Factors influencing the treatment of paper with fluorochemicals for oil repellency

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ABSTRACT

The objectives of this work were to understand why fluorochemicals, added to retard solvent or grease penetration, are more effective in wood-free papers than in mechanical pulp based papers. Newsprint required about ten times more fluorochemical than did Whatman #42 filter paper to achieve solvent resistance. Based on the results of kit tests, contact angle measurements, and X-ray photoelectron spectroscopy using both paper and regenerated cellulose films, it was concluded that about 40% of the added fluorochemical demand of newsprint—compared with filter paper—was due to the higher specific surface area of newsprint. The remaining 60% was due to interference by solvent-extractable material (i.e., pitch). The negative effects of pitch could be partially circumvented by using hydrophobically modified starch in conjunction with fluorochemical.

Application:

The amount of fluorochemical surface application required to obtain solvent-resistant newsprint depends on the specific surface area and pitch content of the paper. Hydrophobic extractives appear to interfere with the uniform spreading of fluorochemical.

PAPER AND PAPERBOARD PRODUCTS are routinely treated with fluorochemicals to limit the rate of penetration by oils, solvents, and other hydrophobic materials *(1)*. Common applications include pet food bags and fast-food packaging. In most cases, only paper products based on chemical pulp fibers are treated. Fluorochemicals are not considered to be cost effective in papers based on mechanical pulps. The objectives of this work were to determine what aspects of wood-containing papers made them less suitable for fluorochemical application and to determine approaches to increase fluorochemical efficiency in mechanical pulp papers.

Fluorochemicals are applied either to the pulp in the wet end or as a size press additive. The wet-end additives, which must be water-soluble or dispersible, are usually low-molecular-weight molecules that contain both hydrocarbon and fluorochemical segments together with a charged group to give water solubility. Two examples of structures are given in **Fig. 1.** In the case of paperboard, fluorine-containing emulsion polymers are generally applied at the size press or calender stack.

A number of generalizations can be made about fluorochemical applications to chemical pulps and fine papers. Fluorochemical addition levels for a given level of solvent resistance increase with increased pulp refining, with increased filler content, and with increased sizing. Refining and filler addition increases the specific surface area of the headbox furnish and thus the fluorochemical demand. Wet-end size dispersions also increase the surface area of the furnish. In addition, sizing influences size press pickup for size press fluorochemical treatment.

Organic solvents and greases do not dissolve or swell cellulose. Therefore, these materials do not diffuse through fiber walls but instead are transported through the pores in paper by capillary forces. The historical method of manufacturing greaseproof paper is to produce a glassine, which essentially has no pores to transport grease through the paper. By contrast, fluorochemical treatment decreases the wettability of the paper structure by solvents and grease; this in turn eliminates the capillary forces.

The surface chemistry of fluorochemical surfaces was extensively investigated by the pioneering work of Zisman and coworkers *(5)*. Contact angle measurements evaluate the interactions of a solvent with a surface; the higher the contact angle, the lower the affinity of a solvent for a surface. The Washburn equation *(3)*, shown as follows, gives an indication of how contact angles influence penetration through porous structures. Ignoring gravity, the rate of capillary forces driven fluid through a horizontal capillary tube of radius R.

$$dh/dt = \gamma R \cos\theta / 4\eta h \qquad (1)$$

where

γ = surface tension
θ = contact angle
η = viscosity
h = distance along the tube.

As the contact angle approaches 90 degrees, the rate of fluid transport approaches 0. The contact angle of corn oil on glassine is 26° *(4)* ($\cos\theta$ = 0.9). Thus, according to the Washburn equation, corn oil penetration will only be slow if the effective pore radius, R, is very small. By comparison, fluorochemical-treated paper has a contact angle of corn oil of 129°*(4)* ($\cos\theta$ = –0.63), which, by

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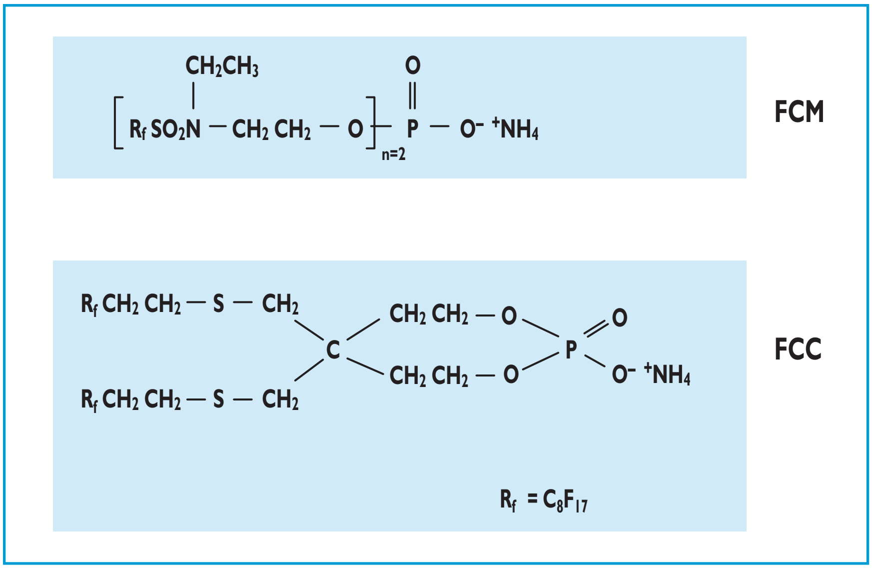
the Washburn analysis, will give no penetration.

Studies with well-defined fluorochemical monolayers have established the molecular requirements for high hydrocarbon contact angles. Zisman's classical experiments consisted of measuring the contact angles of a series of hydrocarbons on a fluorochemical surface. Contrary to theory *(2)*, the cosines of the contact angles are linear functions of the surface tension of the test hydrocarbons. Zisman defined the critical surface tension as the surface tension where the contact angle results extrapolated to cos $\theta = 1$; see **Fig. 2** for examples of Zisman plots. The lowest fluorochemical critical surface tensions of 6 mJ/m^2 (i.e., the most solvent phobic) correspond to surfaces dominated by CF_3 groups, whereas $-CF_2-$ surfaces have a critical surface tension of 18 mJ/m^2 *(5)*. The critical surface tension also decreases from 7 to 4 mJ/m^2 when the chain length of ordered fluorochemical surfactant monolayers was increased from 3 to 8. Thus, fluorochemical chain length is important *(2)*.



1. Structures of the fluorochemicals

Sample name	Pulp type	Origin	Pitch content, %	Comments
NP1	TMP	Beaupre	0.15	Not calendered
NP2	TMP	Beaupre	0.15	Calendered
NP3	SBK (pine) + SGW (mixed swd. and hwd.)	Fort Frances	0.057 (AC) 0.11 (MC)	-
NP4	TMP	Iroquois Falls	0.65	-
BK	-	-	-	From Paprican

I. Summary of newsprint papers

EXPERIMENTAL

Materials

Four newsprint samples were supplied by Abitibi-Consolidated; their properties are summarized in **Table I.** The pitch contents were determined gravimetrically by dichloromethane extraction. Other substrates for fluorochemical treatment were as follows:

- Filter paper: 90 mm diam Whatman #42 ashless
- Cellulose film: 27/32 in. diam dialysis tubing, 100 ft, 12,000–14,000 molecular-weight cutoff dialysis tubing supplied by VWR (Mississauga, ON).

Bleached kraft pulp handsheets were made by standard methods with bleached kraft pulp supplied by Paprican (see Table I).

Two commercial fluorochemicals were used without further purification. One, designated herein as FCM, was FC807 supplied by 3M, and the other, FCC, was Lodyne P208E, supplied by Ciba. Both chemicals are low-molecular-weight phosphate salts; the structures are given in Fig. 1.

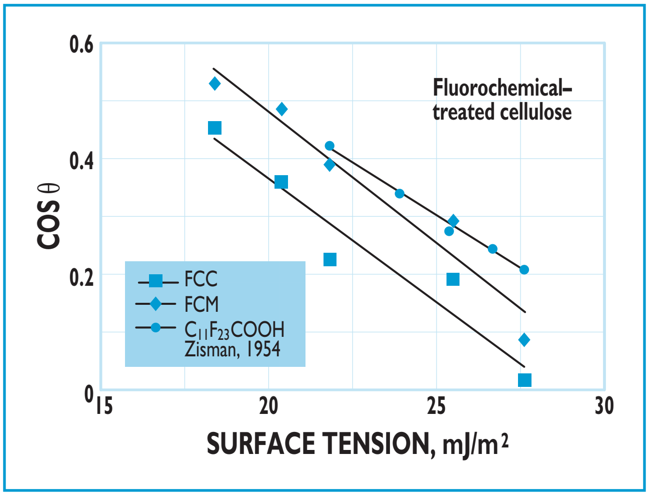
Two commercial starches were used. Soluble starch was supplied by BDH (ACS879), and hydrophobic starch was Filmkote 54, supplied by Nacan Toronto. ^{1}H Nuclear magnetic resonance indicated that the hydrophobic substituent accounted for about 3% of carbons. Starch was dispersed in cold distilled water (2 wt. %), and after 30 min soaking, the suspension was heated to 88°C for 30 min.

Kraft lignin, Indulin C supplied by Westvaco, was used as a model for lignin in mechanical pulp. Fatty acid–rich, distilled tall oil was PAMAK C2 supplied by Hercules, Mississauga, ON. Abietic acid and hexadecane were supplied by Aldrich and were used without further purification. Dichloromethane was supplied by Caledon.

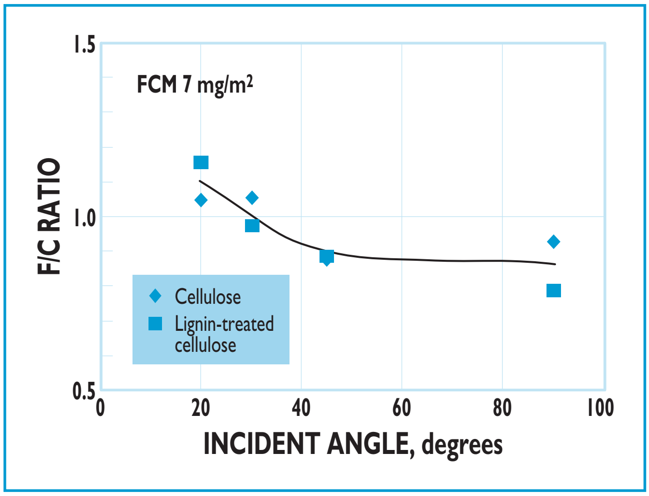
Preparation of cellulose films

Strips of cellulose dialysis tubing were boiled in water three times for 4 hours to remove plasticizers and preservatives. The wet films were stretched over the end of short, 19 mm diam Plexiglas tubes and dried at room temperature.

To prepare lignin-coated cellulose films, 2 g of Indulin C was dissolved in a 100 mL solution of acetone and dioxane (1:2 volume ratio). Cellulose films were soaked in the



2. The contact angle of alkanes on fluorochemical-treated cellulose films as a function of the alkane surface tension. The surface concentrations were 7 mg/m² for both FCM and FCC.



3. The F/C mass ratio, determined by XPS, as a function of incident angle for FCM-treated cellulose and lignin-coated cellulose films. The fluorochemical concentration was 7 mg/m².

Indulin C solutions for 1 day followed by rinsing in distilled water. Films were coated with fluorochemicals by placing 0.25, 0.5, 0.75, and 1.0 mL of fluorochemical solution (0.00012–0.12 wt. %) onto the dried film to give surface coatings in the range 0.04–152 mg/m².

Fluorochemical treatment of paper

Two methods were used to treat paper with fluorochemical. In Method 1, the paper was coated with fluorochemical solution using an RDS #5 Meier grooved rod to control coating thickness. Coated paper was weighed before and after room-temperature drying. In Method 2, the paper was dipped for 30 seconds in a bath of treatment solution, after which it was removed, weighed, and dried. Deionized water or methanol was used to dissolve the fluorochemicals, and concentrations of the treatment solutions were 0.00012–3% by weight.

X-ray photoelectron spectroscopy (XPS) measurements were performed with a Leybold Max200 spectrometer. The results were analyzed with ESCATOOLS Version 4.5, Surface/Interface, Mountain View, CA. Contact angle measurements were conducted under ambient conditions using a Rame Hart goniometer.

Kit ratings were determined using TAPPI Test Method T 559. In this procedure, 12 solutions are prepared from mixtures of castor oil, toluene, and heptane. The most aggressive mixture, corresponding to a kit rating of 12, is toluene:heptane (90:110 by volume), whereas the least aggressive solution, corresponding to a kit rating of 1, is pure castor oil. The test consists of placing a drop of test solution on paper for 15 seconds, after which it is removed by sorption into a tissue. The test is considered a failure if there is evidence of paper wetting by the solvent drop.

RESULTS

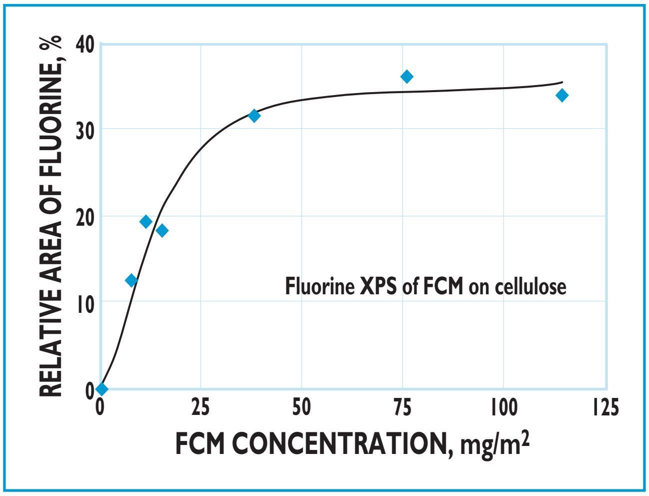
Cellulose films

Cellulose dialysis tubing was used as a smooth model for the surface cellulose fibers. Figure 2 shows the contact angle results for a series of alkanes (hexane, heptane octane, hexadecane, and cyclohexane) as a function of the surface tension of the solvents for two sets of films treated with two commercial fluorochemicals (see Fig. 1 for structures). Zisman's data *(5)* are also shown for a fluorochemical surfactant. The extrapolated critical surface tensions γ_c, corresponding to cos θ = 1, were 8.6 mJ/m² for FCM and 5.1 mJ/m² for FCC. Li *et al.* reported γ_c values of 9–14 mJ/m² for fluorinated derivatives of polyacrylamide *(7)*. They argued that this range corresponded to a mixture of CF_3 and CF_2 groups, whereas γ_c for a pure CF_3 is 6 mJ/m².

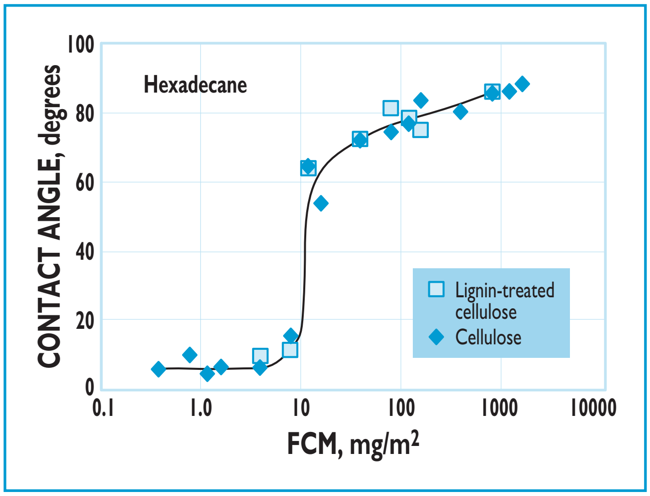
The mole ratio of fluorine to carbon on the films was measured by XPS, and the results are shown as a function of X-ray incident angle in **Fig. 3**. The highest F/C ratio corresponded to the lowest incident angle, indicating that the fluorines were concentrated on the surface. Note that the incident angle roughly corresponds to the depth of the analysis in angstroms. The F/C ratio for the fluorochemical chains on FCM is 2.1, and the ratio for the whole FCM molecule is 1.4. Figure 3 shows that the F/C ratio was about 1.1 on the exterior surface. Therefore, the results in Fig. 3 suggest that a covering of 7 mg/m² gave a surface that was nearly pure fluorochemical. The lignin-coated cellulose gave similar results, suggesting that lignin did not interfere with the orientation of the fluorochemical.

A series of cellulose films was prepared with a range of FC807 surface concentrations, and the films were characterized by XPS. The relative areas of fluorine in the XPS spectra are shown in **Fig. 4** as a function of surface coverage. The surface concentration of fluorine was constant at coverages greater than 40 mg/m².

The contact angle of hexadecane on cellulose films was measured as a



4. The percent area of fluorine in the XPS spectra of cellulose film as a function of the FCM concentration

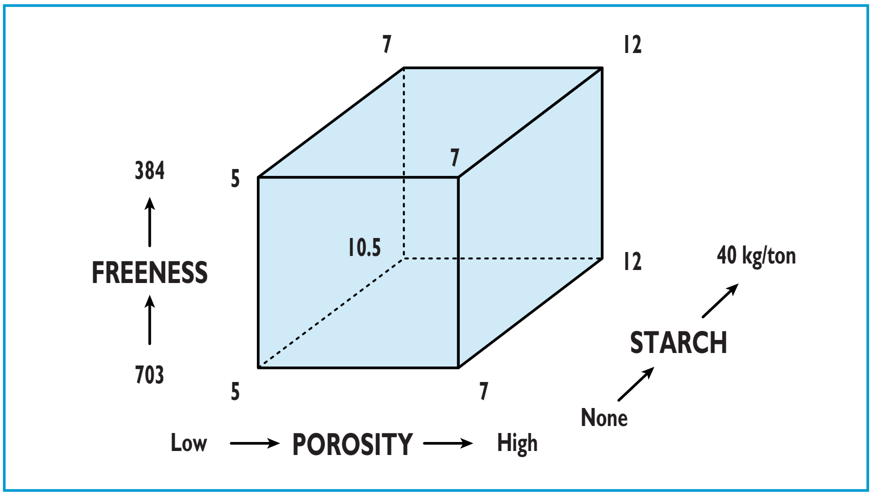


5. Contact angles of hexadecane on cellulose and lignin-treated cellulose as a function of the surface concentration of FCM

function of FCM coverage, and the results are shown in **Fig. 5**. Up to about 10 mg/m^2, the contact angle was less than 20°, whereas higher fluorochemical concentrations gave much higher contact angles. Furthermore, the lignin treatment of the cellulose films had no significant effect on the results.

The onset of the plateau region for the XPS results in Fig. 4 corresponds to coverage at which the hexadecane contact angles increased in Fig. 5. Thus, we conclude that near-monolayer coverage was needed to get a high contact angle.

Results using paper as a substrate, presented in the next section, indicate that resin and fatty acids found in wood can influence the performance of fluorochemicals. This behavior was also reflected in contact angle results. Cellulose films were pretreated with either tall-oil fatty acid or abietic acid followed by FCM, and the results are summarized in **Table II**. FCM-treated cellulose gave a hexadecane contact angle of 85°. Pretreatment of the cellulose film with either fatty or abietic acids caused fluorochemical-treated films to have contact angles of 62° and 66°, respectively. Thus, we conclude that the surfactants interfered with the fluorochemical. The presence of hydrophobic starch in the coating solution partially reversed the negative effects of the fatty and resin acids, whereas there was no benefit in the use of cationic starch.



6. Kit ratings for bleached kraft pulp handsheets (See Table III for details) treated with 5 mg/g FCC using Method I (rod coating). The porosity changes reflect the pressing pressures used to make the handsheets. The starch data shown are for hydrophobic starch.

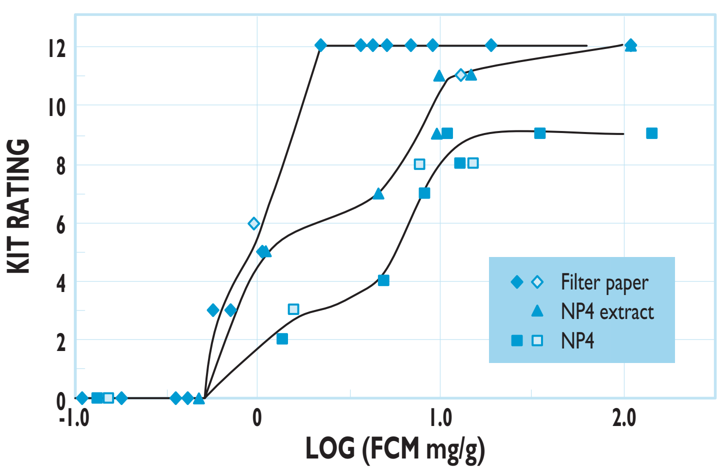
Coating	Fatty acid–pretreated cellulose	Abietic acid–pretreated cellulose
FCM	61	66
Hydrophobic starch + FCM	81	74
Cationic starch + FCM	67	68
No coating	32	61

II. Advancing contact angle of hexadecane (in degrees) on treated cellulose films. Here, 0.5 mL of 12% FCM with 2% starch was dried on the film after fatty or abietic acid treatment. The contact angle of hexadecane on FCM-treated cellulose (i.e., without fatty or abietic acid) was 85°.

Hand-sheet no.	PFI revs.	Calen-dering press., psig*	Avg. bright-ness, % ISO	Light-scat-tering coef.	Opacity, % ISO	Air perme-ability, mL/min	Kit hydro. starch	Kit cationic starch	Kit no starch
1	0	-	86.72	37.33	73.56	920	12	10	7
2	1000	-	85.45	29.95	69.87	1215	12	12	8
3	3000	-	84.68	25.09	65.92	1362	12	12	9
4	6000	-	84.39	22.93	63.94	1367	12	12	6
5	9000	-	83.43	20.74	61.89	1635	12	12	7
11	0	500c	82.02	30.74	72.65	105	12	12	7
12	0	1000c	79.99	26.18	69.52	49.8	12	12	6
13	0	1700c	78.41	21.19	64.53	29.8	10.5	7.5	5
14	0	1000s	81.33	34.72	76.32	103.8	12	12	6
21	1000	500c	79.92	26.63	71.24	116.8	12	11	7
22	1000	1000c	78.22	21.84	66.72	67.8	12	12	6
23	1000	1700c	77.63	18.23	61.87	33.5	10	3	6
24	1000	1000s	79.42	27.50	72.62	116.3	12	12	7
31	3000	500c	77.36	22.53	68.85	144.0	12	12	6
32	3000	1000c	73.14	18.42	65.57	64.3	10	12	5
33	3000	1700c	73.49	15.53	60.12	33.3	11	10	5
34	3000	1000s	76.51	22.51	69.33	198.3	12	12	6
41	6000	500c	76.43	20.93	67.58	153.3	12	11	6
42	6000	1000c	72.77	16.94	63.49	52.5	11	9	5
43	6000	1700c	73.89	14.74	58.53	36.0	5	9	6
44	6000	1000s	76.53	21.88	68.81	207.8	12	12	6
51	9000	500c	74.51	9.94	67.64	185.0	12	5	7
52	9000	1000c	71.87	17.02	64.59	73.5	7	4	6
53	9000	1700c	71.41	14.08	58.97	42.0	7	3	5
54	9000	1000s	74.66	20.25	68.02	271.5	12	9.5	6.5

*c=steel calendered, s=soft-nip calendered

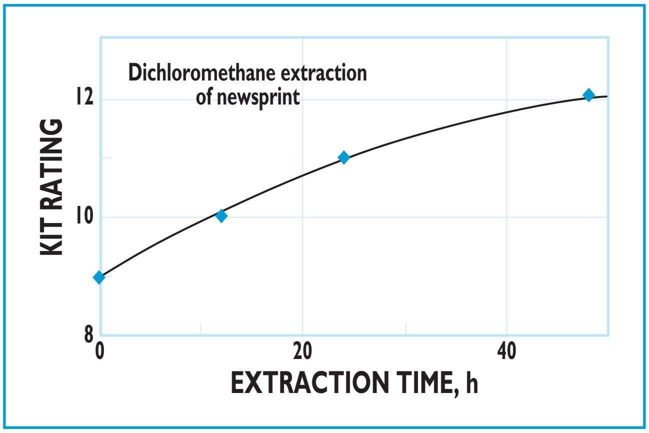
III. Properties of bleached kraft pulp handsheets



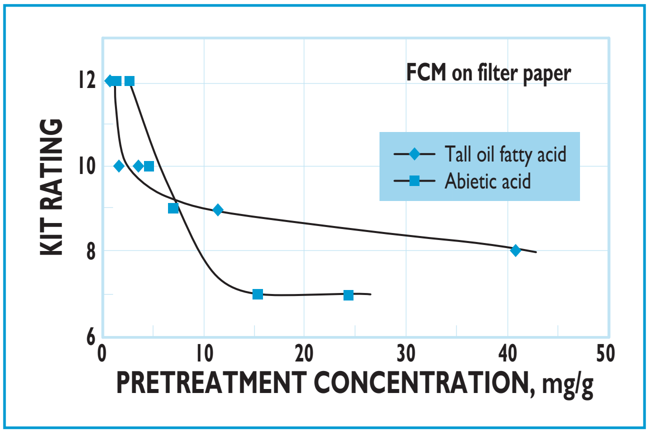
7. Kit ratings for Whatman #42 ashless filter paper, NP4 newsprint, and NP4 newsprint extracted with dichloromethane (48 h) as functions of the coverage with FCM (Method 2). Solid points are FCM dissolved in water, whereas open points are for methanol.

Paper studies

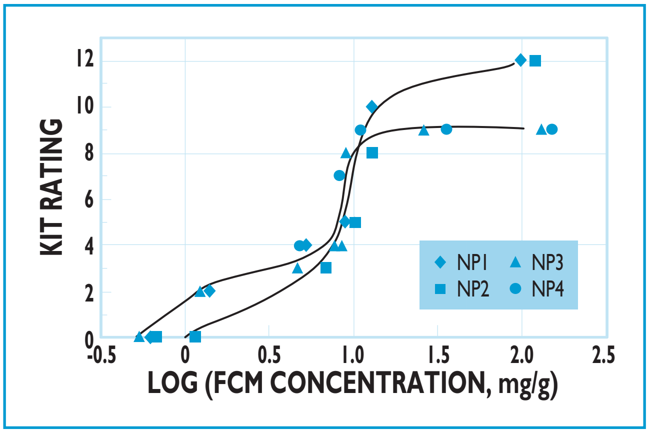
The ability of treated papers to prevent solvent penetrations was evaluated by the "Kit Test," developed by 3M Co. This test measures the penetration of a series of solvent mixtures from castor oil to toluene plus hexane. The higher the kit rating, the more solvent resistant is the paper. A series of handsheets was prepared from bleached kraft pulp by CPPA standard methods. The variables investigated were beating, pressing pressure, and soft-nip vs. steel calendering. The properties of the handsheets and the resulting kit ratings are summarized in **Table III**. The sheets were coated with 1.5% FCC using Method 1 (see "Experimental")



8. Kit rating of standard newsprint as a function of the soaking time in dichloromethane. The extracted paper was treated with 13 mg/g FCM.



9. The influence of fatty acid–rich tall oil and abietic acid on the kit rating of filter paper treated with 6.2 mg/g FCM



10. Kit ratings as a function of FCM coverage for different newsprint samples

to give approximately a 5 mg/g coating. In separate experiments, the coating solutions also contained 2% hydrophobic or soluble starch.

Figure 6 shows kit ratings on the corners of a cube corresponding to extreme values of the variables shown in Table III. Beating and pressing did not substantially influence the kit rating. By contrast, the high hydrophobic starch loading gave a significant improvement in kit rating.

Traditional "grease-proof" fluorochemical-treated papers are formed from lightly beaten chemical pulps similar to filter paper. Kit ratings for treated newsprint are compared with those of filter paper in **Fig. 7**. The filter paper, based on fully bleached chemical pulp, gave the highest kit readings and gave intermediate kit readings at the lowest fluorochemical treatment levels. The newsprint was the most difficult to treat; it gave a maximum kit rating of 9 compared with 12 for filter paper. Furthermore, the newsprint required about one order of magnitude more fluorochemical (~10 mg/g) than did the filter paper to achieve intermediate kit values (6–7), which is adequate for many applications.

Newsprint contains lignin and extractives [i.e., hydrophobic neutral materials, resin, and fatty acids *(8)*] not found in filter paper. The contact angle work on cellulose films suggested that lignin did not interfere with fluorochemical performance. Therefore, it seemed reasonable to propose that the hydrophobic extractives interfered with fluorochemical performance. To test this hypothesis, the newsprint was extracted with dichloromethane to remove some of the extractives. The results in Fig. 7 confirm that removal of some of the extractives increased the fluorochemical efficiency as judged by the kit rating. The papers were treated by dipping them in a bath of fluorochemical, and the uptake was determined gravimetrically. A comparison of the open and filled data points in Fig. 7 suggests that kit ratings were the same regardless of whether the fluorochemical bath was water or methanol. This, in turn, suggests that incomplete dissolution of the fluorochemical or poor wetting of the paper was not the origin of the difficulty in treating newsprint.

The role of extractive removal was further illustrated by measuring the kit rating as a function of newsprint soaking time in dichloromethane. The results, summarized in **Fig. 8**, show that the kit rating increased with soaking up to 48 hours, the longest time studied.

To illustrate the influence of extractives on fluorochemical efficiency, filter paper samples were pretreated with fatty acid–rich distilled tall oil or abietic acid. The kit ratings are shown as a function of tall oil concentration in **Fig. 9**. Both tall oil and abietic acid lowered the kit ratings to values comparable with those observed with newsprint. The abietic acid had a larger effect on the kit rating, although both tall oil fractions were detrimental.

The pitch content of newsprint is a function of the wood species, pulping, wet-end chemistry, and mill closure. **Figure 10** compares kit ratings for different newsprint samples (see Table I for details). Although the pitch contents of the four newsprint samples varied by more than an order of magnitude, all required about 10

Coating	Kit rating (filter paper)	Kit rating (NP4)
FCC	6	4–5
Soluble starch + FCC	12	7
Hydrophobic starch + FCC	12	12

IV. Kit rating of newsprint and filter paper treated by Method 1. The fluorochemical concentration in the paper was about 9 mg/g.

mg/g fluorochemical for intermediate kit values. In addition, the curves were steep and the data noisy in this critical region of kit ratings. NP1 and its calendered counterpart, NP2, showed the best kit ratings at high fluorochemical loadings, although this sample did not have the lowest extractable pitch. Presumably the material interfering with the fluorochemical treatments is only a part of the extractable components. A comparison of NP1 with NP2 indicates that calendering had no effect on fluorochemical performance. It might be expected that this treatment should lower the surface area and thus increase fluorochemical efficiency. However, calendering could also distribute the extractives over the surface, making fluorochemical treatment more problematic.

The mass concentration of extractives in newsprint is typically less than 1%, so it seems reasonable to presume that the role of extractives is related to surface chemistry. Furthermore, it seems reasonable to expect that treating the paper with something before or during fluorochemical treatment might overcome the negative effects. A number of pretreatments were evaluated, and the results are summarized in **Tables IV and V.** In this work, the fluorochemical treatment concentrations were high, and hence very high kit values should be attained. Only hydrophobic starch and carboxymethyl cellulose pretreatments were able to generate very high kit values.

DISCUSSION

Fluorochemical treatment gives solvent resistance by rendering paper surfaces, both internal and external, nonwetting to solvent. For this, the fluorochemical must cover all the surfaces, and the fluorochemical chains on the fluorochemical molecules (see Fig. 1) should be preferentially oriented outward to give a fluorochemical surface. Fluorochemical surfactants and polymers are expensive; therefore, a key issue in technological applications is to achieve the desired effects using a minimum amount of fluorochemical.

Based on the cellulose film results, it is possible to estimate the minimum fluorochemical coverage required for solvent repellency. The XPS (Fig. 4) and contact angle (Fig. 5) results suggest that fluorochemical coverage of about 10 mg/m^2 gives a fluorochemical surface that is not wetted by hexadecane. Thus, in the ideal case, solvent resistance should be attained in paper with fluorochemical loadings of $C = \sigma\ 10\ mg/m^2$, where σ is the specific surface area of the paper. For example, if a paper has a specific surface area of 2 m^2/g, the predicted minimum fluorochemical loading for complete coverage is 20 mg/g (equivalent of kg/metric ton). The results in Fig. 7 shows that a kit rating of 6 requires fluorochemical loadings of 0.97 mg/g for filter paper. If this loading corresponds to 100% fluorochemical coverage, then the specific surface area of the filter paper was about 0.097 m^2/g. Similarly, the extracted newsprint gave a kit value of 7 when treated with $C = 4.5$ mg/g FCM. Based on this analysis, the specific surface area of the newsprint was approximately 0.46 m^2/g. By comparison, the nitrogen BET surface area was 0.9 m^2/g (single-point BET).

This work has confirmed previous claims that newsprint based on mechanical pulp requires much more fluorochemical for solvent resistance than that from bleached chemical pulp. This is in part due to the higher specific surface area of mechanical pulp. However, a key finding in this work, illustrated in Figs. 7–9, is that a dichloromethane-extractable component interferes with fluorochemical treatment. Since the extractives are hydrophobic, these results are similar to the known interference of sizing on fluorochemical treatments of chemical pulps *(1)*.

The detailed mechanism of the interference is not known. One possibility is that hydrophobic regions on the paper are not wetted by the fluorochemical treatment solution. However, since the paper was sub-

Pretreatment chemical	Kit
None	4
1% poly(diallyldimethyl ammonium chloride), Percol 1697, Allied Colloids	9
1% poly(N-isopropylacrylamide), McMaster University	9
1% methoxy-polyethylene glycol 2000, Union Carbide	8
1% Dextran, MW 77,000, Sigma D1390	8
1% ethylene glycol, BDH B10118	9
1%, poly(vinyl alcohol), MW 15,000, Fluka 8138	8
0.5% sodium carboxymethyl cellulose, Aldrich 32,306-2	10
1% sodium carboxymethyl cellulose, Aldrich 32,306-2	12
1% hydroxypropyl cellulose MW 1,000,000 Aldrich 19, 190-6	8

V. Influence of pretreatment chemicals on the kit rating of newsprint NP4 treated by Method 2 with 1.2% FCM to give a coating of about 15 mg/g

merged in the treatment solution and since we used both water and methanol as treatment solutions, all surfaces should have been exposed to fluorochemicals. Therefore, we do not believe that the interference was a wetting problem.

Another possible explanation for interference by the extractives is that the adsorbed fluorochemical does not adopt a good conformation when adsorbed on hydrophobic materials. For example, if the fluorochemical chains were lying on the hydrophobic regions, leaving the more polar part of the molecule facing up, the surface may be wetted by low-energy solvent.

Starch pretreatment or starch addition to the fluorochemical solution gave improved solvent resistance. The starch treatment will fill pores, lowering the specific surface area. Starch may also adsorb onto the more hydrophobic extractives-coated areas to render the surface more hydrophilic and suitable for fluorochemical treatment.

CONCLUSIONS

We reached the following conclusions based on our experiments:

- Based on XPS measurements, a fluorochemical treatment of about 10 mg/m^2 is the minimum required, giving a maximum concentration of fluorine at the air/cellulose interface. Fluorochemical concentrations above 10 mg/m^2 on the regenerated cellulose surfaces give high hexadecane contact angles.
- Pretreatment of the cellulose film with lignin did not influence hexadecane contact angles, whereas tall oil and abietic acid gave lower contact angles.
- Dichloromethane-extractable material renders fluorochemical treatment less effective in papers based on mechanical pulps. We speculate that the hydrophobic extractives induce a less optimal configuration of the fluorochemical at the paper/air interface.
- The cost effectiveness of fluorochemical treatment of newsprint can be improved by using newsprint characterized by low pitch contents and by using hydrophobically modified starch with the fluorochemical.

TJ

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This work was supported by Abitibi-Consolidated. The authors acknowledge Rana Sodhi at the University of Toronto for obtaining the XPS data and Karen Lindstol at Abitibi-Consolidated for help with handsheet preparation and characterization.

Received for review April 3, 1998.

Accepted June 3, 1998.

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