

## Chapter 15c - Studies

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## Chapter 15c - Studies

### Initial Threshold Study for FO solutions

created October 1999, updated April 2005

This study centers on determining what amount of metal would be the threshold for making the highest metal containing print using the Ferric Oxalate (FO) sensitizer. The threshold being that point at which further increase of metal would no longer present a perceivable improvement in the print.

The threshold is dependent on many factors including the paper selected, the area coated, the coating procedure and coating efficiency. It is imperative that the coating coverage and area be determined and the coating mixture be restricted to the area.

Note: Pencil lines are a helpful way to delineate the area.

If one desires more flexibility and less restrictive accuracy, solution concentrations may be used which are higher than the threshold. This may accommodate various papers, inaccuracies in efficiency, coverage, or areas, and some inconsistencies in coating procedure. This convenience will be traded for the cost of some unused metal and sensitizer. Using less material than required to meet the threshold will result in a noticeably weaker print.

#### The Study

The sensitizer was initially mixed as a 30% solution.

7.65 grams Vizcay FO powder (estimated to contain 0.15g Oxalic Acid & 7.50g FO)  
1.00 gram EDTA (Na<sub>4</sub>)  
0.80 gram Oxalic Acid  
H<sub>2</sub>O to make final volume of 25.0 ml when completely dissolved

The drop sizes of all the solutions were determined to be 0.05 ml/drop.  
A bulk base coating mixture was mixed consisting of:

70 drops sensitizer (described above) (30 % solution)  
50 drops K<sub>2</sub>PdCl<sub>4</sub> solution (20.2 % solution, warmed)  
20 drops K<sub>2</sub>PtCl<sub>4</sub> solution (25.7 % solution, warmed)

Both metal solutions must be warmed to keep dissolved. These are the metal solution concentrations for use with a 30% solution of Ferric oxalate. The Metal Solution Formula Calculator may be used to determine the metal solution formulas to use with other sensitizer and concentrations.

Prints were made from the following coating mixtures based on the following sensitizer concentrations.

M = bulk base coating Mixture

W = H<sub>2</sub>O

# of drops	mixture	equivalent % concentration of sensitizer
15	15M	30 %
15	14M+1W	28 %
15	18M+2W	27 %
15	13M+2W	26 %
15	15M+3W	25 %
15	16M+4W	24 %
15	11M+4W	22 %
15	10M+5W	20 %

- Ambient conditions were temperature of 68-70°F, relative humidity of 34%.
- The paper used was Crane's Parchment Business Card Stock (AKA: Cover-90; CP)
- Coatings were by brush into an area 5 inches by 5 inches (25 inches<sup>2</sup> or 161 cm<sup>2</sup>)
- All were dried by the dry method (see Drying the Coating).
- All were exposed with the same negative and a 21-step for 10.25 minutes under UV lamps.
- All were processed the same:
  - ✓ developed in Potassium Oxalate
  - ✓ 2 minutes water bath
  - ✓ 30 minutes total clearing in H<sub>3</sub>PO<sub>4</sub> (3 baths).
  - ✓ Buffered rinse and 10 minute wash.

#### Observations

Note: When discussing results, the #% refers to prints make with the equivalent % concentration of sensitizer solution and associated metal solution.

- ▶ The 20% was noticeably slightly weaker and showed a very slight solarization effect.
- ▶ The darkest areas of the 22% and 24% (as well as the 20%) were not solid (having a "pin holes" sort of look when viewed with transmitted light), and the 25% had a slight hint of this effect, unlike the other prints which were uniformly very solid.
- ▶ The prints were identical other than the above differences.

All of the prints made from a mixture at or above 26% FO in the sensitizer and with the corresponding metal solution were identical by any visual observation. All of the prints below the 26% had some lesser quality observed.

#### Conclusions and Recommendations

It is concluded that for the materials and conditions used, a threshold of 26% is to be expected. Another paper may have a different threshold.

It is recommended that, for the materials and conditions as above, a sensitizer solution with a Ferric Oxalate concentration of 26% be used, along with the respective concentrations of metal solutions. The metal solutions for a given sensitizer may be found using the Metal Solution Formula Calculator or from the tables in Chapter 6, Optimized Formulas for Metal Solutions.

It is alright if a FO concentration slightly greater than 26% is used and may provide some greater flexibility and diversity. However, it must be remembered that at higher concentrations, it can become more difficult to dissolve the metal solutions.

These recommendations are being verified and may change.

## Initial Comparisons of Ferric Oxalate Powders

October 1999, updated April 2005

Several FO powders were compared by measuring specific gravity and pH to investigate any similarities or differences. Some differences were noticed immediately upon the preparation of the solutions and subsequent work attempted to find a reason for those differences. (Note: Later conclusions and study indicate that evaluating prints made from the solutions provided a better understanding than the specific gravity and pH measurements.)

### The Powders

Comparisons were made of Ferric Oxalate (FO) powder from the following sources.

- Bostic & Sullivan (B&S), commercial supplier
- Vicente-M. Vizcay Castro (Vizcay), made by Vicente-M. Vizcay Castro following his preparation procedure
- Jeffrey D. Mathias (JDM), made following Vizcay's preparation procedure

### The Solutions

Solutions were made from the above Ferric Oxalate (FO) powders as described.

### Preliminary Solutions

Initially the B&S and Vizcay solutions were mixed as 16.20 grams FO and 48.0 ml H<sub>2</sub>O. The solutions were shaken intermittently for 24 hours. Due to the large amount of undissolved FO another 2.0 ml H<sub>2</sub>O was added. After another 24 hours of intermittent shaking another 1.0 ml H<sub>2</sub>O was added. It did not seem that the solutions would completely dissolve so they were shaken well and poured into a graduated cylinder and another 1.5 ml of H<sub>2</sub>O was added to bring the total volumes to 60.0 ml (at 78°F). These solutions are what this study refers to as the "Preliminary Solutions".

It was noted that the Vizcay solution had what appeared to be about 4 times the undissolved FO as did the B&S solution at a point where solubility equilibrium was expected.

If these solutions had dissolved completely, they would have been 27% solutions.

These solutions were heated slightly, shaken well and immediately divided into two 30 ml amounts.

For each FO type, one of the 30 ml portions (Preliminary Solution) had the Specific Gravity (SG) and pH measured.

It was felt that Oxalic Acid may be necessary for complete dissolving. For each FO type, the remaining 30 ml portion had Oxalic Acid added at small intervals until complete dissolving and then were termed the "Oxalic Solutions".

#### Oxalic Solutions:

To these solutions (30 ml portions from above), Oxalic Acid was added in an amount of 0.10 gram at a time with shaking and waiting a day or two for dissolving.

The B&S and Vizcay Preliminary Solutions (27%) were found to dissolve completely (at 70°F) when the following amounts of Oxalic Acid were added to the 30 ml of solution.

B&S 0.50 g

Vizcay 1.40 g

These solutions are what this study refers to as the "Oxalic Solutions". The Specific Gravity (SG) and pH were measured.

#### Straight Solutions:

The remainder of the Preliminary Solutions after testing was 23.0 ml. To this 0.50 ml of H<sub>2</sub>O was added and shaken intermittently for 24 hours. The solutions were still not completely dissolved so another 0.50 ml H<sub>2</sub>O was added and shaken intermittently for 24 hours. At this point both FO appeared to be completely dissolved at a temperature of 70°F. These solutions had a concentration between 26.4% (not dissolved) and 25.9% (completely dissolved).

These solutions are what this study refers to as the "Straight Solutions". The Specific Gravity (SG) and pH were measured.

#### EDTA solutions

John Melanson had claimed that EDTA (Na<sub>4</sub>) would allow the ferric oxalate solution to attain a higher concentration. 8 grams of ferric oxalate powder plus 1 gram of EDTA (Na<sub>4</sub>) had H<sub>2</sub>O added in small increments until the material was completely dissolved at a temperature of 70°F (allowing at least 24 hours of intermittent shaking). The total H<sub>2</sub>O added was 22 ml; the total volume of the solution was about 25ml. These were 32% solutions.

These solutions are what this study refers to as the "EDTA Solutions". The Specific Gravity (SG) and pH were measured.

#### Balanced Solutions

With the intention of maximizing the ability to accurately compare powders and investigate the solubility difference when adding oxalic acid, "Balanced Solutions" were made from the

powders. To accomplish this, the amount of oxalic acid assumed in each FO powder was estimated as discussed below in [Estimated Contents of Powders](#). An addition of 4% EDTA (Na<sub>4</sub>) was also used so as to achieve FO concentrations of 30%.

8.45 grams B&S FO powder (assumed to contain 0.91 gram Oxalic Acid & 7.54 grams FO)  
 1.00 gram EDTA (Na<sub>4</sub>)  
 0.04 gram Oxalic Acid  
 H<sub>2</sub>O to make final volume of 25.12 ml

7.65 grams Vizcay FO powder (assumed to contain 0.15 gram Oxalic Acid & 7.50 grams FO)  
 1.00 gram EDTA (Na<sub>4</sub>)  
 0.80 gram Oxalic Acid  
 H<sub>2</sub>O to make final volume of 25.0 ml

7.65 grams JDM FO powder (assumed to contain 0.15 gram Oxalic Acid & 7.50 grams FO)  
 1.00 gram EDTA (Na<sub>4</sub>)  
 0.80 gram Oxalic Acid  
 H<sub>2</sub>O to make final volume of 25.0 ml

These solutions are what this study refers to as the "Balanced Solutions". The Specific Gravity (SG) and pH were measured.

#### Summary of Solutions

Preliminary Solutions	16.20 grams Ferric Oxalate powder, plus 52.5 ml H <sub>2</sub> O Shaken well immediately before measuring (not dissolved, but assumed homogeneous).
Oxalic Solutions	16.20 grams Ferric Oxalate powder, plus 52.5 ml H <sub>2</sub> O, plus amount of Oxalic Acid needed to completely dissolve.
Straight Solutions	25.9 % solutions (FO powder only, no additional Oxalic Acid, assumes 100% pure FO), Completely dissolved.
EDTA Solutions	8.00 grams Ferric Oxalate powder, plus 1.00 gram EDTA (Na <sub>4</sub> ), plus 22 ml H <sub>2</sub> O, Completely dissolved.
Balanced Solutions	30% solution of Ferric Oxalate using estimated contents of powders, plus 1.00 gram EDTA (Na <sub>4</sub> ), plus amount of Oxalic Acid needed to provide identical minimum amounts in all solutions, plus H <sub>2</sub> O to make 25 ml when completely dissolved.

#### Estimated Contents of Powders

It might be assumed that the powders consist only of Ferric Oxalate and Oxalic Acid. These are the only materials introduced in the Vizcay procedure, and these are the only ingredients claimed by Bostic & Sullivan in their product. Trace amounts of Nitric Acid (detected by

odor) and water are likely but assumed negligible.

The initial Oxalic Acid contained in the Vizcay powder can be estimated as follows. The Vizcay preparation provides an additional 2.5% Oxalic Acid. If it is assumed that all of this additional Oxalic Acid remains unreacted, the Vizcay powder can be assumed to contain:

1.92% Oxalic Acid by weight;

98.08% Ferric Oxalate by weight.

It follows that: (% Oxalic Acid in powder) = (extra Oxalic Acid)/(powder produced which includes FO and the extra Oxalic Acid) or

$$0.0192 = (117 * 0.025) / (149.7 + (117 * 0.025))$$

If one assumes that a certain amount of Oxalic Acid is responsible for the ability to completely dissolve the FO powders at a certain concentration (see preparation of Oxalic Solutions), then it is possible to estimate the amount of oxalic acid in the batch of B&S powder.

For this estimate let:

B represent the solution made with B&S powder

V represent the solution made with Vizcay powder

F represent weight of ferric oxalate

O represent weight of oxalic acid included with the powder

A represent weight of oxalic acid in addition to what was in the powder

The weight of powders used to make the Oxalic Solutions was identical, thus:

$$FB+OB = FV+OV$$

From the assumption above, the ratio of the total amount of oxalic acid to ferric oxalate in each solution is identical when the solutions have just the right amount of oxalic acid added to achieve a completely dissolved solution at a given temperature. This is represented as:

$$(AB+OB) / FB = (AV+OV) / FV$$

What is desired is the amount of oxalic acid that would need to be contained in the B&S powder (OB) in order to equate with the amounts of oxalic acid added to achieve complete solubility. The following are known from the Oxalic Solutions and the calculation concerning the Vizcay powder above:

$$\begin{aligned} FB+OB = FV+OV &= 8.10 \text{ grams} \\ AB &= 0.50 \text{ gram} \\ OV &= 0.156 \text{ gram} \\ AV &= 1.40 \text{ grams} \\ FV &= 7.944 \text{ grams} \end{aligned}$$

OB is calculated from (derivation of equation):



$$OB = (FV * (AV+OV) + OV * (AV+OV) - AB * FV) / (FV+AV+OV)$$

$$OB = (7.944*(1.40+.156)+.156*(1.40+.156)-.50*7.944) / (7.944+1.40+.156)$$

$$OB = 0.91 \text{ gram}$$

However, note that the percentages may vary as 0.1 gram of oxalic acid was added at a time for the determination of the Oxalic Solutions. The material had not dissolved with AB = 0.40 and AV = 1.30

$$OB \text{ (low)} = (7.944*(1.30+.156)+.156*(1.30+.156)-.50*7.944) / (7.944+1.30+.156)$$

$$OB \text{ (low)} = 0.83$$

giving 10.3% Oxalic Acid

$$OB \text{ (high)} = (7.944*(1.40+.156)+.156*(1.40+.156)-.40*7.944) / (7.944+1.40+.156)$$

$$OB \text{ (high)} = 0.99$$

giving 12.2% Oxalic Acid

This means that the batch of B&S powder might be assumed to contain:  
 10% to 12% Oxalic Acid by weight;  
 90% to 88% Ferric Oxalate by weight.

## Measurements

### Specific Gravity (SG) of Ferric Oxalate Solutions

#### Equipment:

- balance scale accurate to 0.01 grams
- beaker filled with water (large enough to completely submerge the small sample bottle)
- thin wire
- counter weight to zero scale (as needed)
- sample bottle with cap (small enough to be completely submerged in the water in the beaker)

The sample bottle is filled completely so that there is no air trapped inside.

If the bottle filled with water does not sink in water, then attach a “sinker” (lead) to the bottle for all measurements and consider this part of the bottle weight (the affect is a denser bottle, negative buoyancy).

The thin wire is tied to the sample bottle with the other end looped over the scale hook.

The wire is marked at the level of the water in the beaker when the sample bottle is completely

submerged and not in contact with the beaker. The wire above the mark is considered to contribute part of the tare weight along with the counter weight. The wire below the mark is considered to be part of the sample bottle.

Procedure

- ✓ A) The sample bottle is weighed
- ✓ B) The sample bottle is filled with water and weighed submerged in the beaker with water
- ✓ C) The sample bottle is filled with a solution and weighed
- ✓ D) The sample bottle still filled with the solution is weighed submerged in the beaker with water
- ✓ The Specific Gravity is calculated as:  $SG = (C-A) / [(C-A)-(D-B)]$

Measured Data and Calculated Specific Gravity (SG) (at 64°F) [Measurement Accuracy of 0.01 gram]					
Sample		Weight of Empty bottle (grams)	Weight in AIR (grams) <b>C</b>	Weight in WATER (grams) <b>D</b>	SG (C-A) / [(C-A)-(D-B)] [Error of +- 1.2%]
bottle		6.60 (A)	11.69	3.60 (B)	
Preliminary Solutions	B&S		12.46	4.45	1.17
	Vizcay		12.43	4.61	1.21
Oxalic Solutions	B&S		12.51	4.42	1.16
	Vizcay		12.59	4.47	1.17
Straight Solutions	B&S		12.44	4.35	1.15
	Vizcay		12.48	4.38	1.15
EDTA Solutions	Vizcay		12.74	4.58	1.19
Balanced Solutions	B&S		12.79	4.58	1.19
	Vizcay		12.72	4.61	1.20
	JDM		12.59	4.50	1.18

Specific Gravity Results:

Specific Gravity of Solutions (Error of +- 2%) (temperature of 64°F)			
	B&S	Vizcay	JDM
Preliminary solutions	1.17	1.21	
Oxalic Solutions	1.16	1.17	
Straight Solutions	1.15	1.15	
EDTA solutions		1.19	
Balanced Solutions	1.19	1.20	1.18

Conversion of Specific Gravity into a Solution Concentration Percentage for FO

Page 58 of Dick Stevens' book, "Making Kallitypes" presents an abacus which relates the percent concentration of Ferric Oxalate solutions and specific gravity. From this abacus, the following formula is derived.

$$\% = 157.89474(d-1) \quad (d = \text{specific gravity})$$

Note that the Error is large due to the small volume used to measure the specific gravity.

	% Concentration of Solutions Calculated from the Specific Gravity (Error of +- 7.9%)			% concentration of solutions as made
	B&S	Vizcay	JDM	All solutions
Preliminary solutions	26.8	33.2		
Oxalic Solutions	25.3	26.8		
Straight Solutions	23.7	23.7		25.9
EDTA solutions		30.0		32.0
Balanced Solutions	30.0	31.6	28.4	30.0

## pH of Ferric Oxalate Solutions

### Equipment:

- pH meter accurate to 0.1 pH with automatic temperature compensation and calibration.
- Shot glasses. (Unless probe fits into bottle.)

### pH Results:

pH reference 7.01 measured as 7.0

pH reference 4.01 measured as 4.0

pH of Solutions			
	B&S	Vizcay	JDM
Preliminary solutions	0.4	0.7	
Oxalic Solutions	0.6	0.7	
Straight Solutions	0.7	1.0	
EDTA solutions		0.8	
Balanced Solutions	0.4	0.6	0.5

### Print comparisons:

Prints were made from all but the preliminary solutions. See [Comparing Prints from Ferric Oxalate Powders](#).

## Verification of FO Powder Composition

created October 1999

In order to achieve accuracy and consistency, it is important to begin with an accurately formulated sensitizer to which the metal solution will be balanced. The active Ferric Oxalate content needs to be determined. The Comparison of FO Powders Study demonstrated that FO Powders may not all contain the same amount of or 100% ferric oxalate. That study estimated the contents of some FO powders. The purpose of this study is to verify or develop a better estimate for the ferric oxalate composition of those powders.

FO Powder	% ferric oxalate by weight, estimated (from Comparison of FO Powders)
Vizcay	98 %
Bostic & Sullivan	89 %

Dick Stevens, in his book "Making Kallitypes", presents a method to relate the percent concentration of Ferric Oxalate (FO) solutions with their specific gravity. From this method, the following formula is derived.

$$\% = 157.89474 * (SG-1)$$

where: % = percent concentration of FO solution  
 SG = specific gravity

### Expected Accuracy

In order to achieve enough accuracy, a large enough volume of sensitizer must have its specific gravity measured. The 71 ml of solution measured in this study with dry chemicals weighed at an accuracy of 0.01 grams resulted in a measured Specific Gravity accuracy of +0.4% and a calculated percent concentration accuracy of +-3%. This would mean that a calculated percent concentration of 27.0% could range from about 26.2% to 27.8% (or about 26% to 28%). Any conclusions must consider this range of error, and caution should be exercised whenever differences fall within the error range.

26%

### Sample preparation

Since the Vizcay FO powder has demonstrated the highest content of ferric oxalate, it was selected for this study. Several sensitizer solutions were mixed and measured at the following estimated concentrations. The concentrations were centered around an estimated 26-27% as per the findings of the FO Threshold Study.

The first solution in the following table was mixed and measured; then EDTA was added and the

solution measured again; then Oxalic Acid was added and the solution measured again; then more Oxalic Acid was added and the solution measured again. These steps were to isolate influences of the specific gravity measurement by the Oxalic Acid and EDTA. Next the concentration of the FO is increased incrementally by adding FO powder and measured as indicated in the following table. The slight increase in Oxalic Acid from the powder added should be considered negligible.

Sample	grams Vizcay FO powder	grams FO powder added to previous sample	total grams EDTA (Na4) (% concentration)	total grams Oxalic Acid [including contents of the FO powder, as above] (% concentration of total Oxalic Acid)	grams Oxalic Acid added to previous sample	amount in ml after dissolving by adding H2O	estimated FO concentration (from content listed above)
A	17.37	0.00	0.00 (0%)	0.33 (.47%)	0.00	71	24%
B	18.10	0.73	0.00 (0%)	0.33 (.47%)	0.00	71	25%
C	18.10	0.00	2.13 (3.0%)	0.33 (.47%)	0.00	71	25%
D	18.10	0.00	2.13 (3.0%)	1.07 (1.5%)	0.74	71	25%
E	18.10	0.00	2.13 (3.0%)	1.78 (2.5%)	0.71	71	25%
F	18.10	0.00	2.13 (3.0%)	2.49 (3.5%)	0.71	71	25%
G	18.82	0.72	2.13 (3.0%)	2.52 (3.5%)	0.014	71	26%
H	19.54	0.72	2.13 (3.0%)	2.53 (3.6%)	0.014	71	27%
I	20.27	0.73	2.13 (3.0%)	2.55 (3.6%)	0.014	71	28%
J	20.99	0.72	2.13 (3.0%)	2.56 (3.6%)	0.014	71	29%

Notes: Extra solution was prepared so as to be available to top off contents of the sample bottle as some losses would occur on capping and opening. No record was kept of any losses or displacement of solution due to the addition of solids. The initial mixture (A) required 63.2 ml H<sub>2</sub>O to make the 71 ml sample bottle volume.

The addition of EDTA and / or Oxalic Acid is important as the pure FO will typically only attain a concentration of less than 26% with typical lab temperature and pressure.

### Measurement of Specific Gravity (SG)

#### Equipment:

- balance scale accurate to 0.01 grams
- container filled with water (large enough to completely submerge the sample bottle)
- thin wire
- counter weight to zero scale (as needed)
- sample bottle with cap (small enough to be completely submerged in the water container without touching the container).

#### Preparation:

- ✓ The sample bottle is filled completely so that there is no air trapped inside.
- ✓ If the bottle filled with water does not sink in water, then attach a “sinker” (lead) to the bottle for all measurements and consider this part of the bottle weight (the affect is a denser bottle, negative buoyancy).
- ✓ The thin wire is tied to the sample bottle with the other end looped over the scale hook.
- ✓ The wire is marked at the level of the water in the container when the sample bottle is completely submerged and not in contact with the container. The wire above the mark is considered to contribute part of the tare weight along with the counter weight. The wire below the mark is considered to be part of the sample bottle.

#### Procedure

- ✓ A) The sample bottle is weighed
- ✓ B) The sample bottle is filled with water and weighed submerged in the container of water
- ✓ C) The sample bottle is filled with a solution and weighed
- ✓ D) The sample bottle still filled with the solution is weighed submerged in the container of water
- ✓ The Specific Gravity is calculated as:  $SG = (C-A) / [(C-A)-(D-B)]$

Measurement and Data - temperature of 62-68°F

Measured Data and Calculated Specific Gravity (SG) (at 62-68°F) [Measurement Accuracy of 0.01 gram]						
Sample	Weight of Empty bottle in AIR (grams) <b>(A)</b>	Weight of bottle filled with water submerged in WATER (grams) <b>(B)</b>	Weight of bottle filled with solution in AIR (grams) <b>(C)</b>	Weight of bottle filled with solution submerged in WATER (grams) <b>(D)</b>	<b>SG</b> $(C-A) / [(C-A)-(D-B)]$ [ error of +- 0.4% ]	Temperature (°F)
bottle	77.73	44.22	-	-	-	68
A	-	-	157.43	54.55	1.149	65
B	-	-	157.71	54.95	1.155	68
C	-	-	158.29	55.42	1.161	62
D	-	-	158.48	55.61	1.164	62
E	-	-	158.64	55.82	1.167	62
F	-	-	158.68	55.88	1.168	66
G	-	-	158.96	56.11	1.171	64
H	-	-	159.45	56.59	1.178	64
I	-	-	159.96	56.90	1.182	64
J	-	-	160.63	57.56	1.192	64

Note: The accumulated weights of added solids may not be apparent in (C) as some volume may have been displaced. The sample bottle was always completely filled and capped so as to prevent any air bubbles. However no attempt was made to measure changes in absolute volume measured or volume displaced.



Conversion of Specific Gravity into a Solution Concentration Percentage for Ferric Oxalate using the Dick Stevens' Relationship			
Sample	Estimated % concentration	Measured Specific Gravity [ error of +- 0.4% ]	Calculated % concentration [ error of +- 3% ]
A	24%	1.149	23.5%
B	25%	1.155	24.5%
C	25%	1.161	25.4%
D	25%	1.164	25.9%
E	25%	1.167	26.4%
F	25%	1.168	26.5%
G	26%	1.171	27.0%
H	27%	1.178	28.1%
I	28%	1.182	28.7%
J	29%	1.192	30.3%

#### Analysis

Although within the error, the Stevens' Calculation of percent concentration seems to not agree with the measurements. Before the addition of any Oxalic Acid or EDTA, the values are about 0.5% lower than the estimated, and for measurements after all additions of Oxalic Acid and EDTA, the values are about 1% greater than the estimated. This may be remedied in one of two ways.

- ▶ The Ferric Oxalate made by Vizcay is less pure than estimated.
- ▶ The Ferric Oxalate used by Stevens contained some Oxalic Acid (or other material) which caused his values for concentration to be too high. This could have been caused by a 1% solution concentration of Oxalic Acid in his FO solution.

## Comparing Prints from Ferric Oxalate Powders

created October 1999

Initially done as a test of the Viscay FO manufacturing process, this study complements the study of the Initial Comparisons of Ferric Oxalate Powders. Further comparison is made in the study of the Relative Comparison of FO powders.

The author has used the Ferric Oxalate (FO) powder manufactured by Bostic and Sullivan (B&S) since about 1987. This has been an excellent product in both consistency and quality which was regarded as a standard for this test by which to compare other ferric oxalate.

Working solutions identified during the comparison of several FO powders were made.

First, the FO Test described in the guide was run. The FO solutions behaved as it should and passed test. This test basically just indicates if it is working in general, or perhaps contaminated, or not of high purity.

Second, tests for clearing and fogging were performed. Clearing was complete, with clearing agent and times typically used for the paper selected. There was no noticeable fogging.

Third, identical prints using FO powder made by Vizcay (Vizcay FO), this author using Vizcay's process (JDM FO) and Bostic & Sullivan (B&S FO) were compared (keeping all other things as equal as possible). Prints were made using Crane's Parchment Business Card Stock (AKA: Cover 90) paper. All prints received identical coating technique (by brush), identical exposure, and identical processing using the same negative and a 21-step.

### Preliminary Prints and Results

Four sensitizer solutions (the Oxalic Solutions and Straight Solutions from the Comparison of FO powders) were used to make prints.

The solutions were:

#### Prints from Oxalic Solutions:

- A) 16.20 grams B&S FO powder, plus 52.5 ml H<sub>2</sub>O, plus 0.50 g Oxalic Acid
- B) 16.20 grams Vizcay FO powder, plus 52.5 ml H<sub>2</sub>O, plus 1.40 g Oxalic Acid

#### Prints from Straight Solutions:

- C) 25.9 % solutions B&S FO powder only (no additional Oxalic Acid)
- D) 25.9 % solutions Vizcay FO powder only (no additional Oxalic Acid)

Preliminary observations indicated:

- ▶ Both A & C (B&S powder) are slightly warmer in color than B & D (Vizcay powder).
- ▶ A & C are the same color
- ▶ B & D are the same color
- ▶ A & B (Oxalic Solutions) show more sharpness and better tonal discrimination than their counterparts, C & D (Straight Solutions). It can not yet be determined if the observed effects are due to the Oxalic Acid or the higher solution concentrations. Further study is planned. (See the study Oxalic Acid Concentration in the FO Sensitizer.)
- ▶ A & B (Oxalic Solutions) seem prone to solarization effect in values below zone I.
- ▶ A & B (Oxalic Solutions) have the same speed and contrast.
- ▶ C & D (Straight Solutions) have the same speed and contrast.
- ▶ C & D (Straight Solutions) are almost 1/2 stop faster than their counterparts A & B (Oxalic Solutions) and have the same contrast.

Aside from the color mentioned, no substantial difference was detected in the prints between Vizcay's FO powder and the standard B&S FO powder. Difference were noted in that the prints from the Oxalic Solutions were about 1/2 stop slower, had better sharpness, and had better tonal discrimination than prints from the Straight Solutions.

#### Prints and Results from Balanced Solutions

In order to make an accurate comparison, sensitizer solutions were made having the same concentration of ingredients as best as could be determined from the Comparison of FO Powders study. The Ferric Oxalate was mixed to a solution strength of 30%. The metal solutions were mixed as optimized to be used with the 30% FO.

Prints were made using the following solutions of Ferric Oxalate sensitizer.

#### Prints from Balanced Solutions:

- E) 8.45 grams B&S FO powder (assumed to contain 0.91 g Oxalic Acid & 7.54 g FO)  
1.00 gram EDTA (Na<sub>4</sub>)  
0.04 gram Oxalic Acid  
H<sub>2</sub>O to make final volume of 25.12 ml  
(concentrations: 30% FO, 3.8% Oxalic Acid, 4% EDTA)
  
- F) 7.65 grams Vizcay FO powder (assumed to contain 0.15 g Oxalic Acid & 7.50 g FO)  
1.00 gram EDTA (Na<sub>4</sub>)  
0.80 gram Oxalic Acid  
H<sub>2</sub>O to make final volume of 25.0 ml  
(concentrations: 30% FO, 3.8% Oxalic Acid, 4% EDTA)
  
- G) 7.65 grams JDM FO powder ( assumed to contain 0.15 g Oxalic Acid & 7.50 g FO)  
1.00 gram EDTA (Na<sub>4</sub>)

0.80 gram Oxalic Acid  
H<sub>2</sub>O to make final volume of 25.0 ml  
(concentrations: 30% FO, 3.8% Oxalic Acid, 4% EDTA)

Observations of Prints from Balanced Sensitizer Solutions:

- ▶ E, F, & G have the same speed and contrast.
- ▶ The speed and contrast of E, F, & G (Balanced Solutions) is the same as A & B (Oxalic Solutions).
- ▶ E & F have the same color, G may be barely slightly warmer but very close to E & F.
- ▶ The color of E, F, & G (Balanced Solutions) appears slightly more neutral than the color of B & D.
- ▶ The very high tonal values (Zones above IX) in print G seem to be cleaner and have better definition.
- ▶ The dark values of E, F, & G (Balanced Solutions) are the same and are darker/blacker than A, B, C, & D. Prints from the Balanced Solutions did not show any signs of solarization effect, however the dark values of Zones I and II (where there was no indication of solarization effect in the prints from Oxalic Solutions) were darker/blacker as well.
- ▶ E, F, & G (Balanced Solutions) look identical in all other aspects.
- ▶ E, F, & G (Balanced Solutions) have more sharpness than C & D (Straight Solutions), but not quite as much as A & B (Oxalic Solutions).
- ▶ E, F, & G (Balanced Solutions) and A & B (Oxalic Solutions) have excellent and close to identical tonal discrimination.

Additional prints using sensitizer E, F, & G were made on Bienfang 360 and repeated on the Crane paper with a different negative and the 21-step. Results were identical to and confirmed those above.

No substantial difference is observed between the Balanced prints E, F, & G, except for the slightly better upper highlight definition found in print G. The improved upper highlight definition may be related to preparation conditions of the FO powder; further study is warranted.

Conclusions

Vizcay's preparation procedure allows one to make an unsurpassed, high quality Ferric Oxalate powder suitable for use as a sensitizer with the Pt/Pd process helping produce prints of the highest quality.

The balanced solutions produce identical prints.

## Further Study

Studies are planned to investigate the effects of the amount of Oxalic Acid and pH of the FO sensitizer solution; the threshold of total concentration of the coating mixture, and preparation conditions (including residual HNO<sub>3</sub> content) which may affect highlight values. Other studies of merit could include investigations of other sensitizer solutions and other preparation methods. The measurement of specific gravity should be improved so as to make an accurate method of mixing known Ferric Oxalate concentrations.

## Relative Comparison of FO Powders Using Prints

created December 1999

In order to achieve accuracy and consistency in Pt/Pd prints, it is important to begin with an accurately formulated sensitizer to which the metal solution will be balanced. Determining the absolute active Ferric Oxalate content of a selected powder may be of a higher than desired difficulty level and require sophisticated laboratory equipment. The author considers chemistry operations such as titration to be of a more advanced level than typically practiced by the Pt/Pd printer. A relative comparison was devised and presented below to compare different FO powders and determine a solution concentration for them which would meet or exceed the threshold needed to produce maximum quality prints. The threshold is that point at which no additional metal in the final print can be seen to make a difference.

The Comparison of FO Powders Study indicated that FO Powders are not all the same. That study attempted to estimate the contents of some FO powders. The Verification of FO Powders Study attempted to estimate FO content using the specific gravity of solutions. It was found that these studies could only estimate the composition of the FO powders.

Since those studies, Vicente-M Viscay has sent me three samples of powder and crystalline FO, one being an ultra-fine Ferric oxalate powder. This study investigates the threshold relative to prints using several FO powders and then compares the FO solutions. The study is outlined as follows:

### Procedure:

- ✓ First, identical solutions are made at a high concentration **assuming that all powders are 100% pure FO**. High concentration means one that should be above the threshold. In this study, 30% is used.
- ✓ A coating mixture is made by adding the appropriate metal solution for a 30% FO sensitizer for each FO powder type..
- ✓ Prints are made using these coating mixtures.
- ✓ Prints are made from incrementally diluted coating mixtures so as to determine a threshold level for each FO powder type.
- ✓ The ferric oxalate content of the ultra-fine FO powder is assumed to be as assayed by Viscay.
- ✓ All other FO powders had their ferric oxalate content calculated by normalizing them to have the same threshold relative to the ultra-fine FO powder samples.

The accuracies involved with this study were kept pertinent to the accuracy of Pt/Pd printmaking.

Weights measured to 0.01 grams.

Volumes measured to 0.05 ml (drop size as determined from 200 drops per 10.0 ml)

Sensitizer solutions varied at 1% increments (3% to 4% total volume).

Print evaluations of threshold made by both reflected and transmitted light by eye using strong light.

Sensitizer Solution Components		
Material	Description	Analysis
FO-UF	ultra-fine FO powder Product obtained: Ferric oxalate 6-hydrate Producer: Vicente-M. Vizcay Product number: Exp (15) Quality: Pure; ACS Guarantee: 98,0 - 99.5 % of purity	Guarantee Specifications (general, anions and cations) Ions Limits (always less than .. %) Free oxalic acid: 0.46% Free nitric acid: 0.77% Free water: 0.66% Chloride (Cl <sup>-</sup> ): 0,0005% Phosphate ((PO <sub>4</sub> ) <sup>3-</sup> ): -% Sulphate ((SO <sub>4</sub> ) <sup>2-</sup> ): 0,0050% As: -% Ca: 0,0020% Cd: 0,0010% Co: 0,0010% Cr: 0,0050% Cu: 0,0010% Fe <sup>2+</sup> : 0,0020% K: 0,0050% Mg: 0,0010% Mn: 0,0050% Na: -% N: -% Ni: 0,0010% Pb: 0,0010% Zn: 0,0010%
FO-V	Ferric oxalate hexahydrate Fe <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> .6H <sub>2</sub> O (CAS number: 19469-07-9) Producer: Vicente-M. Vizcay This is the FO powder used in other studies	?
FO-J	Ferric Oxalate powder Producer: Jeffrey D. Mathias Made from Vizcay FO preparation procedure	?
FO-BS	Ferric Oxalate powder Producer: Bostic & Sullivan	?
FO-AC	Ferric Oxalate powder Producer: Artcraft	?

EDTA	ethylene diamine tetra-acetic acid (EDTA). Synonyms: EDTA; Complexone II Molecular Formula: C10H16N2O8 Molecular Weight: 292.25 CAS: 60-00-4 Purity Grade: pure	
H2O	Distilled water	

Paper: Crane's Parchment Business Card Stock (AKA: cover-90; "platinotype")

Coating Mixture:

- 6 drops sensitizer solution (one of those above)
- 4 drops K2PdCl4 metal solution
- 2 drops K2PtCl4 metal solution

Coated area: 127mm x 127mm (5" x 5")

Coated by brush

Exposure: x minutes with UV -BL lamps

Processing:

- 1 minute in standard potassium oxalate bath
- 2 minutes in water bath
- 30 minutes in three clearing baths (2oz 85% H<sub>3</sub>PO<sub>4</sub> per gallon water)
- 1 minute rinse in water with baking soda
- 10 minute wash in water

Nine prints were made for each of the five FO powders in solution concentrations from 30% to 22% in 1% decrements assuming each powder was 100% pure. The threshold was determined by observation of the prints produced by each solution of each of the FO powders.

Results:

FO powder	solution percentage of sensitizer at which threshold is passed by observation of prints	calculated percentage of active sensitizer in powder based on observed threshold
FO-UF	25	98
FO-V	26	94
FO-J	26	94
FO-BS	27	91
FO-AC	26	94