured with the color densitometer (D19C, X-Rite Inc.) after the inks were dried.

Other analyses

Elemental analyses with the use of an X-ray photoelectron microscope (XPS; XR3E2, Vacuum Generators), equipped with monochromated Mg K α X-ray source (1253.6 eV), and scanning electron microscope (SEM; Quanta 200, FEI), equipped with an energy dispersive X-ray microanalyzer (EDX; XFlash 5010 Detector, Bruker Corp.), were carried out. XPS analysis was conducted on both surfaces of the paper samples by the low resolution scanning method. These analyses were already mentioned in our previous article.¹⁹

RESULTS AND DISCUSSION

Calcination and elemental analysis of paper samples

Table 2 reports the ash contents of the paper samples after calcination at 525 °C for 5 hours, as well as the elemental analyses of the corresponding ashes. This table shows that the ash contents of the paper samples remained within the range of 15.0 and 17.1 wt%. In general, the values of this parameter reflect the amounts of inorganic and mineral compounds contained in the base papers

and/or in the coating layers, such as fillers and pigments. The elemental analysis adopted in this study did not cover the detection of oxygen and silicon elements. No fluorine elements were found in the ash components of any of the paper samples, including the oil-proof papers #1 to #5. All the ash samples contained predominantly aluminum and calcium atoms. Samples #1-#5 contained large amounts of calcium and carbon elements, compared to sample #6, while the latter contained more aluminum. These results suggest that the first series of samples (#1 to #5) were mainly filled with calcium carbonate (CaCO₃), whereas sample #6 contained much more kaolin (Al₂O₃·2SiO₂·2H₂O as representative chemical structure). Table 3 gives also the ratio between the main pigments used, *i.e.*, kaolin/CaCO₃.

In fact, these pigments are widely used as fillers for base papers and pigments for coating layers in the papermaking industry.²⁰ Likewise, each ash sample indicated the presence of magnesium, sodium and iron at a low level. Magnesium could originate from talc, a pigment used in coating color due to its softness; iron is a typical kaolin impurity; sodium could originate from residual cation in the chemical pulps used to prepare the paper samples.¹⁹

Water- and oil-proofness evaluations

Figure 2 displays the data on the Stöckigt sizing degrees of the paper samples. In this figure, white and gray bars show the sizing degrees of the non-coated and coated surfaces, respectively. Each paper sample exhibited a sizing degree higher than 20 s on both surfaces. On the whole, all the samples had relatively high sizing degrees when the non-coated surfaces were measured. Figure 2 also shows that samples #1 to #3 possessed relatively higher sizing values, indicating their higher potential of resistance against wetting, and predicting their suitability as paper commodities in packaging applications.

Figure 3 depicts the Cobb₆₀ tests of all the investigated samples. The graph shows that the Cobb values are typical of highly sized surfaces, *i.e.* lower than 20 g/m², except for sample #6, which is the virgin untreated substrate.

In addition, sample #1 displays the lowest Cobb value on both sides. Figure 4 shows the results of the Kit tests aiming at evaluating the oil-proof properties of the paper samples.

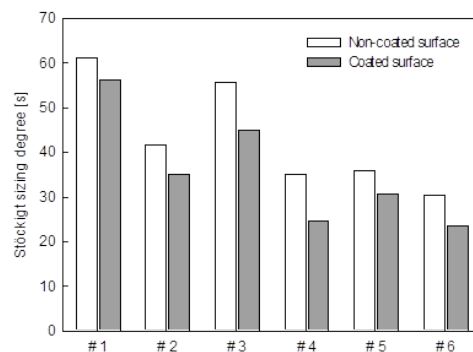


Figure 2: Stöckigt sizing degree of paper samples as water-proofness indices. The specimens were placed with their non-coated surfaces (white bars) or coated surfaces (gray bars) in direct contact with the surface of ammonium thiosulfate (NH_4SCN) solution

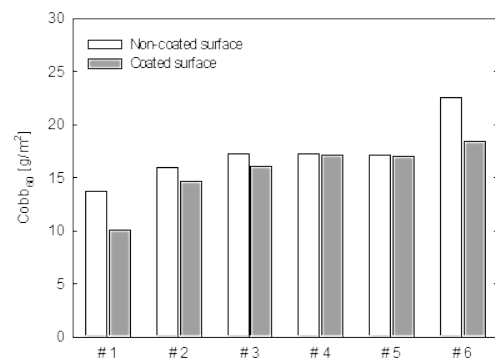


Figure 3: Cobb₆₀ values of paper samples as water-absorption indices

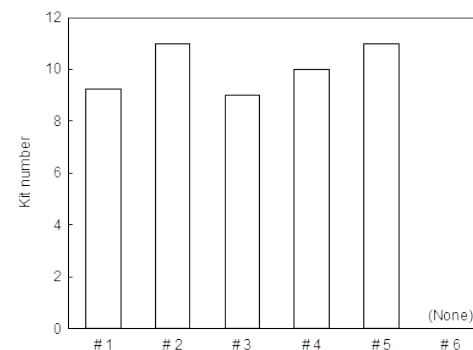


Figure 4: Kit numbers on non-coated surface of paper samples as oil-proofness indices

Table 2
Ash content and atomic composition (wt%)

	Ash content	C	Na	Mg	Al	S	Ca	Fe
#1-OP	15.0	4.04	0.79	0.94	10.66	0.71	14.12	0.50
#2-OP	16.5	4.44	0.80	0.45	11.19	1.00	16.30	0.47
#3-OP	14.9	3.96	1.07	0.48	11.47	0.95	15.35	0.52
#4-OP	14.5	4.52	0.81	1.41	11.35	N.D.*	17.19	0.68
#5-OP	16.1	3.91	1.11	0.88	12.25	N.D.*	16.48	0.43
#6-UT	17.1	0.78	1.06	1.32	18.94	N.D.*	4.02	1.13

*N.D.: Not detected

Table 3
Elemental composition ratio on non-coated and coated surfaces of paper samples (values calculated from the results of peak areas on low resolution XPS spectra)

		C	N	O	F	Na	Al	Si	Ca	Al/Ca	Al/Si	Kaolin/CaCO ₃
#1	Non-coated	52.0	1.1	15.1	31.5	N.D.*	N.D.*	N.D.*	N.D.*	-	-	
	Coated	57.7	1.6	30.1	0.5	N.D.*	4.4	4.0	1.6	2.8	1.1	55/45
#2	Non-coated	47.2	0.8	17.3	34.7	N.D.*	N.D.*	N.D.*	N.D.*	-	-	
	Coated	55.3	1.7	34.3	1.0	0.8	N.D.*	5.9	1.0	-	-	
#3	Non-coated	49.7	0.8	20.1	29.5	N.D.*	N.D.*	N.D.*	N.D.*	-	-	
	Coated	54.2	1.8	32.3	0.6	N.D.*	4.7	4.8	1.6	2.9	1.0	60/40
#4	Non-coated	48.9	1.2	17.7	32.3	N.D.*	N.D.*	N.D.*	N.D.*	-	-	
	Coated	61.0	2.3	27.5	0.4	0.6	2.5	4.4	1.4	1.8	0.6	60/40
#5	Non-coated	48.5	0.4	18.2	32.9	N.D.*	N.D.*	N.D.*	N.D.*	-	-	
	Coated	55.0	2.6	30.8	0.5	0.7	3.5	5.2	1.6	2.2	0.7	62/38
#6	Non-coated	66.4	1.1	30.7	0.5	N.D.*	0.8	0.5	0.1	8.0	1.6	71/29
	Coated	48.0	3.0	35.7	N.D.*	0.8	4.7	6.9	0.9	5.2	0.7	79/21

* N.D.: Not detected

This test was carried out on the non-coated fluorine treated surfaces because the untreated coated counterparts did not display any oil-proof properties.

All the samples exhibited Kit numbers from 9 to 11 on their non-coated fluorine-treated surfaces, except sample #6, since it was not an oil-proof treated substrate.

Ink absorption tests

Figure 5 shows the visual inspection of the ink transfer on the surface of both sides of the tested samples after the ink porosimetry tests, as a function of ink penetration time (7, 15, 30, 60 and 120 s). It is worth noting that the trace of ink drag left beside each ink-transferred area after wiping the surplus ink, corresponds to 0 s application time. Indeed, wiping the ink is an extremely fast process and is considered as 0 s time.

On the non-coated surfaces, paper sample #6 marked a more intense ink-transferred area in comparison with the other five samples. It is clear that the black color intensity on sample #6 became more pronounced with an increase in ink-penetration time. For the coated surfaces, all the samples marked a very light black color within the ink-transferred areas. No remarkable difference was observed among the samples.

Figure 6 shows the values of black color density (BD) within the ink-transferred area after the ink porosimetry tests. These values were measured after the application times of 0-120 s.

On the non-coated surfaces of samples #1-#5, the BD values slightly rose with increasing the application time in the range from 0 to 30 s. Then, the values remained practically constant within a value range of 0.45-0.65. Finally, for sample #6, the BD values on the non-coated surface increased drastically from 0 to 15 s and still kept increasing, although with a lower slope, up to 120 s, to reach about 1.1. On the coated surfaces, no remarkable differences were observed among all the paper samples. Smaller BD values were displayed on the coated surfaces when compared with those related to the non-coated ones. Actually, the BD values for the coated surfaces gradually increased, but they remained around 0.25 even after 120 s.

Elemental analysis of ashes

In the papermaking industries, fillers and pigments are widely added to papers in bulk and in coating layers, in order to increase the opacity, brightness, smoothness, gloss, basis weight and ink-receptivity. As mentioned before, the elemental analyses of ashes (Table 2) show that the main elements were aluminum, calcium and carbon. These data suggest that the coating layer was mainly composed of kaolin (the presence of Al atoms) and calcium carbonate (the detection of Ca and inorganic C atoms). In addition, the presence of a small amount of talc could be deduced from the presence of Mg atoms. These data are in line with those established by XPS analyses, as discussed below.

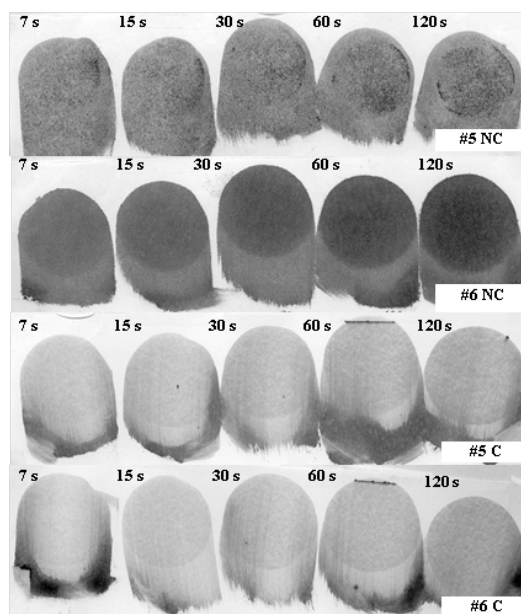


Figure 5: Pictures of ink-transferred areas after the ink-application times of 7, 15, 30, 60 and 120 s on the non-coated (NC) and the coated (C) surfaces of the paper samples deduced from ink porosimetry tests

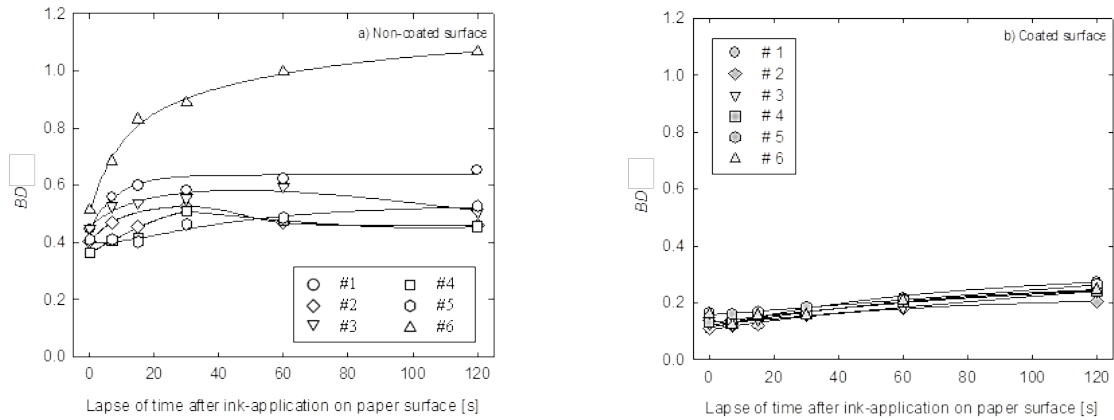


Figure 6: Black color density (BD) on the paper samples after ink porosimetry tests; a) non-coated surface, and b) coated surface

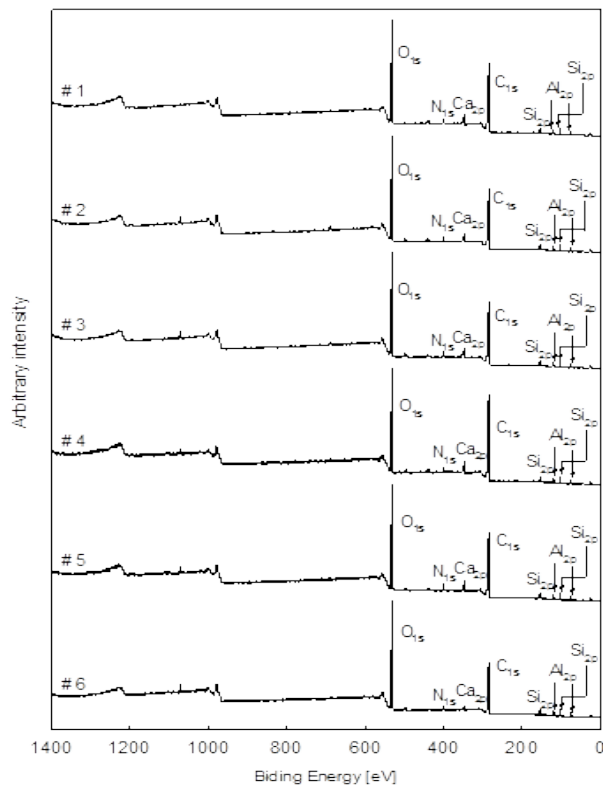


Figure 7: XPS spectra of the paper samples scanned by the low resolution method (coated surface)

Thus, the main pigments are kaolin and calcium carbonate, as expected from common papermaking practices. The ratios between these two pigments were calculated for each sample, as shown in Table 3. Thus, the coated layers for the 5 treated papers were mainly composed of kaolin and calcium carbonate within a ratio of about 60/40 (wt%). For the untreated sample, the kaolin filler was predominant, *i.e.ca.* 80/20.

Figure 7 depicts the XPS low resolution spectra of the coated surfaces. The elemental analyses deduced from XPS are indicated in Table 3.

These surfaces contained aluminum, silicon and calcium atoms, while their non-coated surfaces had almost no traces of these elements, but were constituted mostly of carbon, oxygen and fluorine atoms, as previously reported.¹⁹

The ratio between fluorine and carbon atom (F_{1s}/C_{1s}) was deduced from the corresponding signals in the XPS low resolution spectra, as reported in our previous work.¹⁹ They were found to be: 0.61, 0.73, 0.59, 0.66 and 0.68, for samples # 1 to 5 and close to zero (0.01) for sample #6. These values took into account the sensitivity factor for

the involved atoms. These ratios indicate how rich surface is in fluorine atoms, responsible for oil-repellency power.

Water-proofness evaluation

Paper sample #6 showed, to some extent, a water-proof effect (Figs. 2 and 3) although no oil-proof properties were observed (Fig. 4). These results indicate that sample #6 contained conventional sizing reagents (such as rosin sizes, alkenyl succinic anhydride (ASA or alkylketene dimer (AKD)). Figure 3 displays the result of Cobb₆₀ tests and shows that more than 10 g/m² of water were absorbed by both the non-coated and the coated surfaces of all the paper samples, with a maximum value for sample #6 and a minimum for sample #1. For these two samples, it is possible to discriminate the two sides. As expected, the non-coated surface of sample #6 displayed the highest Cobb₆₀ value, since it is not treated with fluorochemicals.

The Stöckigt sizing test shown in Figure 2 demonstrates that differences between the tested samples, as well as between their sides, can be

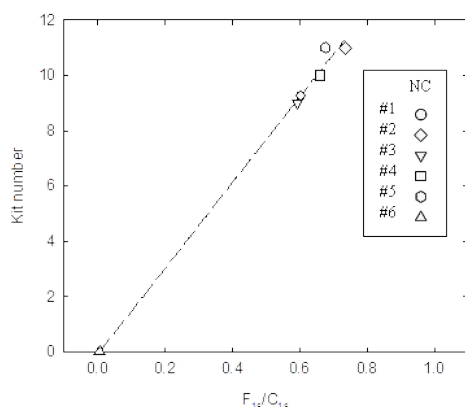


Figure 8: Correlation between the F_{1s}/C_{1s} ratio and the Kit number of the non-coated surfaces of paper samples

Ink absorption evaluation

As described above, Figure 6 shows black color density (BD) on the non-coated and the coated surfaces of the paper samples after ink porosimetry tests. For 30 s of ink penetration, the BD values on the non-coated surfaces of paper samples #1-#5 ranged from 0.45 to 0.65 (Fig. 6). After such a delay, this parameter reached a plateau. Instead, on the non-coated surface of sample #6, the BD values kept increasing and reached a value of 1.06, after 120 s. The coated surfaces displayed a similar

behavior for the all the paper samples. This confirms the similar composition of the coated layers, as established by XPS data. The difference between the two sides is most probably due to the fact that the pore size of the coated layers is generally one hundred times lower than that of the non-coated counterpart.²¹ On the other hand, fluorine layers form a discontinuous film on the non-coated paper surfaces. As a consequence, higher porosity leads to more pronounced ink penetration.

Oil-proofness evaluation

Kit tests were performed on the non-coated surfaces of the paper samples, as depicted in Figure 4. All the samples, except paper #6, displayed values of 9-11, witnessing about their good oil-proof properties. As expected from XPS analysis (previously reported),¹⁹ sample #6 did not show any oil resistance.

Figure 8 displays a good correlation between the F_{1s}/C_{1s} ratios and Kit numbers (Fig. 4) of the paper samples. This finding confirms the efficiency of perfluorated sequences, as oil proof moieties.

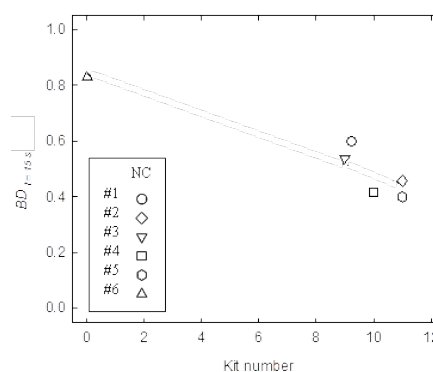


Figure 9: Black color densities at 15 s ($BD_{t=15}$) in ink porosimetry test and Kit number on non-coated paper surfaces

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Figure 9 plots the relationships between the BD values and the Kit numbers (oil-proof indices) on the non-coated surface of paper samples. For the y-axis, the BD values at 15 s were taken in order to relate them with the application time in the Kit solution test, as previously discussed.

As expected, this figure reveals that papers with larger Kit numbers exhibit smaller BD values, while the non-oil-proof sample #6 shows a higher BD value. It could be, therefore, concluded that ink color density was influenced by the oil-proof treatments of the papers. The same tendency was observed (results not shown) when correlating the BD values to Cobb₆₀ results.

CONCLUSION

Five commercial oil-proof papers prepared with fluorochemicals containing six perfluorinated carbon atoms, as oil-repellent reagent, were investigated in terms of elemental analyses, ash content, water- and oil-proof behaviors, XPS and ink absorption evaluation. They were made with the same substrate (here called as untreated sample) and they were treated by surface coating. The elemental analyses of the ashes revealed that each paper sample contained inorganic compounds, such as fillers, pigments. XPS analyses allowed the evaluation of the relative amount of fluorine atoms on the surface of paper samples. In Stöckigt sizing, Cobb₆₀ and Kit tests, all the paper samples containing fluorochemicals showed both high water- and oil-proof effects, while in the fluorine-free paper sample a certain level of water-proof features was found, but no oil-proof properties were observed. As expected, the ink absorption tests showed that the non-coated surface of the fluorine free paper displayed large ink retention, whereas the coated surfaces of all the paper samples displayed small ink absorption.

This paper also shows that fluorine bearing sequences associated with this type of fluorochemicals do not migrate to the coated side, thus preventing printability defects, which makes them a serious potential candidate for substituting the old (banned) families.

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