Radiochemical study of *z*-directional mobility of varnish in paper

Sujit Banerjee, Kyle R. Reed, Ronald C. Hooper, Roger H. Van Eperen, Barry Crouse, and John T. Moynihan

ABSTRACT: The penetration of ink components into paper was studied by applying three ink formulations containing ^{14}C-tagged varnish to paper. Surfaces of the treated papers were ground to provide a uniform gradient in thickness from one side of the sheet to the other. The relative mobility of pigment and varnish were measured on the ground sheets. Varnish penetrated to a greater depth than the pigment for the three inks studied. The pigment content of the ink was an important factor in dictating varnish ingress.

KEYWORDS: Bond papers, ink absorption, penetration, radiochemistry, varnish, Z direction.

The degree of penetration of ink components into paper is an important factor in ink adhesion and wear, especially in situations where the surface of the ink film is exposed to physical abrasion. Penetration is governed by properties such as paper porosity, ink viscosity, and the strength of the ink–paper interaction.[1] It is likely that separation of ink components occurs as ink penetrates into paper, since the mobility of the various components on cellulose must differ considerably. Our interest in print permanence led us to examine the relative penetration of pigment and varnish into bond paper.

Experimental technique

The varnish in the ink cannot be detected in the presence of the pigment by conventional spectroscopic techniques such as Fourier transform infrared spectroscopy (FTIR). Accordingly, we investigated the feasibility of using radioactively tagged varnish, which would considerably improve detectability. Three varnishes (Varnishes A, B, and C) currently in industrial use were tagged with ^{14}C as follows.

Approximately 250 g of each varnish was heated to 150°C, 0.5–1 mCi of 1,4-[^{14}C] succinic anhydride (8 mCi/mmole) was added, and the mixture was stirred for 0.5 h under a nitrogen blanket. The varnish contains free hydroxyl groups, some of which are esterified by the anhydride.[2] Since the molecular weight of the varnish is about 3000 amu, the addition of a small amount of the tagged ester group should make no material difference to the properties of the varnish. This is particularly true for Varnish C, since succinic anhydride is used in its preparation.

Drawdowns of the three formulations were prepared and air-dried for seven days. In order to determine their *z*-directional penetration into paper, we ground the surface of the paper at an angle, so that the thickness of the sheet uniformly decreased from one end to the other. This was done by positioning the treated papers on a sheet grinder with the mounting block angled at a horizontal gradient of 0.353 mils/in. The sheet was held to the block with a slight vacuum and was ground by rapidly drawing a grinding wheel rotating at 7200 rpm across its surface. The sheets were then exposed to X-ray film (X-OMAT) for two weeks.

Results

Photographs of the ground papers are presented in the upper panel of **Fig. 1.** The dark areas in these photos are caused by the pigment. The top edge

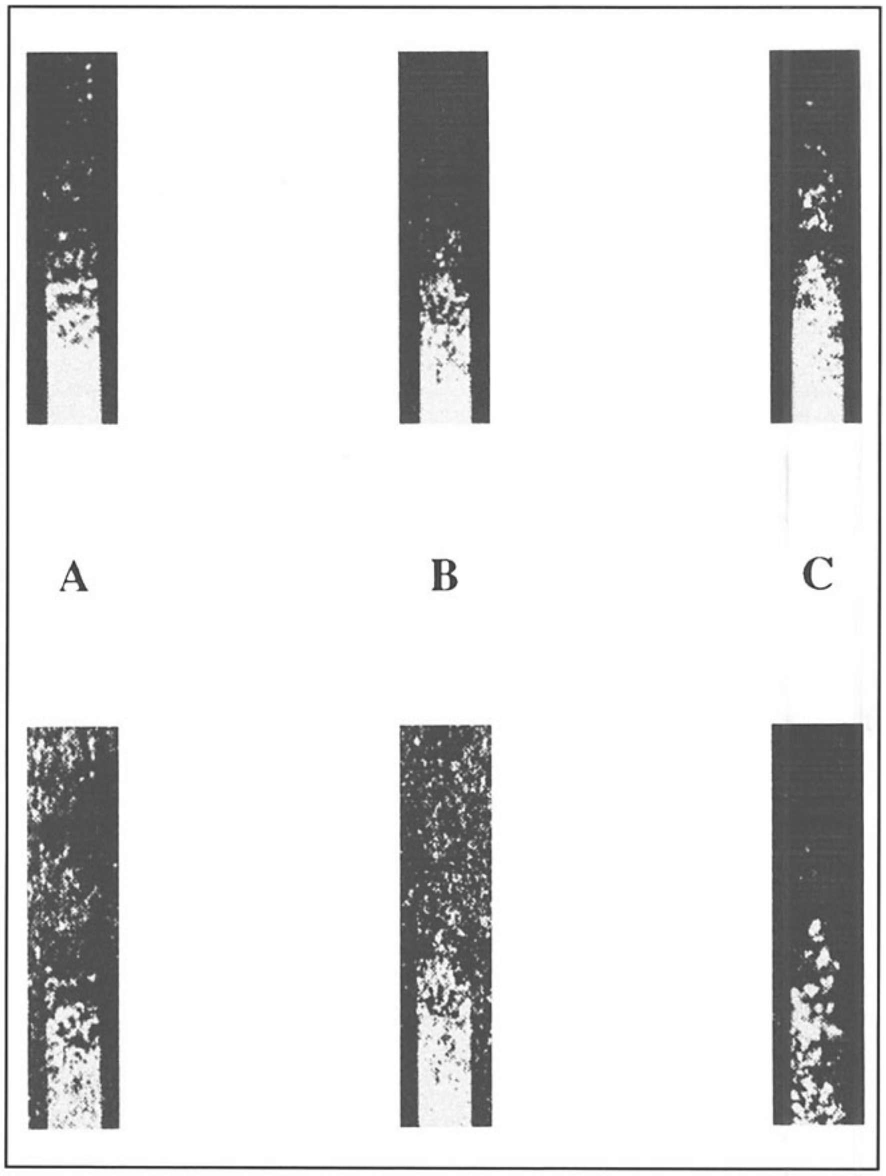
Banerjee, Reed, Hooper, Van Eperen, and Crouse are affiliated with the Institute of Paper Science and Technology, 500 10th St. NW, Atlanta, GA 30318. Moynihan works as a consultant, 12473 Marstan Moor, Herndon, VA 22071.

[1]Levlin, J. E. and Nordman, L., "Advances in Printing Science and Technology," Vol. 4, Paper in the Printing Processes, Pergamon, New York, 1967, pp. 33–55.

[2]Lambourne, R., "Paint and Surface Coatings," Wiley, New York, 1987.

of the sample is its thickest point, with the grinding track becoming progressively more visible as the surface is removed. The lower panel of Fig. 1 shows the corresponding developed X-ray prints. The dark areas reflect the presence of radioactive varnish, and it is clear that the degree of penetration is Varnish C > Varnish B ≈ Varnish A. Clearly, the varnish penetrates substantially deeper than does the pigment.

1. Photographs (upper panel) and radiographs (lower panel) of paper surfaces after application of ^{14}C-labeled ink. The inked surfaces have been ground to reduce sheet thickness uniformly from the top edge (thickest point) to the bottom edge (thinnest point).



Varnish penetration

In order to quantify the radioactivity on the ground paper, discs were punched from the samples at 1-in. intervals using a standard office punch. The discs were suspended in a scintillation cocktail and counted in duplicate for ^{14}C in a Beckman liquid scintillation counter. The results are provided in **Table I.** Although the count rate was not quench-corrected, the results can be interpreted on a relative basis, since the degree of quenching was very similar for all the samples. The counts are relatively unchanged up to a depth of about 2 mils, after which they decrease sharply. This was surprising, since we had expected a progressive decrease in the number of counts as the radioactive varnish was ground off.

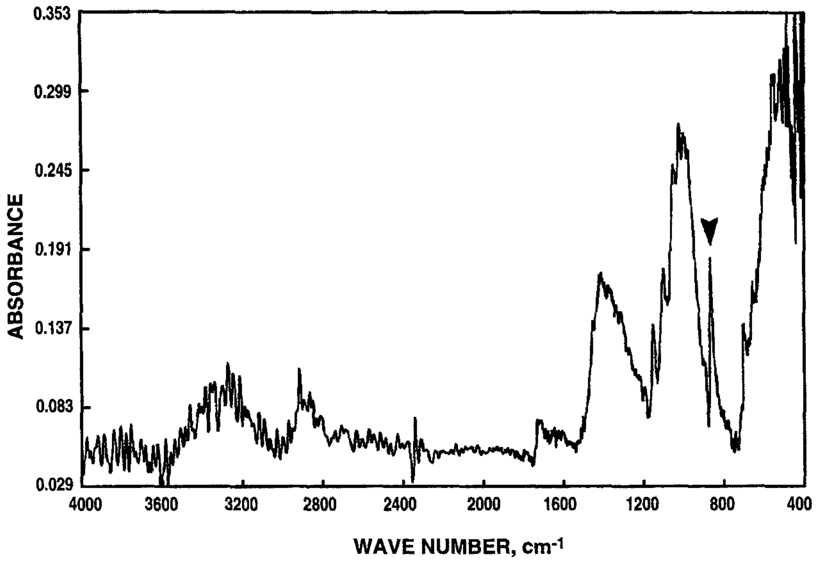
It seems that the activity in the body of the paper is quenched, while activity on the surface is not. In other words, only the surface counts are registered. This is reasonable, since the discs were dropped into the scintillation vial as is, i.e., without maceration. It appears that varnish A penetrates evenly to 1.4 mils, Varnish B to 1.8 mils, and Varnish C to at least 1.7 mils. Furthermore, a substantial fraction of the varnish penetrates to 2.1 mils and presumably beyond in at least two, and very probably in all three, drawdowns. In contrast, the penetration of pigment is about 1.3 mils in sample A, 1.1 mils in sample B, and only 0.8 mil in Sample C. These results are fully consistent with the X-ray film data and confirm the deeper penetration of the varnish. The liquid scintillation data are more precise than the radiographs and reveal the slightly greater penetration of Varnish B over Varnish A.

A potential concern with the grinding process is that the pressure of the grinding wheel might force the varnish and pigment applied into the body of the paper, thereby leading to an artificially high penetration. The high speed of the grinding wheel makes this scenario unlikely. Nevertheless, in order to verify the integrity of the grinding process, a sample was positioned at a gradient of 0.59 mil/in. to the hori-

I. Penetration of radioactive varnish into paper as measured by scintillation counts

Penetration, mils	Counts/min Varnish A	Counts/min Varnish B	Counts/min Varnish C
0	207	304	...
0.35	206	307	2180
0.70	212	264	1914
1.05	208	278	2009
1.40	199	277	1735
1.75	134	294	1949
2.10	107	217	...

2. Infrared spectra of ink on paper. The marked signal at 872 cm^{-1} is characteristic of the pigment used.



II. Penetration of pigment into paper as measured by the ratio of pigment signal intensity (872 cm^{-1}) to paper signal intensity (1000 cm^{-1}) at six levels of penetration*

	Penetration, mils					
	0.35	*0.70*	*1.05*	*1.40*	*1.75*	*2.10*
Regular paper						
Standard ink	0.79	0.71	0.66	0.53	0.09	0
	1.0	0.92	0.68	0.43	0.17	0
Modified ink	0.66	0.78	0.54	0.35	0.07	0
	0.56	0.55	0.37	0.24	0	0
Embossed paper						
Standard ink	0.73	0.52	0.43	0.46	0.32	0.05
	0.66	0.75	0.53	0.29	0.32	0.09
Modified ink	0.67	0.78	0.78	0.67	0.13	0
	0.75	0.68	0.52	0.53	0.09	0

*The two sets of values for each ink–paper combination are replicates.

zontal and ground in both uphill and downhill directions in parallel channels. Both grindings gave the same value for the depth of penetration of the pigment, thereby confirming the integrity of the technique.

Pigment penetration

While the penetration of radioactive varnish was easily quantifiable, a method for measuring the degree of pigment ingress was not available. We felt that reflectance infrared spectroscopy might provide a basis for such a measurement, and we conducted a feasibility study using two types of paper (regular and embossed) and two types of ink (standard and modified).

Drawdowns were prepared and surface-ground as previously described. ATR (attenuated total reflectance) spectra were taken of spots at 0.35-mil-depth intervals. Results are illustrated in **Fig. 2.** Comparison of pigmented and unpigmented areas showed that a signal at 872 cm^{-1} was characteristic of the pigment, whereas the broad envelope at about 1000 cm^{-1} was associated only with the paper. Thus, the ratio of the heights of the two signals provides a measure of the amount of pigment on the paper. These ratios are provided in **Table II** for the two papers considered.

Penetration of both inks was similar for the regular paper. Penetration was even to about 0.7–1 mil, after which it decreased sharply. Embossed paper was obtained by running the paper through the relief plates but without ink, so that the reverse side, when printed, was contoured to reflect the image of the printing plates. Surprisingly, ingress into the embossed paper appeared to be greater than that in the regular sample, especially for the standard ink. We believe the phenomenon to be real, since it replicates well. Possibly, the unevenness of the embossed surface causes channeling, which gives rise to the higher value.

Application of the varnish in the absence of pigment led to substantially greater penetration in both regular and embossed papers. Evidently, the pigment retards the mobility of the varnish by associating with it.

Summary

We have shown from both the X-ray and the liquid scintillation data that varnish penetrates paper to a greater degree than does the pigment. The relative difference depends, in part, on the pigment loading in the varnish. Using a simple spectroscopic technique to measure pigment coverage on paper, we have found that the embossing process seems to augment pigment penetration, possibly due to channeling. These results should be interpreted on a relative rather than on an absolute basis. Actual penetration during a press run is less, since the contact time between the ink formulation and paper is much lower. For example, surface-grinding of conventionally printed matter showed that pigment ingress was less than 0.5 mil.

Received for review Feb. 5, 1993.

Accepted March 20, 1993.