# COMPARISON OF LABORATORY WATER PICKUP TESTS WITH ACTUAL PRESS PERFORMANCE

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Abstract: Water pickup results from the mixmaster and the litho break are compared to results obtained from a production press. The difficulties encountered in sampling and a GC method for water, IPA, and EGBE are described.

The goal of this work was to learn which of two commonly used laboratory water pickup tests, the mixmaster or the litho break, correlated best with results from an actual press run. We were aware of three studies, cited by Fetsko in her excellent review of ink/water interactions (Fetsko, 1986), which measured the water content of inks taken from a lithographic press. A study of metal deco inks by Cartwright and Harden (1965), found 3-5% water in inks from the form roller. A study by Lindquist of news inks in 1976 found 12-15% water in inks from the form roller most distant from the water fountain and 24-34% water in inks from the form roller closest to the water fountain. Cunningham and Moore (1984) studied sheetfed offset inks and found a 4 to 22% water content in inks from the fourth form roller (presumably the most distant from the Dahlgren form).

In the first study, we did not know from which form roller the ink sample was taken, or the sampling technique used. In the second study, the roller locations were known but we still did not know how the samples were obtained. In the third study, the authors stated the samples were taken while the press was running. We have sampled inks from running presses and from running litho breaks and these samples contained more water than the same ink sample taken after the press or litho break had been stopped and the roller patted dry. Also, the variation in water content from the moving system was greater than that obtained from the stopped system. We believe that the process of sampling ink from a running roller train is an emulsification process itself and will lead to high and erratic water values.

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The sample size quoted in the third study was only 50-70 mg so even small droplets of water incorporated during the sampling process will have a large effect on water content.

Since laboratory tests measure contained water, we wanted to analyze only for contained water and not surface water. We are convinced that the rollers must be stopped and patted dry to avoid high readings caused by inadvertent emulsification and surface water inclusion.

A great deal of the cited work was done with conventional dampeners or continuous dampeners using isopropanol. Also, these works were concerned only with water pickup. We wanted to measure the alcohol pickup of the ink and now that alcohol substitutes are being used on an ever increasing basis, we wanted to measure the butyl cellosolve content also.

The question: "What is the water pickup of ink on a lithographic press?", raises several other questions:

1. What press?
2. What location on the press - form rollers, plate, ink fountain?
3. What fountain solution?
4. What rollers?
5. What plates?
6. What blankets?
7. What inks?

To answer these questions, we enlisted the aid of the Fort Dearborn Lithograph Company, a quality label printer who has pioneered the use of alcohol-free fountain solutions. One of their former employees, Bernie Kelly, now retired, had researched fountain solutions, inks, rollers, plates, and blankets and had already determined the most suitable combination that would allow the use of an alcohol substitute. Fort Dearborn runs alcohol-free three shifts a day, 5 days a week and has done so for over 10 years.

The first press test was run on a 64 inch Royal Zenith Planeta - complete details are in appendix 1. Samples were taken from the Dahlgren form roller - called DF - and the form roller furthest from the Dahlgren form roller - called OF. We really wanted to obtain samples from the plate but the quantity of ink on the plate was

too small for the analyses we were capable of doing. It seemed that an average of the values found on samples from the OF and DF would approximate the values on the plate.

The most commonly used laboratory test in the US ink industry is the mixmaster test. The most widely used mixmaster is known as the Duke and the test is commonly called the Duke test. There are two usual methods of running the Duke. One is to add 50 g of ink and 50 ml of FS to the bowl and then mix the slurry for 5 minutes at 90 RPM. The second, described by Surland (Surland, 1980), consists of adding 15 ml of FS to 50 g of ink and mixing this for 1 minute at 90 RPM. This process is repeated for 10 minutes and water pickup versus time is obtained. The second test method is the litho break test (Tasker et al, 1983). In this method 2.94 ml of ink are distributed on the rolls of the litho break, fountain solution is placed in contact with the ink, and samples are analyzed periodically for water. This method also gives water pickup versus time. In both of these methods, a number can be assigned to the rate of water pickup (k) and a second number (a) can be assigned to the ultimate water pickup. The Duke test involves measurement of water pickup by weight while the procedure cited called for the use of the Karl Fischer method because the sample size was small (about 300 mg).

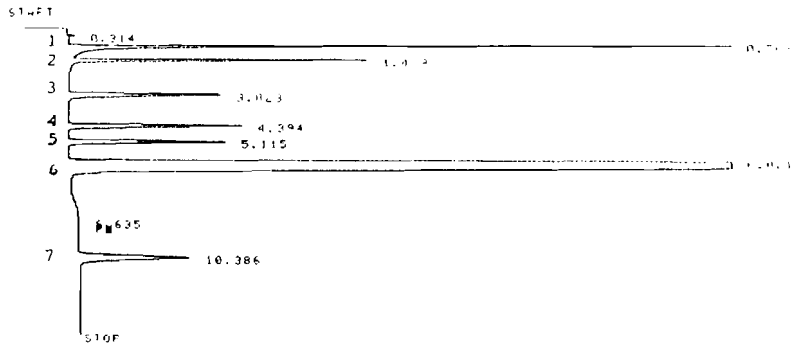


**Figure 1.** Gas chromatogram of water (1), methanol (2), ethanol (3), isopropanol (4), n-propanol (5), tetrahydrofuran (6), and EGBE (7).

Neither of the methods as described can measure the level of other fountain solution components such as isopropanol or butyl cellosolve. Since we were interested in the pickup of these two components also, we developed a GC method to measure water, isopropanol, and butyl cellosolve contents in an ink. The method resolves water, methanol, ethanol, isopropanol, n-propanol, tetrahydrofuran, and ethylene glycol mono n-butyl ether (EGBE) well - see figure 1.

Quantitation of water, methanol, isopropanol, and EGBE in standard solutions was performed by measuring the signal response of a thermal conductivity detector for 1 to 20 microgram injections of these hydroxyl compounds.

Plotting amount of substance on the x axis versus ln (signal) on the y axis revealed a parabolic curve of the type:

$$H_2O = \ln \text{signal}^2 \qquad (1)$$

Taking logs of both sides, we get:

$$\ln (H_2O) = 2 \ln\ln \text{signal} \qquad (2)$$

Using linear regression for six data pairs we find:

$$\ln\ln \text{signal} = .122 \ln(H_2O) + 1.99 \qquad (3)$$

with a correlation coefficient of r = 0.99996.

Similar equations were found for methanol, isopropanol, and EGBE - see data in Table 1.

$$\ln\ln \text{signal} = b \ln x + a$$

| x | b | a | r |
|---|---|---|---|
| $H_2O$ | 0.122 | 1.99 | .99996 |
| MeOH | 0.166 | 2.03 | .9959 |
| IPA | 0.104 | 2.01 | .9945 |
| EGBE | 0.081 | 2.06 | .9959 |

**Table 1.** Constants for equations relating signal response to quantity using a packed column and TCD.

Our procedure consists of adding the sample to a tared vial, reweighing, adding 2 ml of tetrahydrofuran (THF) which contains 0.160 to 0.240 g methanol (known to three decimal places) per gram THF. The sample is dissolved by shaking on a paint shaker, and then transferred to an autosampler vial. Five microliter volumes are then injected onto the column with the conditions maintained as described in appendix 2.

The water found in the 5 µl sample is found from:

$$H_2O=\exp((\ln\ln \text{signal}-1.99)/.122) \qquad (4)$$

The MeOH, IPA, and EGBE are found similarly; the limit of detection of these substances is about 250 nanograms using a TCD.

We used this analytical method on samples taken from the 64 inch Planeta. After a job had been running for about 6 hours, the fountain inks were removed and the retained lots of ink were put on the press. The press was then restarted and the job was run for 30 minutes. At this point the press was stopped and samples were taken from the OF and DF rollers as described-see figure 2.

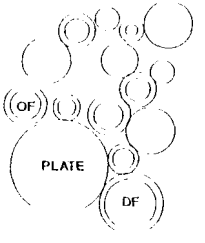


**Figure 2.** Roller train sample points.

The results are listed in Table 3.

| | Y | | R | | B | | K | |
|---|---|---|---|---|---|---|---|---|
| | OF | DF | OF | DF | OF | DF | OF | DF |
| 7 MIN | 0.00 | 0.54 | 0.88 | 0.98 | - | - | - | - |
| 25 MIN | 0.39 | 0.65 | 1.35 | 0.78 | 0.55 | 1.08 | 0.53 | 0.94 |
| 60 MIN | 0.86 | 3.50 | 1.01 | 1.28 | 0.43 | 1.02 | 0.48 | 0.70 |
| 120 MIN | 1.42 | 2.34 | 0.94 | 1.16 | 0.64 | 1.16 | 0.51 | 0.76 |

**Table 3.** Water analysis of press samples.

These results, 0.4 to 3.5% water, <0.3% IPA, and <0.3% EGBE are surprisingly low - considerably lower than the

values obtained from the studies on news inks and sheet-fed offset inks reported previously - and lower than expected based on our mixmaster and litho break testing. Several reasons for the low readings were considered.

1. Volatiles might have evaporated from the emulsion in the sealed vial prior to dissolving the sample in THF for analysis. Water is a very small molecule and can escape even from apparently tightly sealed containers. A sample of emulsion prepared on the litho break was transferred to two vials. One vial was analyzed immediately. The second was aged 24 hours prior to analysis.

| | $H_2O$ | EGBE |
|---|---|---|
| Immediate | 4.8 | 0.31 |
| 24 Hours | 5.0 | 0.34 |

These results indicate that water was not lost through volatilization after the vial was sealed.

2. Volatiles might have evaporated from the THF - dissolved sample while waiting on the autosampler. The yellow sample, which had the highest water content, 3.5%, was reanalyzed in triplicate 48 hours after preparation.

| Sample Age | | $H_2O$ |
|---|---|---|
| 2 hours | | 3.5 |
| 48 hours | Run 1. | 3.5 |
| | Run 2. | 3.6 |
| | Run 3. | 3.4 |

Apparently dissolved samples do not gain or lose water from sealed vials while standing on the autosampler.

3. Volatiles might have evaporated from the form rollers prior to sampling. While we were careful to sample the yellow ink as soon as possible after stopping the press, the inks were always sampled in the order: yellow, red, blue, and then black. Since the yellow ink had the highest water content and the black ink the lowest and since the time between sampling the first color, yellow, and the last color, black, ranged from 10-15 minutes, it seems that evaporation is a likely explanation for the low water values - especially for the blue and

black inks.

| Time-Min. | 120 |
|---|---|
| Yellow | 1.88 |
| Red | 1.05 |
| Blue | 0.90 |
| Black | 0.64 |

**Table 4.** Average water content of ink samples from press - (OF + DF)/2.

To see how quickly water evaporated from a roller train, the black ink was emulsified on the litho break using water + KSP-500. A portion of the ink was removed from the roller immediately (30-40 seconds) and the remainder was allowed to stand on the rollers for an additional fifteen minutes.

| | |
|---|---|
| Immediate | 7.9% |
| 15 Minutes Old | 0.5% |

Clearly the time elapsed between stopping the rollers and sealing the sample into the vial is critical. Another series of tests was run to learn the rate of water loss from the rollers. The red ink was run on the litho break for five minutes using G7AV/25% IPA and patted dry. Elapsed time between stopping the litho break and sampling was about 30 seconds. This is as fast as we were able to get a sample and drying the rollers took almost all of this time. The samples were then analyzed by GC.

| Elapsed Time | $H_2O$ | IPA |
|---|---|---|
| 30 | 5.4 | 1.1 |
| 180 | 2.5 | ND |
| 330 | 1.3 | ND |
| 600 | 0.1 | ND |

From this test, we estimate we have about 20 seconds after drying the rollers to get a sample containing at least 90% of the original water, but the data does not allow us any estimates on time for IPA content.

We then reran the press test on the red ink and sampled the ink as soon as possible after stopping the press. This time ranged from 20 to 40 seconds which is less than or equal to the elapsed time on the litho break. The results are listed in table 5.

| Red Ink/KSP 500 | | |
|---|---|---|
| Time-Min. | OF | DF |
| 30 | 6.2 | 5.1 |
| 60 | 6.9 | 2.7 |
| 90 | 4.9 | 2.8 |
| 120 | 5.2 | 4.7 |
| 150 | 5.8 | 6.4 |
| Mean | 5.8 | 4.3 |

**Table 5.** Water pickup from second press run.

After the 150 minute sample was taken the press was allowed to stand for one and three minutes and samples were taken.

| 150 Minute Red/KSP 500 Sample | | |
|---|---|---|
| Time Lapse After First Sample | OF | DF |
| 0 Min | 5.8 | 6.4 |
| 1 Min | 1.2 | 1.2 |
| 3 Min | 1.1 | 1.2 |

**Table 6.** Effect of delayed sampling on water content.

Roughly 80% of the emulsified water is lost from the rollers in the first minute after stopping. The ink film thickness on the press rollers was estimated to be about 6 microns and about 33 microns on the litho break. The thinner ink film may explain why water evaporates faster from the press rollers than the litho break roller.

The etch was found to contain 8.7% EGBE which would amount to 0.27% of the fountain solution in the first press test and 0.13% in the second test. None was detected in the samples listed in Tables 5 and 6. One sample was taken through the roller guard while the press was running to see if samples taken this way do contain high values for water. In fact, numerous free droplets of water were clearly visible in this sample which confirms our contention that this method is not reliable for measuring contained water. An analysis of this sample gave 10.6% water and 0.07% EGBE-subtantially higher than the values listed in table 5.

| Time-Min. | KSP 500 | Tap Water |
|---|---|---|
| 1 | 18.3 | 18.3 |
| 2 | 30.4 | 32.0 |
| 3 | 37.1 | 39.9 |
| 4 | 41.5 | 45.2 |
| 5 | 43.7 | 47.7 |
| 6 | 46.5 | 50.2 |
| 7 | 47.7 | 51.0 |
| 8 | 48.9 | 52.0 |
| 9 | 49.9 | 52.8 |
| 10 | 50.7 | 53.6 |

**Table 7.** Fountain solution content versus time from the mixmaster.

The same lot of red ink was tested on the Duke and the litho break with 8 oz KSP 500 etch/gallon water. These tests were also run using plain tap water. See tables 7 and 8.

| Time-Sec. | KSP 500 | Tap Water |
|---|---|---|
| 5 | 3.3 | 6.7 |
| 15 | 4.3 | 9.5 |
| 40 | 3.1 | 15.0 |
| 60 | 5.4 | 16.5 |
| 80 | 5.6 | 17.1 |
| 180 | 6.0 | 18.7 |
| 300 | 6.2 | |
| 600 | 6.6 | |

**Table 8.** Water content versus time from the litho break (by GC).

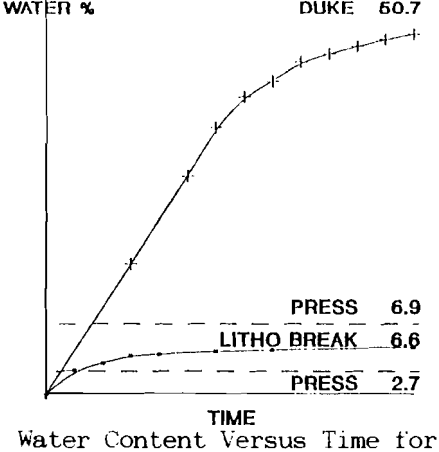


**Figure 3.** Water Content Versus Time for Duke and Litho Break Compared to Press Results.

In this study, the water content, 6.0-6.6% of the red ink sampled from the litho break at 3-10 MIN, agreed reasonably well with the water content of 5.8-6.4% found in the 150 min press samples. While the mixmaster test is useful in diagnosing a number of press problems (Surland, 1980), it gives unrealistically high values of water content compared to the values obtained from press samples in this and other studies (Cunningham & Moore, 1984).

**Summary:**

1. To avoid trapping various quantities of surface water in small ink samples, the press should be stopped and patted dry before sampling.

2. Sampling must be performed very quickly (less than 30 seconds) after stopping the press to minimize evaporation of volatiles from the rollers.

3. The GC method can detect about 500 nanograms of EGBE. Since we inject a 5 microliter volume of about 50 micrograms ink/microliter and we did not detect EGBE, it must be present at less than 0.2%.

4. The litho break gives water contents similar to samples taken from the form rollers of the press while the mixmaster gives much higher values.

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1983. "Water Pickup Test for Lithographic Inks." TAGA Proceedings (Technical Association of the Graphic Arts, Rochester) pp. 176-190.

## Appendix 1
## Press Conditions

| Type | 1st Trial Royal Zenith Planeta | 2nd Trial Man Roland Rekord |
|---|---|---|
| Size-Inches | 64 | 41 |
| Dampeners | Continuous | Continuous |
| Rollers-DF | Akorn PVC | Akorn PVC |
| Hardness Shore A | 26 | 26 |
| Speed | 6,700 IPH | 10,000 IPH |
| Blankets | Zippy 600, Conv. | Zippy 400, Conv. |
| Plates | Kodak Neg. | Kodak Neg. |
| Etch | Rosos KSP-500-M3 | Rosos KSP-500-M3 |
| Concentration | 8 Oz/Gal. | 4 Oz./Gal. |
| pH | 3.7 | 4.1 |
| Conductivity | 2800 | 2400 |

## Appendix 2
## GC Conditions

| | |
|---|---|
| Column | Chromosorb 102<br>80/100 Mesh<br>6'x1/8" SS |
| Carrier Gas | He: 35 ml/Min. |
| Oven | $120^{O}$C (2 MIN)<br>$240^{O}$C $20^{O}$/MIN |
| Injection | Splitless |
| Injection Temp | 225 |
| Detector | TCD |
| Detector Temp | 250 |