

## Chapter 15b - Studies

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## Chapter 15b - Studies

### Empirical Verification of the POP Process Equation and Optimization of the Solutions

created August 1999

What exactly occurs during the POP process is not fully known. In order to verify the POP Process Equation and optimize the solutions used in the coating, an experimental test was conducted. Conditions and parameters were carefully controlled and recorded. The ability to make consistently identical prints is a must for this type of test. Evaluations were made based on the study of actual prints. Prints were compared side by side and with standard DOP prints.

Some of the data in this test were obtained as part of a larger more comprehensive study. The interest at this point was to study the Lithium double salt of Palladium and two types of sensitizer on three frequently used substrates and to verify empirically the process equations.

#### PROCEDURE:

For these comparisons the following materials and conditions were used. Only Palladium solutions were used; no tests were made with Pt so as to limit parameters. All subsequent reference is by the respective notations given.

#### SUBSTRATES:

The following substrates were chosen as they are ones used often and represent some diversity.

B = Hunt Co., Bienfang 360

CP = Crane's Parchment Business Card Stock (Lot No. 5302) ("Cover 90")

SI = Sea Island Fabric

#### COATING CHEMISTRY:

The notation used is [sensitizer - contrast agent - Pd salt - Pt salt]

sensitizer [# of drops, type], types used were:

FO ..... Ferric Oxalate 27% solution

AFO40 ... Ammonium Ferric Oxalate 40% solution

AFO60 ... Ammonium Ferric Oxalate 60% solution

Pd solution [# of drops, type of salt, approximate % solution], type of Pd salt used was:

Li ... Lithium -  $\text{Li}_2\text{PdCl}_4$

Pt salt - none was used in order to eliminate a variable

contrast agent - none was used in order to eliminate another variable

The following coatings were evaluated for this test.

6FO-6Li36-0-0	6AFO40-6Li36-0-0	6AFO60-6Li36-0-0
6FO-6Li30-0-0	6AFO40-6Li30-0-0	6AFO60-6Li30-0-0
6FO-6Li24-0-0	6AFO40-6Li24-0-0	6AFO60-6Li24-0-0
6FO-6Li18-0-0	6AFO40-6Li18-0-0	6AFO60-6Li18-0-0
6FO-6Li12-0-0	6AFO40-6Li12-0-0	
6FO-6Li6-0-0	6AFO40-6Li6-0-0	

#### AMBIENT CONDITIONS:

Other testing and experience has shown the POP process to be only consistently dependable at an ambient relative humidity (RH) below 65% and an ambient temperature below 75°F. The ambient temperature for this study was between 68°F and 73°F. The ambient relative humidity was set at 62% +/- 3%.

#### EXPOSURE:

Exposure was identical for all prints under artificial lamps (as described in this guide). This was approximately the exposure this negative would typically get. The time was kept constant so that speed and contrast could be readily compared using a 21-step. It would have been just as valid to match the print and 21-steps and note time differences, although it would have been difficult and cumbersome to accurately define any contrast differences. Consideration was made when evaluating prints as to any differences in speed and contrast. Results have been verified using other negatives and printing times that give the optimum print.

#### PROCESSING:

Processing was standardized but tailored for each type of substrate and sensitizer.

For FO on CP:

- Developer was Potassium Oxalate 1 minute
- Rinsed in tray of water for 2 minutes
- Cleared in Phosphoric acid baths for total of 30 minutes

For AFO40 on CP:

- Developer was tray of water for 2 minutes
- Cleared in Phosphoric acid baths for total of 20 minutes

For FO on B:

- Developer was Potassium Oxalate 1 minute
- Rinsed in tray of water for 2 minutes
- Cleared in Phosphoric acid baths for total of 15 minutes

For AFO40 on B:

- Developer was tray of water for 2 minutes
- Cleared in Phosphoric acid baths for total of 15 minutes

For FO on SI:

- Developer was Potassium Oxalate 1 minute

Rinsed in tray of water for 2 minutes  
Cleared in Phosphoric acid baths for total of 12 minutes  
For AFO40 on SI:  
Developer was tray of water for 2 minutes  
Cleared in Phosphoric acid baths for total of 12 minutes

water = 0.5um filtered tap water  
Phosphoric acid bath = 2oz 85% H<sub>3</sub>PO<sub>4</sub> in 1 gal. water  
The clearing times were determined by the method outlined in this guide.

## OBSERVATIONS:

### EVALUATION:

Prints were compared by looking at, after dry, in "normal" light and direct sunlight (reflected and transmitted). The overall evaluation was to judge the quality of the print with emphasis on darker areas. The same image of a dark stairway with lots of shadow details and texture was used. Also included in the print was a "21 step".

### AFO40 SERIES

The series of AFO40 for Li6 to Li36 showed a transition from a noticeably weak and muddy Li6 print to a healthy Li24 print with no further improvements in the Li30 and Li36 prints. The AFO60-Li30 and Li36 prints showed a bit more substance. There was a definite distinction between the Li18 and Li24 prints. These results are significantly helpful as an empirical tool to finding the process equation (discussed later). These prints all had the same color and speed. The contrast seemed to increase about 1 grade mostly from Li6 to Li18 and a little more to Li24.

### AFO40 vs AFO60

A difference was noted between the AFO sensitizer solutions of 40% and 60%. Differences were only noted for the Li36 and Li30 coatings. No difference was detected for the Li24 and Li18 coatings. (Recall that the number indicates the % solution of Li<sub>2</sub>PdCl<sub>4</sub>.) These findings proved to be significantly helpful as an empirical tool to finding the process equation (discussed later). Due to this importance, these prints were repeated and found to give consistent results.

A final comparison was made with the best of the AFO40 and AFO60 prints. Those were the AFO40-Li24 and the AFO60-Li36. These prints seemed to have equivalent speed. The AFO60-Li36 seemed to have 1/4 grade (or less) more contrast. Both had excellent solid dark areas with the AFO60-Li36 looking slightly more solid. The AFO40-Li24 was slightly warmer and the AFO60-Li36 was very neutral in color (although not perfectly neutral). Although both prints could be considered acceptable, the AFO60-Li36 had a bit more substance and depth. Portions of the image looked more alive in the AFO60-Li36 print.

### FO SERIES

These prints with the FO sensitizer and Li metal salt all showed the same speed and contrast. The

prints exhibited an interesting orangish brown color much more obvious in the FO-Li18 and FO-Li24 prints. FO-Li6 was weak and muddy and FO-Li12 was not far off from the mud. FO-Li18 through FO-Li36 were fairly identical. These findings verify the DOP process equation.

#### FO vs AFO

Comparison was made with the FO-Li24, AFO40-Li24, AFO60-Li36 prints. The FO prints seemed to be a slight bit slower. The prints showed the same contrast up to about Zone VI where the AFO prints then went on to show about 1 grade more contrast. The FO prints were definitely warm in color with the AFO prints close to neutral.. The FO prints had more solid dark areas and exhibited more depth and substance than the AFO40 prints. The AFO60-Li36 prints seemed to have the same depth and substance of the FO prints; the differences being the color and the contrast in the upper values.

#### FINDINGS:

##### THE POP EQUATION:

From the POP Process Equation it is calculated that the AFO40 should be totally used with a  $\text{Li}_2\text{PdCl}_4$  solution of 24.49% indicating that an additional amount of  $\text{Li}_2\text{PdCl}_4$  would be unused. In the AFO40 prints, quality increased from the Li6 to the Li24 and then was constant to Li30 and Li36. This would indicate a "point of saturation" between Li18 (18%) and Li24 (24%). Recall that Li24 is an abbreviation and that the percentage has been rounded to 2 digits. The actual percentage of <24> to four digits was <24.49>. Li24 is the solution of 24.49%. This "point of saturation" data supports the balance of one for one as given by the process equation.

In the AFO60 prints, print quality compared with AFO40 prints was improved in the Li30 and Li36 but remained the same in Li24 and Li18. This would indicate a "point of saturation" between Li24 and Li30. This AFO60 data is consistent with the AFO40 data and also supports the balance of one for one as given by the process equation.

#### CONCLUSIONS

- ★ The POP and DOP processes rely on a use of one molar equivalent of metal double salt for every molar equivalent of sensitizer. If less metal (by way of a weaker metal solution) is used, the result is a weaker print.
- ★ The DOP process seems to require much less metal (by way of a weaker metal solution) than the POP process to get desirable results.
- ★ The POP process can achieve unique effects, such as a neutral or cool color, but seemingly only at the expense of using much more metal (by way of a stronger metal solution).

This study is used to set what the concentrations for the metal solutions should be for a given sensitizer solution. These can be found as the calculated formulas in the Chapter 6 section, Optimized Formulas for Metal Solutions. Further study of the amount of metal that is actually required to optimize the print quality for POP is addressed in a further study, Verification of Metal Solution Optimization.

## Verification of Metal Solution Optimization

created August 1999, updated October 1999

An empirical study (Empirical Verification of the POP Process Equation) to determine the appropriate ratio of metal double salts to sensitizer for the POP (Printing Out Process) Pt/Pd process equation supported a ratio of one-to-one. The solution concentrations for various metal double salt solutions were then calculated. That study produced prints which demonstrated that for given sensitizer solutions (40% and 60% Ammonium Ferric Oxalate [AFO]) certain metal solution concentrations existed that below which produced progressively weaker prints and above which produced identical prints. These metal solution concentrations corresponded to those as calculated.

A question remained as to what amount of metal would be the threshold for making the highest metal containing print using the AFO sensitizer. The threshold being that point at which further increase of metal would no longer present a perceivable improvement in the print.

For the DOP (Develop Out Process), the Ferric Oxalate (FO) sensitizer provides a limiting function as it can only be mixed to about a 27% solution under standard conditions (25°C, 1 atmosphere pressure). To date all attempts have demonstrated that the highest concentration of FO (27%) and the respective calculated metal solutions produces the highest quality prints. If lower concentrations are used, noticeably weaker prints are observed. It might be stated that any threshold for DOP cannot be attained due to the limit set by the maximum strength of the FO solution.

Note: With the addition of oxalic acid or EDTA, the FO solution can be mixed stronger than 27%. However, studies of the FO sensitizer have demonstrated it to achieve an optimum solution strength of between 24% and 26% depending on the quality of the FO powder and the substrate used. See the studies Threshold for FO Solutions, Comparisons of Ferric Oxalate Powders, and Verification of FO Powder Composition.

For AFO, a solution strength of 60% is easily obtained. However a limit comes into play in that this 60% solution with the corresponding calculated metal solution produces a coating solution which begins to have problems, including:

- streaks in the print from brush marks because of the thick solution;
- crystallization of the coating mixture if not applied immediately after mixing;
- graininess in the prints perhaps from unnoticed crystallization;
- bleeding of metal from the print in the water pre-clearing bath.

Questions emerge as to what is the limiting concentration of the FO and AFO sensitizers, and does a metal amount threshold occur within these limit. The purpose of this study is to answer these questions and formulate a coating recommendation for POP using AFO. Other studies, referenced above, provide coating recommendations for DOP using FO.

The Study:

Prints were made from the following coating mixtures (see end of Preparing the Coating Solution for a description of nomenclature used).

The AFO was a solution of 60%.

The Li<sub>2</sub>PdCl<sub>4</sub> was a solution of 36.73%.

The W indicates H<sub>2</sub>O.

Coating Mixtures Use for Study				
	A	B	C	D
1	6AFO60-6L36-0W			
2	5AFO60-5L36-2W			
3	4AFO60-4L36-4W	6AFO60-6L36-6W		
4	3AFO60-3L36-6W	6AFO60-6L36-12W	4AFO60-4L36-8W	
5	2AFO60-2L36-8W	6AFO60-6L36-24W	4AFO60-4L36-16W	3AFO60-3L36-15W
6	1AFO60-1L36-10W	6AFO60-6L36-60W	4AFO60-4L36-40W	3AFO60-3L36-30W

- The mixtures of the A column start at 60% (A1) and diminish in concentration through 40% (A3) to 10% (A6).
- The mixtures of the B column are diluted identical to their counter parts of the A column but keeping an identical amount of metal as the first mixture (the calculated 60% AFO mixture).
- The mixtures of column C are diluted identical to their counter parts of the A and B columns while keeping an identical amount of metal as in the calculated 40% AFO mixture.
- The mixtures of column D are diluted identical to their counter parts of the A, B, and C columns while keeping an identical amount of metal as in a 30% AFO mixture (A4).
- Each of these mixtures was coated into an identical area of about 25 square inches (enough room for a 4x5 negative a 21-step). Keeping the area of coverage constant is critical, and in order to accomplish this for some of the mixtures in the B and C columns, a different coating method was devised (see the Quasi Multi-Coating Method below).

The purpose of column A was to observe an incremental decrease in the concentration of coating mixture solutions. It is important that the sensitizer to metal solution ratio remains one-to-one as this was determined to be proper from previous study.

One purpose of columns B, C, and D was to compare the dilution of the coating mixture at values of 60%, 40%, and 30% AFO with the reduction of mixture (column A).

Another purpose of columns B, C, and D was to investigated changes in total metal content independent of mixture concentration and without problems associated with the stronger solutions.

This investigates a row such as 4, 5, or 6.

- Ambient conditions were temperature of 73-75°F, relative humidity of 65-67%.
- The paper used was Crane's Parchment Business Card Stock (AKA: Cover-90; CP)
- Single coatings received a very brief pre-mist; multi-coatings received no pre-mist.
- All were coated by brush and "Wet" dried (see the Wet Dry Drying Study.)
- All were exposed for 12 minutes under UV lamps. A6 was repeated with a longer exposure to verify that the weakness was not from speed loss.
- All were processed the same:
  - ✓ 2 minutes water bath
  - ✓ 20 minutes total clearing in H3PO4.
  - ✓ Buffered rinse and 8-10 minute wash.

Observations:

General Observations

- ▶ Strength and Depth of image (dark values) B5 & B6 had excellent strength and depth with good solid dark areas more so than all the others.
- ▶ B3, C4, C5, & C6 had excellent strength and depth with good solid dark areas more so than the A group but not quite as much as B5 & B6.
- ▶ A2 & A3 had excellent strength and depth with good solid dark areas but not quite as much as those above.
- ▶ A4 had very good strength and depth with good solid dark areas but noticeably less than those above
- ▶ A5 was slightly weak.
- ▶ D5 & D6 were definitely weak, not as weak as A6 but weaker than A5.
- ▶ A6 was definitely weaker than all.
- ▶ A1 & A2 were the only prints to "bleed" metal into the water (pre-clearing) bath.
- ▶ A1 was not included in this comparison as some weakening was noticed likely due to other factors.

Overall Substance and Presence

- ▶ B5, B6, C4, C5, A2, & A3 showed the most Substance and Presence.
- ▶ A6, D5, and D6 showed the least Substance and Presence.
- ▶ B5 came the closest to matching (identical) the Substance and Presence of a DOP print.

Image Color

- ▶ A1, A2, & A3 were neutral color; A4, A5, & A6 were barely slightly warmer.
- ▶ B3 & B4 were neutral color; B5 & B6 were slightly warmer.
- ▶ C4, C5, & C6 were in-between the neutral and warm colors with C5 the warmest.
- ▶ D5 & D6 were neutral color.

Image Graininess of large tonal areas (21-step)

- ▶ A1 was noticeably grainy; A2, A3, & A4 slightly grainy; A5 & A6 were smooth.

- ▶ B3 was slightly grainy; B4 barely showed some grain; B5 & B6 were smooth.
- ▶ C4 barely showed some grain; C5 & C6 were smooth.
- ▶ D5 & D6 were smooth.

#### Paper Surface

- ▶ The surface of B6 was slightly rougher (probably due to the long brushing of five coats).
- ▶ The surfaces of those receiving three or four coats (B5, C6, & D6) felt barely, but noticeably, rougher.

#### Speed

- ▶ All the coatings seemed to be close to the same speed. Too close to be evaluated by the 21-step, however a few appeared slightly darker throughout the print (B5, B6, & C5).

#### Contrast

- ▶ A1 through A6 showed a graduated change in contrast with A6 being about 1 grade more contrast.
- ▶ The B group showed the same gradation of contrast with B6 being the highest but about a half grade less than A6.
- ▶ The trend followed in the C and D groups (6 the most contrast); and in each row, A having the most contrast. In all rows the contrast progressively changed about one and a half grades.
- ▶ Two coats by the Quasi Multi-Coating Method consistently produced a half grade less contrast than a single coat.

#### **Quasi Multi-Coating Method**

This author has had mixed results from multiple coatings in the past. A thought was that some of the past difficulties could have been related to drying the mixture and then re-coating. Coatings of mixtures containing 50 % to 100 % additional mixture had been brushed into the same areas without problems. So it was supposed that additional mixture could be added to the coating before it dried completely. (Hence the term Quasi.)

The Quasi Multi-Coating Method is basically as follows:

- ✓ Pour out a typical amount of mixture on to the paper as with a single coating;
- ✓ Brush this into the area desired as if it were a single coating;
- ✓ Allow to dry beyond the point of loss of gloss, but before complete dryness (rather damp);
- ✓ Pour out some more of the mixture (about the same amount);
- ✓ Brush this into the area desired as if it were a single coating;
- ✓ Allow to dry beyond the point of loss of gloss, but before complete dryness (rather damp);
- ✓ Continue until all of the mixture is used.
- ✓ Dry to desired dryness.

Each pouring should be enough to completely coat a layer over the full area. Do not extend any

mixture beyond this area. With this Quasi Multi-Coating Method, it is of the utmost importance that the coating be restricted to the correct area and completely fill the area each partial coating. Spreading the mixture too thin (past the area) will result in a weakened coating which, if at the threshold, will produce a weakened print. Not spreading the mixture to fully to cover the area will result in a stronger coating in some places and may produce non-uniformities in the final print.

The coating of mixture B6 was accomplished with five pourings (5 quasi coats) and took a little more than half an hour to coat and dry. These coatings produced excellent prints. All of the A group had one coat; B5 had three coats; B4 two coats; B3 one coat; C6 four coats; C5 two coats; C4 one coat; D6 three coats; D5 one coat. Drying times are significantly lengthened with multiple coats.

A few of the coatings showed some difficulty (large lighter blotchy areas) which was likely because of too much drying of the first coating. Those coatings were repeated, taking care not to over dry, and produced excellent results. It was also noted that none of the prints (including the 5 coat) showed any signs of solarization effect.

## Discussions

### COVERAGE:

Consistency of the coating coverage is of critical importance. Coverage is expressed as cm<sup>2</sup>/ml and defined as:

$$[\text{Coverage}] = [\text{area of coating in cm}^2] / [\text{number of drops of sensitizer at specified solution concentration}] * [\text{ml per drop}]$$

An increase in coverage will weaken the print, and a decrease in coverage will waste chemistry. Because multiple coatings may be made and may use a diluted mixture, the total number of mixture drops is not an accurate reference. The appropriate reference is the number of drops of sensitizer solution, which is identical to the number of drops of metal solution. The purpose of coating is to get a known amount of active chemicals evenly distributed throughout the coated area. Coverage indicates that amount.

Coverage will vary by paper and must be determined for each paper. Knowing the coverages will permit the easy transition from one paper to another without the worry of insufficient chemistry. The Coverage for the paper used in this study is calculated as follows.

$$\text{Coverage of CP} = 161 / 6 * 0.05 = 1.34 \text{ cm}^2/\text{ml}$$

This means that an 8x10 with half inch borders (100 inches<sup>2</sup> or 645 cm<sup>2</sup>) will require the number of drops of sensitizer as follows.

$$\text{drops} = [\text{area coated}] / [\text{Coverage}] * [\text{ml per drop}] = 645 / 1.34 * 0.05 = 24$$

Add to this amount of sensitizer, an identical number of drops of the appropriate metal solution(s), an optional drop of contrast agent, and any optional dilution water, to make a coating mixture for an 8x10 on CP.

#### THRESHOLD:

Column A alone indicates that A4 (a 40% AFO solution with respective metal solution) may be close to the threshold.

When evaluating the rows, it is noticed that column D (a 30% AFO solution with respective metal solution) is far below the quality of column C (a 40% AFO solution with respective metal solution)

Columns B (a 60% AFO solution with respective metal solution) and C (a 40% AFO solution with respective metal solution) are very close. In row 6, B is definitely better than C. In rows 4 and 5 the prints look identical with B5 being a bit warmer.

It is suspected that the appearance of depth and substance may be enhanced by a slight warm color. Without this color B5 and C5 would look identical.

Without finer tuning, it is most likely that the 40% AFO solution with respective metal solution is the closest to the threshold (30% being definitely too weak). It is possible that slightly less than 40% may be used and should be verified.

#### QUASI MULTI-COATING:

It appears that multiple coatings by the method above may produce a fuller advantage of the materials than a single coat. C5 appears superior to C4 and A3 (especially considering smoothness).

Two coats by the Quasi Multi-Coating Method consistently produced a half grade less contrast than a single coat. However, further coats showed an increase in contrast, suspected to be caused by an overriding influence of dilution.

#### Further Data and Discussion

Additional data was sought from coatings based on a 35% AFO solution with respective metal solution. To accomplish this two prints were made with the following coating mixtures.

- 12 drops of the mixture 7AFO60-7L36-10W
- 24 drops of the mixture 7AFO60-7L36-36W

Note: For reference 7AFO60-7L36-10W is the equivalent of 12AFO35-12L21 which is twice the amount needed for the area coated.

The prints fit into the above assembly of prints where expected. These prints were extremely close

to C4, C5, and A3. They were noticeably better than D5 and D6 and slightly better than A4.

These prints appear to be of a quality good enough to consider them closer to the threshold than those of the 40% AFO.

These prints had a neutral color and did not appear to have as much depth or substance as B5 and B6. However, it is becoming more convincing that the depth and substance perceived is a function of other than only the amount of metal in the print (i.e., the color has some influence).

### Conclusions and Recommendations

A reminder that this information is paper specific. The sensitizer solution strength (and the associated metal solution) and coating mixtures for other papers should be evaluated by this or a similar procedure. However, the ratio of sensitizer to metal solution will remain unchanged.

It is unlikely that a change to another type of metal solution will influence these results, if that metal solution is the calculated optimized solution for the solution of sensitizer (see Optimized Formulas).

For POP, a 35% AFO solution with respective metal solution provides enough metal to reach the discussed threshold and should be the coating mixture used and applied as either a single coat or a two coat Quasi Multi-Coating.

This translates to the following coating solutions and equivalent coating mixture recommendation.

AFO made as a 35% solution (AFO35).  
Li<sub>2</sub>PdCl<sub>4</sub> made as a 21.43% solution (L21).  
Na<sub>2</sub>PdCl<sub>4</sub> made as a 24.05% solution.  
K<sub>2</sub>PdCl<sub>4</sub> made as a 26.7% solution.  
K<sub>2</sub>PtCl<sub>4</sub> made as a 33.9% solution.

Note: Metal solutions may be mixed or interchanged freely.

For single coat:

(#drops) (AFO) - (#drops) (metal solution)[ - 1 drop (contrast agent)] optional

For double Quasi Multi-Coating:

(#drops) (AFO) - (#drops) (metal solution) - (2 times #drops) (H<sub>2</sub>O)[ - 1 drop (contrast agent)] optional

An advantage of the double Quasi Multi-Coating:

As some of the metal solutions above will not stay in solution (unless heated), they could be mixed at half their concentration, twice the #drops put into the mixture, and a #drops deleted from the H<sub>2</sub>O.

For double Quasi Multi-Coating with metal solutions at half their strength:

(#drops) (AFO) - (2 times #drops) (metal solution) - (#drops) (H<sub>2</sub>O)[ - 1 drop (contrast agent)] optional

#### Additional Pondering

Not only has this study been paper dependent, results are also affected by coating efficiency. The Wet Dry Drying Study has roughly predicted a coating efficiency of 81% for the brushing techniques used. A different brushing technique or the use of a rod may have a different coating efficiency. A higher efficiency would allow the solution strengths to be reduced, and a lower efficiency would require the solution strengths be increased. It is highly recommended that a standardized coating technique be practiced and used at all times.

An important aspect of this study has been to determine and to have technique to consistently put the maximum beneficial (threshold) amount of metal into the coating.

## Wet Dry Drying Study

created August 1999

The purpose of this study was to investigate any differences that may have existed between exposing a coating that has been dried “Wet” or “Dry”.

Drying "Wet" means that the relative humidity (RH) of the coating was at ambient and relatively high (typically 60-70% RH) when exposed. Drying is accomplished by blowing ambient air over the coating until just dry and letting RH of the coating come to that of the ambient.

Drying "Dry" means that the ambient RH was relatively low (preferably less than 40% RH) and the print dried by blowing air with medium heat over the coating to dry as much as possible. This method is that which is also referred to as drying to “bone dry”. The dried coating is quickly put in the contact frame and exposed so as to keep driest.

Note: A method to check if the RH of a paper has reached equilibrium with the ambient, is to place the paper on a scale accurate to 0.01 grams and observe the movement. An increase will indicate an increasing RH in the paper; while a decrease will indicate a decreasing RH in the paper.

This study was made after preliminary work from other studies and early on demonstrated some interesting results.

- ▶ It became apparent that the paper may change water content rather quickly.
- ▶ Solarization effects may occur - which are addressed later.
- ▶ A printout which was unusually very dark and of extremely high contrast was only seen with the “wet” dried coatings at an ambient temperature of 82°F. However, this high of a temperature produced its own problem as discussed in Solarization later.
- ▶ Pre-humidification of the paper had to be re-thought and is also discussed later in Solarization.
- ▶ As a result of preliminary study, the “Dry” portion needs to be repeated.

All weights were measured with an Ohaus Cent-O-Gram mechanical quad balance scale accurate to 0.01 grams.

### Ambient Conditions

For the “Wet” part, the temperature was 72°F and the relative humidity 62%RH for A, B, C, and D; and the temperature was 75°F and the relative humidity 68%RH for E.

For the initial “Dry” part, the temperature was 77°F and the relative humidity 45%RH for A, B, C, and D. Plans are to repeat the “Dry” portion keeping the RH below 40%.

Materials and Procedure

- ✓ Paper was Crane's lot # 5302 (AKA parchment Business card stock, Cover 90, "platinotype"). Paper was cut to slightly larger than area to be coated.
- ✓ This paper was chosen as it is a thick paper having a capacity to hold moisture.
- ✓ Coating was 9 drops FO (27% solution), 6 drops  $K_2PdCl_4$ (19% solution), 3 drops  $K_2PtCl_4$  (24% solution), 1 drop Ammonium Dichromate (0.25% solution).
- ✓ This coating mixture is typically used.
- ✓ Coating mixture was weighed.
- ✓ Paper was weighed.
- ✓ Paper was humidified only briefly on the coating side with a sonic mister. (See discussion of Solarization later.)
- ✓ Paper was weighed and verified that there was no increase in weight. (See discussion of Solarization later.)
- ✓ Coatings were applied by brush and covered enough area for a 4x5, and a 21-step.
- ✓ Coated paper was weighed.
- ✓ Coatings were dried by one of the methods above.
- ✓ Dried coated paper was weighed.
- ✓ Coating exposed for 10 minutes with BL type lamps through a negative and 21-step.
- ✓ Exposed paper weighed.
- ✓ Developed in Potassium Oxalate (1 minute)
- ✓ Rinse/Pre-clear in water bath (2 minutes)
- ✓ Cleared with phosphoric acid baths for a total of 30 minutes
- ✓ Rinsed in buffered water, washed, dried
- ✓ Dried, finished print weighed.

Weighing Data

Drying "Wet" - weight in grams					
	A	B	C	D	E
mixture weight	1.25	1.25	1.25	1.25	1.25
pre-misting	4.91	4.76	4.46	4.15	6.08
pre-coating	4.91	4.76	4.46	4.15	7.01
post-coating	5.93	5.82	5.47	5.12	7.08
post-drying	5.25	5.02	4.72	4.44	6.34
post-exposure		5.01	4.68	4.39	
final	5.00	4.86	4.55	4.28	6.04

Drying "Dry" - weight in grams - Data questionable due to Pre-misting				
	A	B	C	D
mixture weight	1.25	1.25	1.25	1.25
pre-misting	9.26	8.73	8.71	8.71
pre-coating	9.39	9.12	9.08	9.39
post-coating	10.24	10.00	9.92	10.29
post-drying	9.04	8.75	8.72	8.92
post-exposure	9.10	8.75	8.76	8.98
final				

"Dry" data will be obtained in which the pre-misting is omitted or reduced so that no gain in weight is detected, with the RH kept below 40%.

Calculations:

Drying "Wet" - changes of weight in grams					
	A	B	C	D	E
Due to misting	0.00	0.00	0.00	0.00	0.03
Due to coating	1.02	1.06	1.01	0.97	1.01
Start to Dry	0.34	0.26	0.26	0.29	0.26
Due to exposure		-0.01	-0.04	-0.05	
Start to final	0.09	0.10	0.09	0.13	

Drying "Dry" - changes of weight in grams - Data questionable due to Pre-misting				
	A	B	C	D
Due to misting	0.13	0.39	0.37	0.50
Due to coating	0.85	0.88	0.84	0.90
Start to Dry	-.22	0.02	0.01	0.03
Due to exposure	0.06	0.05	0.04	0.06
Start to final				

The weight of the coating chemistry minus water except for the  $6\text{H}_2\text{O}$  attached to the FO is calculated to be about 0.0203 grams assuming none lost.

## Observations

### SOLARIZATION

- ▶ "Wet" prints A and B showed no solarization.
- ▶ "Wet" print D barely showed a minute solarization.
- ▶ "Wet" print C showed very little solarization.
- ▶ "Wet" print E showed some solarization. The RH of E was intentionally forced upwards;
- ▶ "Dry" prints that received a strong pre-coating misting showed solarization.

Note: "Dry" prints will be repeated without a weight gain from pre-coating misting.

In every example the solarization did not show while the prints were wet from processing; only after drying did the solarization become apparent. This hiding of the solarization is suspected to be related to the depth that the coating has penetrated the paper; when wet, greater depth is viewed into the paper. (This is also why prints appear to have greater depth and substance when wet.)

Whether what is happening is actually solarization is not known. What had been observed, and now related to certain conditions, appears similar to a solarization. What is important is that this effect can be avoided or significantly reduced by controlling a couple of the parameters. It is expected that different papers will behave differently, so the conditions set forward in this study only apply to the paper used.

Previous experimentation demonstrated that the solarization effect was only observed at higher ambient temperatures (82°F) and when the pre-coating misting was overabundant. When the ambient temperature was kept lower than 75°F and care was given so as to only just barely mist the paper prior to coating, no or very little solarization was observed. All other parameters had been kept constant.

It has been known for some time that papers generally coat better when cold, and that more mixture is required to coat the same area at a higher temperature. It is suspected that the higher temperature encourages the chemistry to soak deeper into the paper. This is paper dependent; and is much more noticeable in a thicker paper which absorbs moisture.

It has been thought that pre-coating humidification of most papers was beneficial as it made the paper more susceptible to accepting the coating. However, this must now be re-thought, as too much humidification (misting) may now promote this solarization effect. It is suspected that a rise in relative humidity above the ambient will encourage the coating chemistry to soak too deeply into the paper. At a temperature of 73°F, an over misted paper led to solarization, whereas no misting provided an excellent print with no signs of solarization.

The solarization effect is suspected to be caused by the deep absorption of coating chemistry into the paper. It is desirable to get the chemistry into the paper, but it appears now to a certain limit. This limit can be controlled by a joint effort of command over the temperature and the pre-coating misting. Each paper will have its own characteristics. For the Crane paper used in this study, it is suggested that the ambient temperature be kept below 75°F. For any paper it is suggested that the misting be quick enough to not increase the weight of the paper (measured to at least 0.01 grams).

#### PRINTOUT

Another effect of the higher temperature was a dramatically increased printout. This printout was extremely high contrast and dark. It is thought the this printout would produce a better separation of shadow detail. This increased shadow detail was observed in some prints, however these prints also exhibited a large amount of the solarization effect. It would now become a balance of shadow detail versus solarization. It does seem that the solarization could be controlled to the very darkest areas while the increased shadow separation could result in an overall benefit to the print. This was not attempted for this study; the temperature was kept in the low to mid seventies and all tests kept misting to a minimum so as to not cause an increase in weight. This printout may have merit and should be studied further.

#### PRINT COMPARISONS

To be completed after obtaining "Dry" data.

It is suspected that prints will be almost identical, but more data must be collected to verify this. And, this is expected to be paper dependent.

#### WEIGHT COMPARISONS

To be completed after obtaining "Dry" data.

A weight of interest here is the start-to-finish which is expected to give an indication of the difference in water content between the "Wet" and "Dry" methods. If it is assumed the the "Dry" method produces no weight increase, the amount of water in the "Wet" method, for the given ambient conditions, would average 0.28 grams. Plans are to obtain this weight for several ambient RH, and determine the temperature sensitivity, IF... If there is a notable change observed in the print. Thus far it is suspected that prints will be almost identical.

#### CHEMISTRY CONSUMPTION

Considering "Wet" prints only.

Note that not all of the coating chemistry was delivered to the paper as some was soaked up by the brush and some stuck to the shot glass. If it is assumed that the chemistry delivered to the paper is (weight of post-coat)-(weight of pre-coat) or delta due to coat, this would indicated that a bit more than 81% of the chemistry was delivered to the paper.

#### Conclusions:

Temperature and pre-coat misting can be controlled so that the solarization effect can be avoided or minimized.

To be completed after obtaining "Dry" data.