

WATER PICK-UP TEST FOR LITHOGRAPHIC INKS

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Abstract: Previously proposed laboratory tests for predicting the performance of inks on a lithographic press don't always work. Three new tests are proposed and discussed. These tests sometimes predict failures when the older tests predict success.

Prior to doing the work outlined in this report, we were familiar with four laboratory tests for determining the water pick-up of lithographic inks: the mixmaster test, Surland's refinement of the mixmaster test (1980), the Litho Break tester (Thwing Albert), and a method for determining the final water pick-up of a litho ink (Degussa, 1972).

After making inks which passed these tests but still failed in the field, we developed three new tests for predicting the performance of an ink on a lithographic press. These tests and their application to an ink that works and to an ink that fails are the subject of this report.

Test 1. Delta Plastic Viscosity

The first test, called Delta PV, is performed by distributing 2.94 ml of ink on a Litho-Break tester, and then contacting the ink with fountain solution for five minutes at 100 RPM and 20 psi roller pressures. After removing surface moisture with a paper towel, a sample of ink is removed and fall times are measured with two different weights on a falling rod (Thwing Albert). Plastic viscosity (PV) is calculated and compared with the initial plastic viscosity. A large difference in plastic viscosity between the

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non-emulsified ink and the emulsified ink indicates difficulty in color control across the sheet and throughout the run.

Three UV inks were submitted to us. One ran with no difficulty, but great difficulty was experienced in running the other two.

Most of the constituents of a UV ink are soluble in isopropanol, so it is natural to expect the ink to extract isopropanol from the fountain solution and undergo a decrease in viscosity.

Results using this test method on the three inks are shown in Table 1. Two of the inks showed dramatic decreases in plastic viscosity while one showed a slight increase, which is well within the experimental error of our plastic viscosity determination.

The ink which showed little or no decrease in viscosity after emulsification was the ink that ran well, while the inks that showed a large decrease in viscosity after emulsification were the two that were difficult to run.

Test 2. The a-k Fit

Our second test, which we call the a-k fit, consists of distributing 2.94 ml of ink on the Litho-Break, contacting the ink with fountain solution for various periods of time, and analyzing the emulsion for water by Karl Fischer.

Procedure:

Emulsify the ink on a Litho-Break tester in which a variable speed motor (Dayton) is substituted for the standard motor. Operating conditions are:

RPM	100
Roller Pressures	All 20 psi.
Water Tray	Full
Ink Volume	2.94 ml

After running for 5 seconds, separate the rollers and remove the water pan immediately. Dry the surface moisture with a paper towel and take an ink sample of 100-300 mg from the center of the bottom roller.

Transfer the sample to a tared vial (Aldrich), seal, and weigh. Add 2 ml chloroform, seal, and weigh again. Disperse the sample and use a 2 ml syringe to transfer the contents to a Karl Fischer titrator (Brinkmann). Weigh the empty vial and the syringe before and after sample transfer. Operating conditions of the titrator are:

Flask Solution	3 chloroform/ 1 methanol
Time to endpoint:	30 seconds
Percent Full scale milliamps:	82

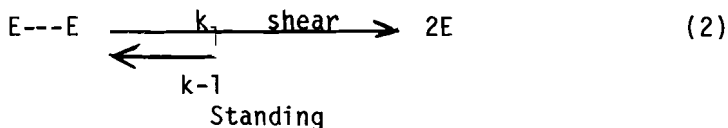
Run a blank of the chloroform and standardize the Karl Fischer reagent. The percent of water is calculated using equation (1).

$$\%H_2O = \frac{(ml \text{ titrant-blank}) (factor)}{(\frac{wt. \text{ ink vial}}{wt. \text{ chloroform}}) \times wt. \text{ transferred}} \times 10 \quad (1)$$

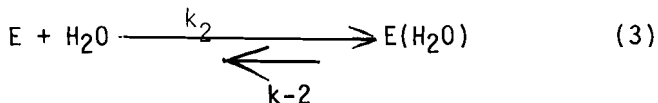
Run this test for 0, 5, 15, 40, 60, and 80 seconds with water as a fountain solution. With isopropanol solutions, run at 0, 5, 20, 40, and 60 seconds.

Values obtained on four heat-set and four sheet-fed process inks determined with water as a fountain solution are shown in Table 2.

The data can be rationalized by assuming that there are emulsifiers (E) in the ink that weakly bond to each other (E--E). On shearing, these bonds break apart; on standing they reform, but the rate of breaking during shear is greater than the rate of formation on standing.



This assumption is justified by the known thixotropic behavior of inks. Once an emulsifier is liberated, it can rapidly emulsify water and slowly release it in a very slow step. The emulsion is designated E(H₂O).



Then

$$\frac{d[E(H_2O)]}{dt} = k_2 [E] [H_2O] - k_{-2} [E(H_2O)] \quad (4)$$

In equation (4), water is present in large excess and is essentially constant, so it is incorporated into a new constant, k_3 . The term $k_3 [E]$ is expected to be very large compared to $k_{-2} [E(H_2O)]$, so this latter term is dropped. With these assumptions, we have:

$$\frac{d[E(H_2O)]}{dt} = k_3 [E] \quad (5)$$

This equation is the differential form of an equation exhibiting first order kinetics; see Wiberg (1964); its integrated form is:

$$\ln \frac{E}{E-X} = k_3 t \quad (6)$$

At this time we are unable to measure E . However, we can measure the ultimate water pick-up on an ink (generally 5-25%) and we postulate that the ultimate water pick-up represents E . We designate the ultimate water pick-up as "a", so the final equation is:

$$\ln \frac{a}{a-H_2O} = kt \quad (7)$$

or

$$H_2O = a [(1-EXP(-kt))] \quad (8)$$

We use equation (7) to calculate the best "a and k" values for a given ink. Generally, we discard the 80 second value and recheck a questionable value. Values for "a and k" found for the eight inks are shown in Table 3.

All eight inks listed in Tables 2 and 3 have run on a wide variety of commercial presses printing all sorts of forms with virtually no complaints, so one might assume that other inks with these "a and k" values will also run well.

While this may be a necessary condition for an ink to run, it does not appear to be sufficient as we have made inks that pass this test, but still failed on a press.

Generally, we believe that inks with high "a" values require low "k" values, so that even if an ink can ultimately pick up a large amount of water, it does it so slowly that the ink never does pick up a large amount of water under press conditions. Conversely, we feel that an ink with a high "k" value requires a low "a" value.

Test 3. Emulsified Water Particle Size

Our third test is the easiest to run. Again we emulsify 2.94 ml of ink on the Litho-Break under the same conditions we described previously. After two minutes, we dry off the surface moisture, take a small sample, draw it down on a microscope slide in a fairly thin film, and observe the size of the emulsified water particles at 1250 power (Zeiss).

With the four heat-set inks, the particle size never exceeds two microns. With the four sheet-fed inks, the particle size never exceeds eight microns.

Using this test, we have observed inks with emulsified water particles as large as thirty microns. These inks will run at slow press speeds. At normal press speeds (400-500 feet per minute) however, the inks fail, as the densitometer readings cannot be maintained.

In order to pass this test, an ink made for a high speed press should emulsify water in spheres no larger than two microns, while an ink made for a slower press should emulsify water in spheres no larger than ten microns.

Application of Tests to Two Inks

We will now show the application of these tests to two inks, one which runs on a lithographic press, and one that doesn't. These inks were made with identical levels of the same driers, additives, and let-down vehicle. The only difference was the flush color.

The delta PV test showed no significant difference between the two inks. See Table 4.

Results of the a-k fit show little difference between the two inks, whether water or water/isopropanol is used as a fountain solution. See Tables 5 and 6.

Microphotographs of the emulsified water particles show a major difference between Ink A and Ink B. See Figures 1 and 2. Ink A contains many droplets in the one to two micron range and the largest is eight microns. Ink B however, contains many droplets in the five to eight micron range with the largest at twenty microns.

Discussion

The Delta PV test measures a gross change in PV of an ink from the non-emulsified state to the completely emulsified state. It is a crude measure of $\Delta PV / \Delta H_2O$, the rate of change of viscosity with water pick-up. If this number is large, then the viscosity and flow of the ink will change rapidly with slight changes in water pick-up, so it is natural to expect that a large Delta PV value can cause color control problems throughout a run.

When an a-k fit has been found for an ink, we believe it fairly accurately describes the real change in water content of an ink versus time, whether on a Litho-Break or on a real press. Inks appear to emulsify water by first-order kinetics, and also appear to have a limit on how much water they can emulsify.

We feel we have a good method for measuring the true water pick-up of an ink, but really why should the presence or absence of water or rate of water pick-up of an ink affect the performance of that ink on a press? If an ink picks up water, and the viscosity and other physical properties remain unchanged, we believe the ink would print as well with water as it would without water.

One reason printers and inkmakers continually talk about water as an enemy, is that physical properties of an ink rarely remain constant as the ink picks up water. It is the change of a key physical property with water pick-up that causes the problem.

Inkmakers and printers know that a poor grind can cause piling on a press. If there are not too many particles above eight microns, the ink will not cause trouble. In some cases two percent of a wax with a particle size of ten to fifteen microns is added to an ink and no apparent problems arise. Inkmakers know that large quantities of such a wax (say twenty percent) won't print, not even in the lab.

When inks absorb twenty percent of water and most of that water is present in the form of spheres ten microns or larger, it is reasonable to expect this ink to print nearly as poorly as an ink with twenty percent of a ten micron wax.

There is a difference. A wax is a non-deformable particle whereas a water particle is deformable. The ink with twenty percent of fifteen micron wax won't print at high or low speeds. The ink with twenty percent of fifteen micron water may print at slow speed, but not at high speed.

The gap between rollers is estimated to be one micron (MacPhee, 1976). Obviously some eight to fifteen micron particles can go through this nip or else large quantities of wax would be accumulating on presses everywhere. We assume that the press is capable of delivering a small quantity of large particle size constituents in any given time.

If this quantity is small, the ink will run initially. If this quantity is large, the ink won't run initially. If this quantity is small, but becomes large as the ink is run, the ink will run initially, but fail in a short time, especially on light forms.

Acknowledgements

Mr. James Wyatt led us to the measurement of water particle size with his observations on the change in opacity of an ink on the form roller of a lithographic press.

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TABLE 1. CHANGE IN PLASTIC VISCOSITY OF
THREE INKS ON EMULSIFICATION
WITH 75% WATER, 25% ISOPROPANOL

	INK A	INK B	INK C
PV BEFORE EMULSIFICATION	280	300	320
PV AFTER EMULSIFICATION	140	310	160
DELTA PV	-140	+ 10	-160

TABLE 2. WATER PICK-UP VERSUS TIME
ON EIGHT PROCESS INKS

TIME, SECONDS	0	5	15	40	60	80
HEAT-SET						
BLACK % WATER	0.0	3.9	5.1	10.6	13.0	12.9
BLUE	0.0	2.7	5.7	9.3	11.9	13.4
RED	0.4	2.7	5.6	12.0	14.7	15.1
YELLOW	0.0	3.5	4.5	4.6	5.7	5.6
SHEET-FED						
BLACK	0.1	1.8	5.6	12.0	14.8	17.3
BLUE	0.3	2.7	7.9	13.6	16.9	18.6
RED	0.6	1.4	5.1	7.5	8.2	8.1
YELLOW	0.0	2.3	7.1	12.9	14.4	17.2

TABLE 3. a AND k VALUES ON EIGHT PROCESS INKS

	a	kx10 ²
HEAT-SET		
BLACK	16.0	3.2
BLUE	14.0	2.9
RED	19.0	2.5
YELLOW	5.6	5.2
SHEET-FED		
BLACK	20.0	2.3
BLUE	20.0	3.0
RED	8.5	5.7
YELLOW	15.5	4.6

TABLE 4. DELTA PV RESULTS FOR TWO INKS

	INK A	INK B
PV BEFORE EMULSIFICATION - POISE	247	384
PV AFTER EMULSIFICATION	236	391
DELTA PV	- 11	+ 7

TABLE 5. a-k FITS FOR TWO INKS WITH WATER AS FOUNTAIN SOLUTION

TIME, SECONDS:	0	5	15	40	60	80	a	k x 10 ²
INK A % H ₂ O	0.2	3.2	7.8	12.7	15.5	16.2	16.7	4.2
INK B	0.2	3.0	6.2	12.5	14.1	13.5	15.5	4.1

TABLE 6. a-k FITS FOR TWO INKS USING DAHLGREN TYPE FOUNTAIN SOLUTION

FOUNTAIN SOLUTION = 75% WATER/25% ISOPROPANOL

TIME, SECONDS:	0	5	20	40	a	k x 10 ²
INK A % H ₂ O	0.2	1.3	4.0	6.2	7.3	5.2
INK B	0.2	2.4	3.8	6.5	7.6	4.7

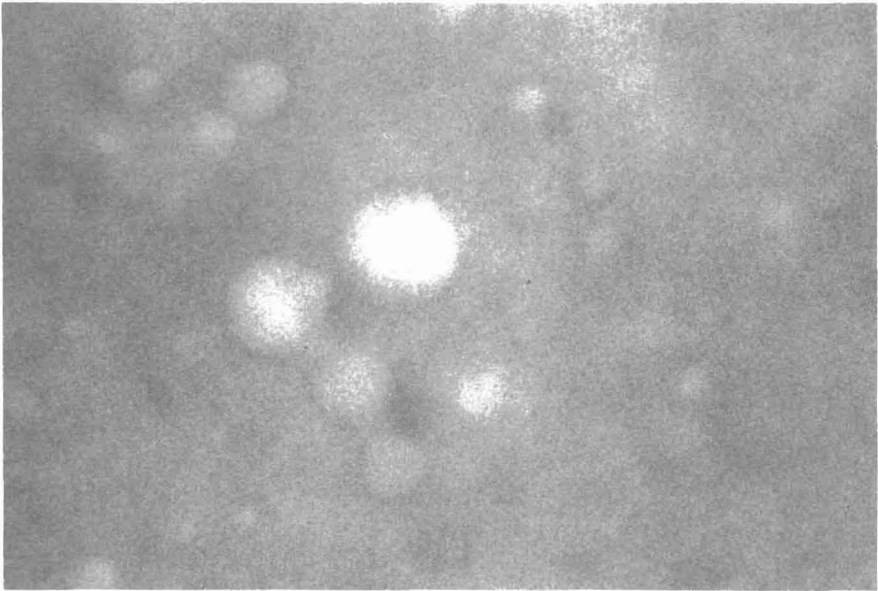


FIGURE 1. INK A AFTER EMULSIFICATION

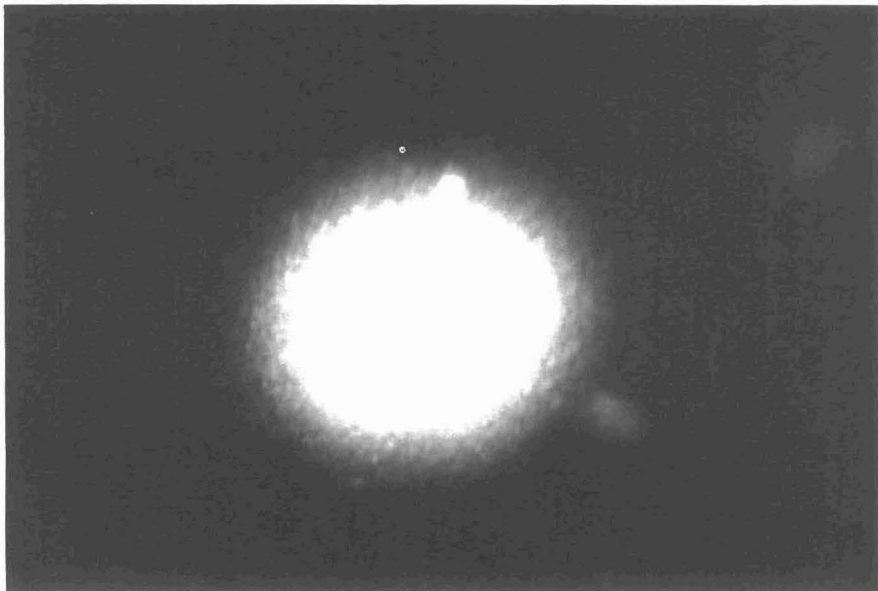


FIGURE 2. INK B AFTER EMULSIFICATION

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Milwaukee, WI 53201

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Brinkmann Instruments Co.
110 River Road
Des Plaines, IL 60016

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Karl Fischer Automat E547.

Carl Zeiss, Inc.
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2711-A Curtiss St.
Downers Grove, IL 60515

Objective 46 19 11-9902
Eyepieces Kp1 W 12, 5X/20

Dayton Electric Manufacturing Co.
5959 Howard Ave.
Niles, IL 60648

Variable speed motor 2Z846A

Thwing Albert Instrument Co.
10960 Datton Road
Philadelphia, PA 19154

Litho-Break Tester Model 123-1.
Viscometer Model LR-2