Chapter 15 - Studies

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Study of Oxalic Acid Concentration in the FO Sensitizer

created October 1999

The purpose of this study was to determine what (if any) effects are related to the amount of Oxalic Acid in the Ferric Oxalate (FO) sensitizer solution.

A low Oxalic Acid solution was needed for the base of this study. The Vizcay "EDTA Solution" from the Comparison of FO Powders study was modified so as to provide a 30% FO solution.

8.00 grams Vizcay FO Powder (estimated to contain 0.15 g Oxalic Acid & 7.85 g FO)
1.05 gram EDTA (CAS: 60-00-4)
H_2O to make 26.2 ml when completely dissolved

The composition of this Base Solution contains concentrations of

30% ferric oxalate
4% EDTA (CAS: 60-00-4)
0.587% oxalic acid

The metal solution formulas used with this 30% FO sensitizer can be determined using the Formula Calculator or Quick Formula Table in Chapter 6, Optimized Formulas for Metal Solutions. A coating mixture was mixed consisting of:

7 drops sensitizer (described above) (30 % solution)
5 drops K_2PdCl_4 solution (20.2 % solution, warmed)
2 drops K_2PtCl_4 solution (25.7 % solution, warmed)

The remaining Base Solution had oxalic acid added, another coating was produced, and this was repeated until the following coating mixtures were made containing the following concentrations of Oxalic Acid. The pH of the sensitizer solution was measured, but not of the coating mixture. There were concerns that pH measurement of the relatively small amounts of coating mixture might alter the amount of the coating mixture as the probe can carry off several drops.

% concentration Oxalic Acid in sensitizer solution	pH (± 0.1)
0.587	0.6
1	0.3
2	0.1
3	0.0
4	0.0
5	0.0
6	0.0
8	0.0
10	0.0

- Ambient conditions were temperature of 66ºF, relative humidity of 34-36%.
- 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 inches2 or 161 cm2)
- All were dried by the dry method (see Drying the Coating).
- All were exposed with the same negative and a 21-step for 10.5 minutes under UV lamps.
- All were processed the same:
  - ✓ developed in Potassium Oxalate
  - ✓ 2 minutes water bath
  - ✓ 30 minutes total clearing in H_3PO_4 (3 baths).
  - ✓ Buffered rinse and 10 minute wash.

Observations

At first look all the prints seemed identical. Closer observation revealed that:

- ‣ As Oxalic Acid concentration increased the speed may decrease by about 0.125 stop from 0.587 to 10. This is not a large change, but noticeable on the 21-step.
- ‣ Prints with Oxalic Acid concentrations above 2% seem to have better tonal discrimination and separation (perhaps from an edge effect) and better sharpness.
- ‣ Prints with Oxalic Acid concentrations above 5% seem to be fuzzier (perhaps from some increased graininess, increasing with 10 having the most). The fuzziness offsets (6%) and then more than offsets (8% & 10%) any gain in sharpness.

Conclusions

Oxalic Acid concentration from 2% to 5% in the sensitizer solution may be beneficial providing better sharpness and better tonal discrimination with higher concentrations progressively causing graininess. The resulting effects are very slight.

Study of the Clearing of Pt/Pd Prints

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This study has documented some very significant findings concerning the clearing of Pt/Pd prints. This study makes use of the revised clearing test involving the use of Potassium Ferricyanide as an indicator. Thanks to John Melanson for suggesting the use of this indicator.

Several past observations have been made and verified and can be considered general trends concerning clearing.

- Most thin papers clear better and/or faster than thicker papers.
- POP type prints using Ammonium Ferric Oxalate sensitizer may clear in about half the time of DOP type prints using Ferric Oxalate sensitizer. This from previous work and not investigated further in this study.
- Prints made with a lower solution concentration of the coating ingredients will clear slightly faster. However, it must be remembered that a certain threshold concentration must be used to avoid weak prints. This from the Threshold Study.

The most significant finding with this study is that an addition of Oxalic Acid and EDTA to the sensitizer solution dramatically reduces clearing times. (See the procedure and results below for details.)

Only single agents were used for this study. It is suspected that a series of multiple agents might provide improved clearing, however the possibilities of combinations are numerous and may become a mute point at the conclusion of this study.

CRITICAL CONSIDERATIONS:

It is most important that the following be considered carefully as they can have a dramatic influence on clearing investigation. All relate to fogging, which may appear to be incomplete clearing.

- A safe light MUST be used. Work lights must be tested to assure that they will not fog the coating. Sodium vapor lights are an excellent choice.
- Coating brushes should be kept clean. Old sensitizer material can get into the print causing a fogging effect. Brushes should be rinsed well in distilled water and squeegeed dry with a paper towel after each use. Brushes should then be stored in a light tight box or bag.
- Fresh developer should be used. Developer that has been used for many prints may contain exposed material that may react with or lodge onto coatings causing a fogged appearance.

This was a culprit in this study resulting in a lack of clearing in a reasonable time. When new developer was used, the repeated tests showed dramatically improved clearing. It should be routine practice to replace the developer rather than continuously replenish.

- Cross contamination can be a problem. The initial clearing indicator of a 10% solution of Potassium Ferricyanide proved to be too sensitive. Uncoated samples were processed along with the other samples and although nothing could be detected without the indicator, the indicator would show some blue. Cross contamination is suspected to occur from used developer, rinse, clearing baths, and especially wash water. When samples were processed individually with fresh solutions and wash water, the false indications did not occur. However, it was not practical to process hundreds of samples with individual fresh baths and washes. Thus, a 1% solution of Potassium Ferricyanide was prepared and applied by smearing a little on with a clean, fresh Q-tip.

  Notes: If a Q-tip with indicator solution touches an uncleared sample, it can produce false blue indications on a cleared sample. Also it is recommended to use a dropper to drop indicator solution onto the Q-tip, without touching. Do not dip the Q-tip into the solution. Also any trace of metal in the Potassium Ferricyanide solution may give a false blue color.

- Evaluation was made relative to any indication on uncoated samples. This cross contamination is not critical for individual prints, but should be a consideration for producing archival prints. The final clearing bath and wash water should always be fresh. Also it must be remembered that the clearing indicator can be so sensitive as to give false indications and should be checked and referenced with a uncoated control.

MATERIALS:
For simplicity, only one paper was used, Crane's paper (lot# 5302). This is a thick and traditionally long to clear paper (typically 40 to 60 minutes, sometimes longer). Other papers may have different clearing times and/or respond to various clearing agents differently.

Several clearing agents were tested. Water was 0.5 um filtered tap water.

Code (used for this study)	Agent	Description
P	Phosphoric Acid (H_3PO_4)	2 ounces of 85% reagent grade per 1 gallon water
C	Citric Acid	20 grams per 1000 ml water (2% solution)

S	Sodium Bisulfate	20 grams per 1000 ml water (2% solution)
F	Sprint Fixer Remover	label directions (1 part plus 9 parts water)
E	EDTA (Na4)	40 grams per 1000 ml water (4% solution)
W	water	0.5 um filtered tap water

Notes: HCl (Hydrochloric Acid) was not included because previous use has demonstrated that it can bleach the highlights of the print. However, the HCl may work fine (without bleaching) at the shorter clearing times this study demonstrates and should not be dismissed without further testing.

Potassium Meta Bisulfite worked well but gave off too much sulphurous fumes so was eliminated from most of the tests and is not reported.

Several Ferric Oxalate powders were investigated. However, results were a factor of the additives rather than the powder used. The Vizcay powder was selected as its composition and purity is best known. The addition of Oxalic Acid and EDTA to the sensitizer made a significant difference in clearing ability. 3% Oxalic Acid was included because previous study indicated an advantage of having from 2% to 5% and 3% is typically used. 3% EDTA was initially selected being the same concentration as the Oxalic Acid. When used together, 1% EDTA was found to be more than adequate.

The EDTA was subsequently reduced to a range of 0.04% to 0.1% from the 1% used in the Clearing Study. The reason was that some "bleeding" of the metals may occur in the print noticeable as washing off or flowing through the substrate. The "bleeding" did not occur at the lower amount.

Sensitizer and Additives Tested	
Sensitizer Code	Description
V	Vizcay Ferric Oxalate at 24% (Vizcay's preparation procedure)
VO	Vizcay Ferric Oxalate at 24% plus Oxalic Acid at 3%
VE	Vizcay Ferric Oxalate at 24% plus EDTA at 3%
VOE	Vizcay Ferric Oxalate at 24% plus 3% Oxalic Acid plus 1% EDTA

for example:
VOE = 24.00 g FO + 3.00 g Oxalic Acid + 1.00 g EDTA + H_2O to make 100 ml

EDTA used as a sensitizer additive was ethylene diamine tetra-acetic acid
Synonyms: EDTA; Complexone II
Molecular Formula: C10H16N2O8
Molecular Weight: 292.25
CAS: 60-00-4
Purity Grade: pure
Note: This is NOT the same EDTA(Na4) used as a clearing bath. The EDTA(Na4) tested as a clearing bath was some sent to me by John Melanson.

The metal salt solutions were K_2PdCl_4 (16.2%) and K_2PtCl_4 (20.6%) in a ratio of 5 parts Pd and 2 parts Pt. The strengths of these solutions is that calculated to work with the 24% FO sensitizer strength.

PROCESSING:
All samples were processed as follows:

- ✓ coating mixture mixed (as for a 4x5 print)
- ✓ brush coated (with coating edges indicated and as instructed in Test for Clearing)
- ✓ dried
- ✓ identified with marks and then cut into samples
- ✓ 1 minute in Potassium Oxalate (developer and all baths at ambient temperature)
- ✓ 2 minutes in water
- ✓ # minutes in clearing agent
- ✓ 5 minute wash in water
- ✓ dried
- ✓ evaluated
- ✓ exposed for 12 minutes with UV lamps (about double typical printing time)
- ✓ Potassium Ferricyanide (1% solution) applied (smeared on with clean Q-tip) to part of coated area
- ✓ 2 minutes rest
- ✓ 10 minute wash to remove all yellow from Potassium Ferricyanide
- ✓ dried
- ✓ evaluated

Note: If one uses a different developer or different conditions, those should be used for the test.

IDENTIFICATION & NOMENCLATURE:
Samples are referred to as X# where
X = the code letter of the clearing agent
# = number of minutes in the clearing agent

Observations of the evaluations are coded as follows:

CODE	color	Description
For areas without Potassium Ferricyanide: (colors shown are approximate)		
x		no sample
0		identical to uncoated paper
1		very faint gray color (the slightest distinction)
2		light gray color
3		gray color
4		light brown or light yellow-brown color (may include gray)
5		brown or deep yellow-brown color (similar to coating color)
For areas with Potassium Ferricyanide: (colors shown are approximate)		
no code		no change
a		faint blue color
b		blue color

Note: Consideration should be given for unnecessary cross contamination and any slightly "0a" rated samples might be considered completely clear.

For example:

3b - means the coated area was a gray color and the area with Potassium Ferricyanide was a blue color.

1 - means the coated area was only a very faint gray color and the area with Potassium Ferricyanide showed no change (remained a very faint gray color).

OBSERVATIONS:
The following clearing results as a function of agent and time are shown for several sensitizers. The last data set compares use of an old developer.

Time (minutes) >	5	10	15	20	30	40
For V sensitizer (FO only):						
P	5b	4b	x	3b	2b	1a
C	5b	4b	x	3b	1b	1b
S	5b	4b	x	3b	2b	1a
F	2b	1b	x	1a	0a	0a
E	4b	3a	x	2a	2	2
W	5b	5b	x	4b	4b	4b
For VO sensitizer (FO + OA):						
P	2b	1b	x	1b	1b	1a
C	1b	1b	x	1a	1a	0a
S	2b	2b	x	1b	1b	1a
F	1b	1b	x	0	0	0
E	1a	1a	x	1a	0	0
W	3b	1b	x	1b	0b	0b
For VE sensitizer (FO + EDTA):						
P	1a	1a	1	0	0	x
C	1a	1	1	0	0	x
S	x	x	x	1a	0	x
F	1a	1a	0	0	0	x
E	1a	0a	0	0	0	x
W	x	1b	x	x	1a	x

Time (minutes) >	5	10	15	20	30	40
For VOE sensitizer (FO + OA + EDTA):						
P	0a	0a	0a	0a	x	x
C	0a	0a	0a	0a	x	x
S	0a	0a	0a	0	x	x
F	0a	0a	0	0	x	x
E	0a	0a	0	0	x	x
W	1b	1b	0b	0a	x	x
For comparison, with old developer VOE gave the following results:						
P	2b	2a	2a	2a	1a	x
C	2b	2b	2a	1a	1a	x
S	2b	2b	1a	1a	1a	x
F	2	2	1	1	1	x
E	2	2	2	2	1	x
W	2a	2a	2a	2	2	x

CONCLUSIONS:

★ The addition of either Oxalic Acid or EDTA to the Ferric Oxalate (FO) sensitizer solution improved clearing and reduced clearing times.

★ Best clearing results were obtained when both Oxalic Acid and EDTA were added. Note that even water (without any clearing agent) cleared completely in 20 minutes plus wash when both Oxalic Acid and EDTA were added.

★ A used developer can dramatically hinder clearing.

★ The choice of sensitizer additive and a fresh developer is more important to good clearing than the choice of clearing agent.

RECOMMENDATIONS:

★ For proper clearing of Pt/Pd prints it is recommended that Oxalic Acid (3%) and EDTA (0.04%) be added to the Ferric Oxalate sensitizer solution.

Notes: Previous work from the Threshold Study has shown the addition of up to 5% of Oxalic Acid to the sensitizer does not seem to degrade the quality of the print.

Work subsequent to this study reduced the EDTA from 1% to 0.4% then added 8/2001: Further study of the "bleeding" of metal during processing has indicated that too much EDTA seems the culprit. It is now recommended that EDTA in the sensitizer be kept to a solution strength of between 0.04% and 0.1%. The actual amount can vary with different papers, so the smallest amount of EDTA to add to the sensitizer to assist with clearing should be determined for each paper.

★ Since Potassium Meta Bisulfite produces a strong sulphurous odor (especially when used in an open tray), it is NOT recommended as a clearing agent.

★ Sprint Fixer Remover is a good choice for the selected paper as it provided the best and fastest clearing in every case. A different paper may favor another clearing agent.

★ A total wash time of 10 minutes with at least one change of fresh water is recommended.

★ Recommended times for clearing the selected paper (CP) are:
- 10-15 minutes for the Sprint Fixer Remover or EDTA(Na4) giving a total processing (develop through wash) time of 23-28 minutes.
- 15-20 minutes for Sodium Bisulfate giving a total processing (develop through wash) time of 28-33 minutes.
- 20 minutes for Phosphoric Acid or Citric Acid giving a total processing (develop through wash) time of 33 minutes.

★ It should be routine practice to replace the developer after a large amount of coatings while replenishing for developer carried off by prints.

Have a clear day.

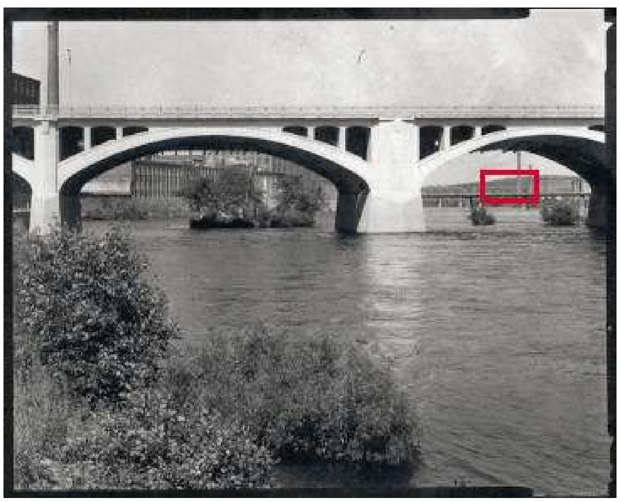
A Look at Grain in the Film and Details in the Print

created December 2000 (original data May 1986)

A negative with more pronounced grain can allow for better detail in the Pt/Pd print. It seems that edges of tones in a Pt/Pd print are better discriminated when there is adequate grain in the negative.

The same scene is recorded on films having different grain. Of the films selected, Tri-X has a good amount of grain and Tech-Pan has almost no grain. Pt/Pd prints are made from each negative and compared. The negatives have been reversed for ease of comparison. Please be aware that some of the details of interest are on the order or smaller than the resolution of the scan (1200 ppi); the originals viewed with a magnifier demonstrate this effect better than these scans.

The selected portion of the full 4x5 negative is as approximately indicated here:

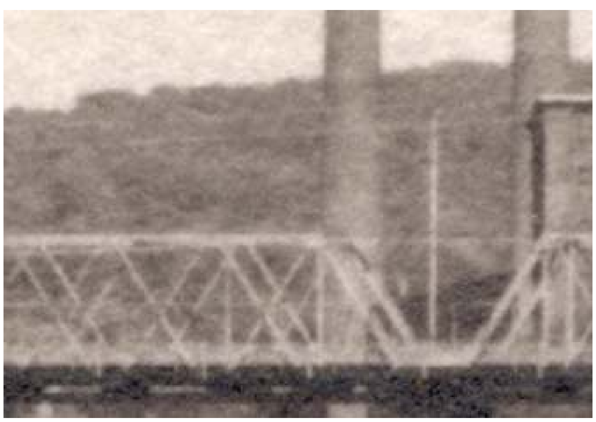


A Look at Grain in the Film and Details in the Print

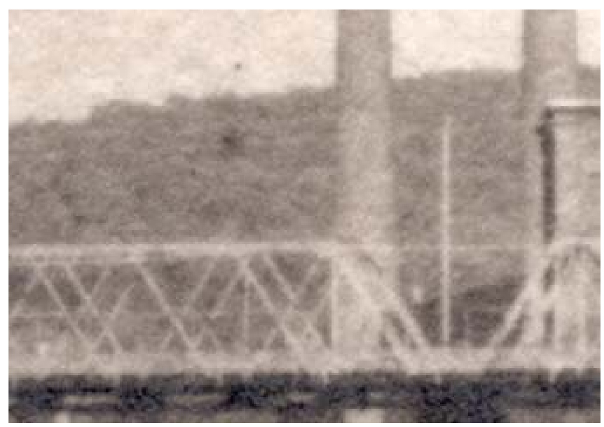
Portion of Tri-x negative.

Portion of Tech-Pan negative.

Notes: Note better details in the Tech-Pan negative.
What looks like grain in the negatives (above) is only artifacts of the scan.
What looks like grain in the prints (below) is the texture of the paper surface.



Pt/Pd print from Tri-X negative.
This print has better detail than the print from the Tech-Pan negative. The power lines are especially better discerned when viewed with a magnifier.



Pt/Pd print from Tech-Pan negative.
The power lines merge in places even when viewed with a magnifier. Also note less of an edge definition of the stacks, and less bridge detail.

Note: No sharpening was used in any of the images. The negatives and prints were scanned at 1200 ppi. Many differences are outside of the scan resolution, but can be observed with a magnifier.