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A RADIOCHEMICAL STUDY OF THE Z-DIRECTIONAL MOBILITY OF VARNISH IN PAPER

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A Radiochemical Study of the Z-Directional Mobility of Varnish in Paper

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Tappi J.

Abstract

The penetration of ink components into paper was studied by applying ink containing ^{14}C labeled varnish to paper, surface grinding the treated paper and measuring the relative mobility of pigment and varnish. The varnish was found to penetrate more than the pigment for the three inks studied, with the pigment content of the ink being an important factor in dictating overall varnish ingress.

The degree of penetration of ink components into paper is an important factor in ink failure. 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.

The varnish cannot be detected in the presence of the pigment by conventional spectroscopic techniques such as Fourier transform infrared spectroscopy (FT-IR). Accordingly, we investigated the feasibility of using radioactively tagged varnish, which would considerably improve detectability. Three varnishes (designated as Varnish A,B,C in this study) currently in industrial use were tagged with ^{14}C as follows. Approximately 250 g. of each varnish was heated to 150^{o}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 hours 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 were 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/inch. 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, and the developed print is illustrated in Fig. 1 (lower panel). The top edge of the sample is its thickest point; the grinding track becomes progressively more visible as the surface is removed. 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. A photograph of the ground paper is included in Fig. 1 (upper panel); here, the dark areas are caused by the pigment. Clearly, the varnish penetrates substantially deeper than does the pigment.

In order to quantify the radioactivity on the ground paper, disks were punched from the samples at 1" intervals using a standard office punch. The disks 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 1. 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 about two 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, but that on the surface is not. In other words, only the surface counts are registered. This is reasonable since the disks were dropped into the scintillation vial as is, ie., 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 mil in sample A, 1.1 mil in sample B, and only 0.8 mils 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 better 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 mils/inch to the horizontal, 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.

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 above, and spectra were taken in the attenuated total reflectance (ATR) mode of spots at 0.35 mil depth intervals. Comparison of pigmented and unpigmented areas showed that a signal at 872 cm^{-1} (Fig. 2) 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 2 for the two papers considered.

Penetration of both inks were similar to that of the standard ink 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.

In 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. We have devised a simple spectroscopic means to measure pigment coverage on paper, and 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 printed matter showed that pigment ingress was less than 0.5 mils.

References

1. Levlin, J.E., 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.

Captions to Figures

Figure 1: Photographs (upper panel) and radiographs (lower panel) of paper surface ground after the application of labeled ink.

Figure 2: Infra red spectra of ink on paper. The marked signal is characteristic of the pigment used.

TABLE 1: Penetration of Radioactive Varnish into Paper

Penetration (mils)	counts/min Varnish A	Varnish B	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	-

TABLE 2: Variation of the 872 cm^{-1} and 1000 cm^{-1} intensity ratio with pigment penetration[a]

Penetration: (mils)	0.35	0.70	1.05	1.40	1.75	2.10
<u>regular paper</u>						
std. 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
<u>embossed paper</u>						
std. 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

[a]the two sets of values for each ink-paper combination are replicates

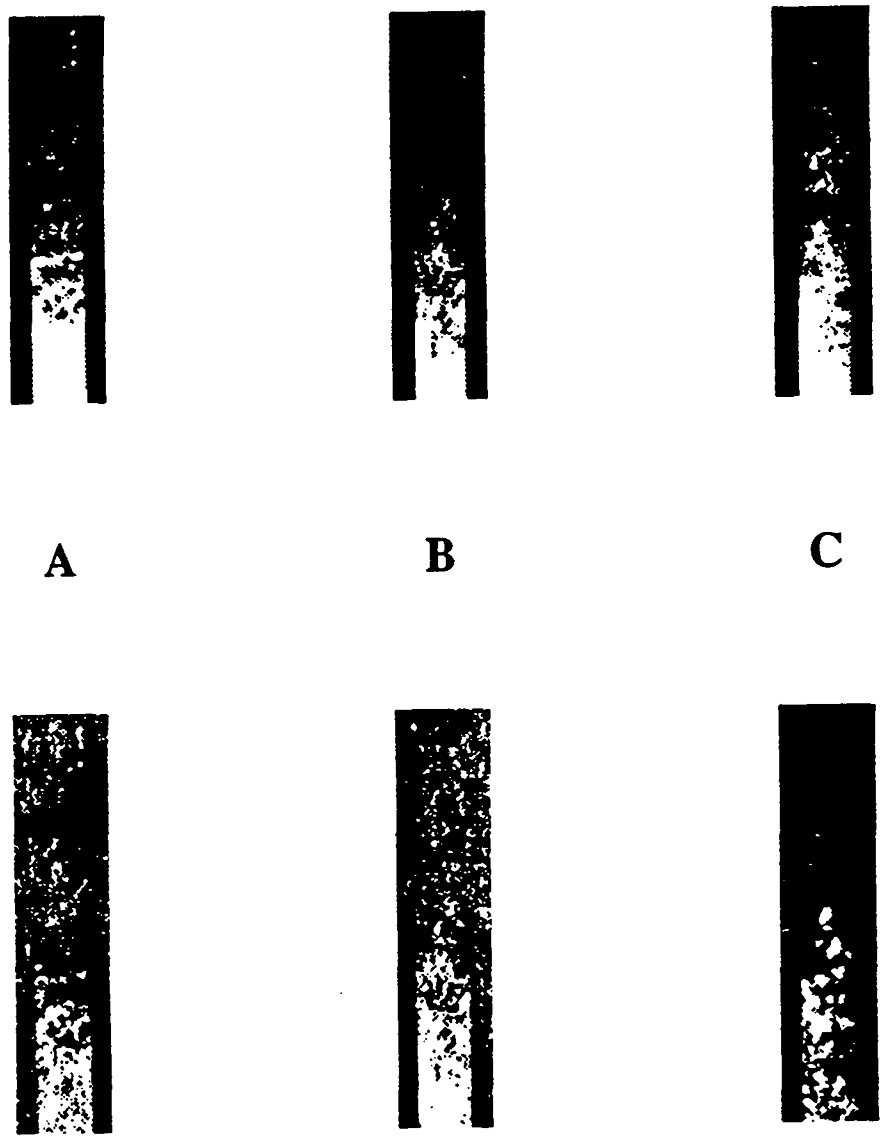
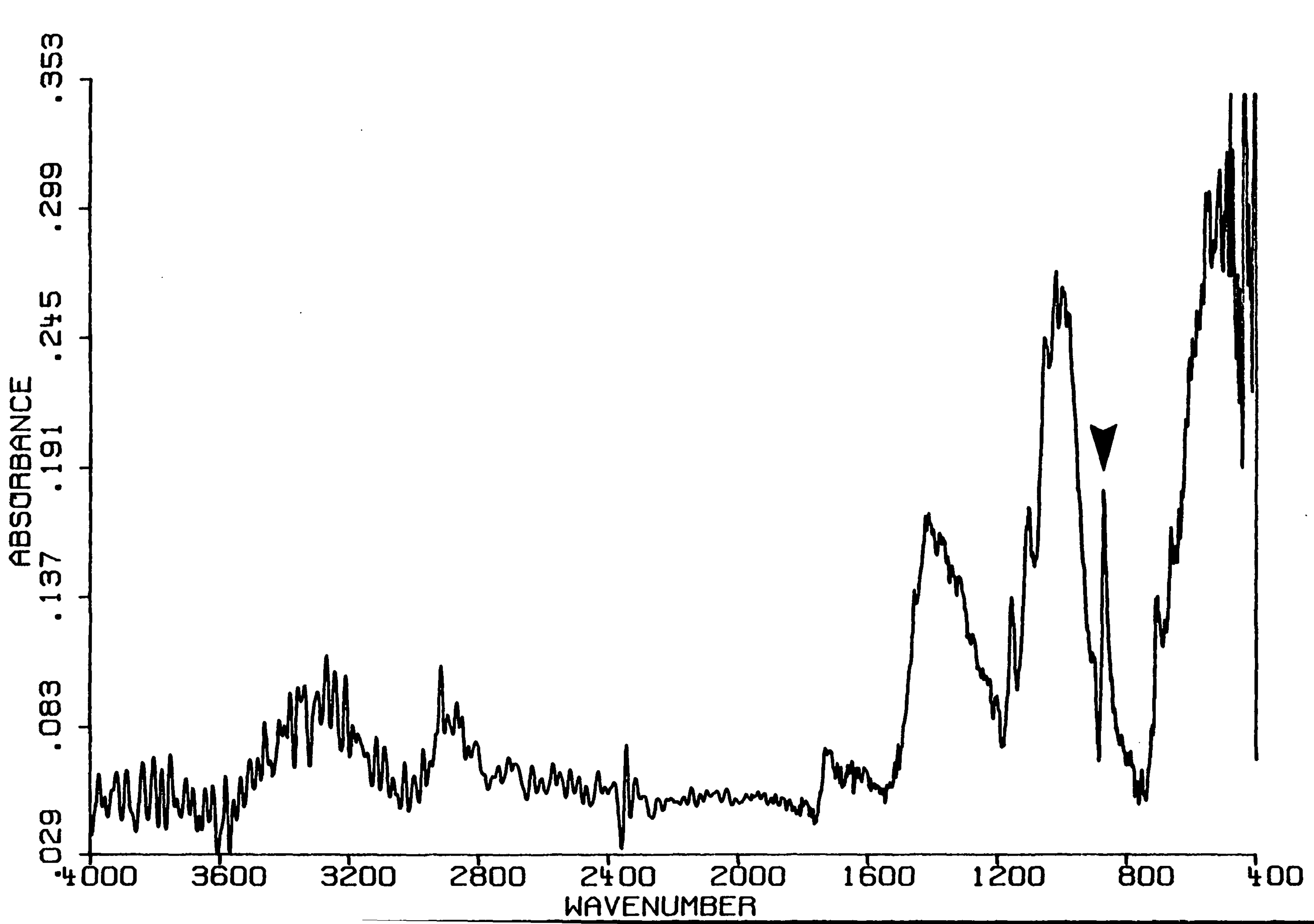


Figure 1.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ABSORBANCE
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WAVENUMBER