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The Removal of Low Concentrations of Heavy Metals from Photographic Processing Effluents Using a Modified Crovex Silver Recovery Metallic Replacement System

John W. Miller Jr

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THE REMOVAL OF LOW CONCENTRATIONS OF HEAVY METALS FROM PHOTOGRAPHIC PROCESSING EFFLUENTS USING A MODIFIED CROVEX® SILVER RECOVERY METALLIC REPLACEMENT SYSTEM

by

John W. Miller, Jr.

A thesis submitted in partial fulfillment of the requirements for the degree of Bachelor of Science in the School of Photographic Arts and Sciences in the College of Graphic Arts and Photography of the Rochester Institute of Technology

April, 1982

Signature of the Author...........................................................

Photographic Science and Instrumentation Division

Certified by.................................................................

Paul D. Berg

Thesis Advisor

Accepted by.................................................................

Ronald Francis

Coordinator, Undergraduate Research

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ROCHESTER INSTITUTE OF TECHNOLOGY
COLLEGE OF GRAPHIC ARTS AND PHOTOGRAPHY

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THE REMOVAL OF LOW CONCENTRATIONS OF HEAVY METALS FROM PHOTOGRAPHIC PROCESSING EFFLUENTS USING A MODIFIED CROVEX® SILVER RECOVERY METALLIC REPLACEMENT SYSTEM

by

John W. Miller, Jr.

Submitted to the Photographic Science and Instrumentation Division in partial fulfillment of the requirements for the Bachelor of Science degree at the Rochester Institute of Technology

ABSTRACT

Parameters have been established for effective removal of low concentrations of silver and cadmium from photographic processing effluents using a CROVEX® silver recovery metallic replacement system. Parameters include: total photographic processing effluents (composed primarily of wash effluent, fixer, and developer), residence time, pumping pressures, and maximum heavy metal input. Techniques using these parameters yield silver and cadmium removal approaching 98%.
ACKNOWLEDGEMENTS

I would like to thank the E. I. DuPont de Nemours Co. for the numerous use of equipment, time, and facilities. Thank you to all the people of the DuPont Company who helped with this thesis especially Paul D. Berg who served as my research advisor and Larry B. Friar who helped with substantial technical information.
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INTRODUCTION

Photographic processing effluent may contain potentially toxic chemicals, some of which are heavy metals.\textsuperscript{1,2} Heavy metals found in photographic processing effluent include: zinc, cobalt, cadmium, chromium, copper, and silver.\textsuperscript{3,4} Silver, along with chromium (found in reversal and color processes) are major concerns of the photographic industry because of higher silver prices and regulations governing heavy metal discharge.\textsuperscript{5}

Most forms of silver found in photographic effluent include: silver metal, silver thiosulfate, and silver sulfide which are harmless to the environment and are easily removed by treatment plants. Other forms of silver such as silver nitrate are extremely toxic because of reactions with other compounds that may reduce oxygen levels that help to break down sewage components.

Regulatory agencies do not differentiate between various silver forms, but prohibit disposal above specified concentrations.\textsuperscript{6,7} In 1977 Kodak surveyed 108 municipalities selected according to size and geographical location as a cross section. The results found: \textsuperscript{8} Table 1

\begin{tabular}{l l}
No Silver Limit at all & 72 cities \\
Remainder did have a limit & 36 cities \\
Average of the 36 & 2.8 ppm \\
\end{tabular}
Concentrations are normally expressed in parts per million (ppm). Used fixer contains 2000-6000 ppm silver and after common electrolytic silver recovery treatments contains 100-1000 ppm. Wash water typically contains several ppm of silver and other heavy metals. Effluents from color processing are usually low in silver concentration but are substantially higher for black and white negative processing. Common values encountered are far above the U. S. Public Health Services limit of .05 ppm limit for drinking water and exceed permissible values in many municipal sewer codes.\(^9\)

Until recently, attention to silver recovery has been directed towards methods for recovering silver from concentrated silver bearing solutions, such as used photographic fixers for small photographic processing facilities. The bulk of the literature addresses techniques for this type of recovery and low level recovery for large photographic processing facilities.

Increasingly stringent sewer codes, high silver prices, and environmental concerns have directed attention to ways to remove any silver, present in low concentrations, from photographic processing effluent, including wash water.

Several methods are available for silver recovery.
The most common methods can be classed as electrolytic, chemical precipitation, reverse osmosis and ion exchange, and metallic replacement.

Electrolytic recovery is fast, yields high purity silver, has low maintenance, and requires electrical power. Electrolytic recovery is popular; however, silver levels are not reduced easily below 200 ppm.\textsuperscript{10,11}

Chemical precipitation reduces silver levels below 10 ppm and is most effective. The disadvantage is the need of a skilled chemical operator. Chemical precipitation does not work well on dilute solutions.\textsuperscript{12,13}

Reverse osmosis and ion exchange systems help conserve water and energy; however, they require an initial high capital outlay and are usually suitable only for large processing laboratories.\textsuperscript{14}

Metallic replacement is a method which depends on the known chemical principle that a metal, in elemental form, will replace a metallic ion from a compound in solution if the compound is a metallic ion lower in the electromotive series.\textsuperscript{15,16,17,18}

Many types of metals have been found to be suitable for metallic replacement. The metals most useful are composed of copper, iron, aluminum, zinc, and bronzes. The lighter metals, however, generate sulphide when the effluent is on the alkaline side through interactions with sulphite usually
present, and are rarely employed.\textsuperscript{19,20,21} Iron, being relatively inexpensive and effective, is most commonly used in the form of steel wool. Steel wool is a readily available material, forms large surface areas, is cheap, and is a fast precipitator. Iron, being high in the electromotive series, will remove silver and other heavy metals from processing effluent.\textsuperscript{22,23}

In simple theory, two atoms of silver will exchange for one atom of iron:

\[
\text{Fe} + 2\text{Ag}^+ \rightarrow 2\text{Ag} + \text{Fe}^{++} \quad (1)
\]

that is one part (by weight) of iron should produce 3.86 parts of silver. This theoretical rate cannot be achieved in practice because of long residence times, difficult pH control, and nonuniform solution mixing.

When fixer is acid, with pH between 5 and 6, the acid is found to etch the iron surface. The first reaction when acid fixer meets the steel wool is the formation of iron sulphide:

\[
2\text{H} + \text{S}_2\text{O}_3^- \rightarrow \text{H}_2\text{S} + \text{SO}_3^- \quad (2)
\]

\[
\text{Fe}^{++} + \text{H}_2\text{S} \rightarrow \text{FeS} + 2\text{H}^+ \quad (3)
\]

\[
\text{Fe} + 2\text{H}^+ \rightarrow 2\text{H} + \text{Fe}^{++} \quad (4)
\]

with a reduction of the thiosulphate to hydrogen sulphide.
and sulphite (eq. 3) and the precipitation of ferrous sulphide (eq. 4).

The ferrous sulphide will exchange readily with the silver to form silver sulphide (eq. 5).

\[ \text{FeS} + 2\text{Ag}^+ \rightarrow \text{Fe}^{2+} + \text{Ag}_2\text{S} \]  

(5)

The sludge formed in the metallic replacement process contains silver, iron and a substantial portion (15%) of sulphur.

Metallic replacement can be used to remove silver from wash water. Wash water is usually used in relatively large volumes, many times that of fixer for example. These large volumes have restricted the application of metallic replacement systems, which use steel wool, because canisters employed cannot tolerate the high throughput volumes required to treat a processor sized system. To handle the flow rates, a pump must be used to place the effluent under pressure. Normal cartridges cannot be used because of high pressures which cause leaks.\textsuperscript{24}

There are several metallic replacement systems for handling the large flow rates and pressures suitable for treating wash water. The Kodak Chemical Recovery Cartridge, Type 3\textsuperscript{25} is one, and the DuPont CROVEX\textsuperscript{®} Silver Recovery Cartridge is another.\textsuperscript{26} Both systems are similar in application; however, the Du Pont system has capabilities for
higher volumes and flow rates (10 - 12 gal./min. vs. 3 - 4 gal./min. for the Kodak system). Because of this high throughput capacity, the Du Pont system was chosen for this proposal.

The Du Pont CROVEX® silver recovery system was designed to work with the Dupont CROVEX® Wash-off Processors to recover silver from the processor's effluent.

CROVEX® film products work on the basis that silver halide, when developed in a gelatin layer with a tanning developer will harden the gelatin in the exposed areas. The unexposed portions of the gelatin will remain soft. The unexposed portions are washed-off the film by water at a temperature of 110 degrees F. and 60 psi. Hence the term wash-off becomes used.

The effluent contains water in large quantities with lower concentrations of silver halide in gelatin. The CROVEX® cartridge removes the silver halide by injecting the effluent with fixer. The silver halide is converted to silver thiosulfate. The effluent then passes through the cartridge filled with steel wool. The silver is removed through metallic replacement.

Theoretically, a metallic replacement system will recover more than 99% of less active heavy metals in the effluent.
Realistically, only 85% of the silver available is recovered using a metallic replacement system due to unfavorable conditions such as short residence times. Optimum conditions of permissible concentration, pH, pressure, and residence time for the recovery of heavy metals from processing effluent are not described in the literature.

The hypothesis of this study is that by establishing operating parameters on these variables (above) for the CROVEX® Filter Cartridge System, workable ranges for an
economic application in small photographic processing facilities can be made for the removal of silver and other heavy metals through metallic replacement.

**EXPERIMENTAL**

Modifications to the CROVEX® cartridge for this experimental work included the removal of the replenishment pumps and plumbing to simulate a film processor's effluent flows and electrolytic silver removal from fixer prior to cartridge processing.

![Diagram of CROVEX® Cartridge Field Layout](image)

*Figure 2: CROVEX® Cartridge Field Layout*

The effluent flowing from a processor has a pH that is dictated generally by the wash water pH, except in the case
of a chemistry dump. Since the wash water does control the effluent pH, the effluent averages a pH of 7 (or whatever the pH of the wash water; generally averages 6-8). The effect of pH on metallic replacement using iron is shown below.

Figure 3: Ag/Fe recovered vs. pH of effluent

At a pH of 6 to 7, metallic replacement using iron shows the highest rate of exchange with silver. When the pH goes up from 7 to 8 the exchange rate drops significantly as seen from figure 3.

Because small facilities have little control over
effluent pH, it will not be controlled here, but only monitored. Wash water, the major component of effluent should control the pH to about 7.

Pressure in the cartridge system between the collection tank and cartridge is controlled by the pump. With no restriction on the cartridge lines, the pump exerts a pressure of 5 psi. To study the effects of pressure on recovery of heavy metals a pressure gauge and control valve were installed between the pump and the cartridge.

With the valve, the pressure could be varied in the cartridge from 0-5 psi. The study was limited to 2-5 + .25 psi because pressure less than 2 psi created long (2 minute) transfer times between the holding tank and cartridge.

An advantage to a pressurized system is the mixing action created by the pressure and the decreased chance of channeling, where the effluent forces several paths through the steel wool lowering the chance of reaction between the steel wool and effluent.

Figure 4a: Cartridge channel effect Figure 4b: Cartridge mixing action
The mixing action promotes faster reactions by allowing fresh iron surface area to be exposed to incoming effluent.

The residence time of the effluent in an actual field operation is dependent upon a processor's wash flow rate. As the flow rates of a processor are increased, the filter cartridge system must handle the effluent faster.

The cartridge system's holding tank holds 6 gallons of effluent. When the tank fills to the six gallon level, a float switch activates the pump. When the tank level drops, a lower float switch shuts off the pump.

The residence times requires a reflection of field processors effluent flow rates which depend upon the manufacturer's recommendation. Flow rates averaged between 1½ and 4 gallons of wash water per minute, according to several film processor manufacturers. Converting the flow rates to residence time for the cartridge system, indicates residence times from 1½ to 4 minutes should be studied.

Water temperature was kept at 70° ± 2°F, a reasonable "room temperature" environment.

Concentration of silver in the effluent was varied by dilution of the used silver laden fixer entering the holding tank. Concentrations should be determined by the amount of dilution. The range of study was chosen to be from 25 to 330 ppm of silver and/or cadmium because actual field processors differ by chemistry, films processed, and replenishment rates.
Samples collected for analysis of the system were taken from the used fixer tank, effluent holding tank, and cartridge system effluent line. The measurements for pH and temperature took place in the system holding tank.

Silver was analyzed according to ANSI PH 4.37-1975 pages 9 and 37, using a Beckman atomic absorbtion spectrophotometer in the Du Pont Co., Rochester analytical lab. Calibration of the spectrophotometer was performed using standards of 2 and 3 ppm of silver. Error level ± 5%.

Cadmium analysis was performed using a Siemens x-ray analyzer and a Rochester built liquid emulsion analyzer. Calibration was performed using standards of cadmium at 1000, 500, and 125 ppm. Error level ± 2%.
Blank samples were made by dilution of non-silver laden fixer (fresh) and water to determine noise levels in both testing systems.

Effective effluent pump cycles for the unit were determined to be 6 cycles for a true reading from the cartridge. The value of 6 cycles was obtained by running a constant volume of effluent as well as a constant value of silver concentration for a series of 12 cycles. Effluent from the cartridge was tested after every cycle. When a plateau was reached in outgoing effluent silver level, more testing would not be needed.

![Graph of Ag ppm vs. Test Cycle](image)

**Figure 6:** Silver level of effluent vs. Test Cycle

The plateau should be reached once the previous cartridge effluent was replaced with the new effluent being tested.

The experimental design was a $2^3$ Factorial varying residence time, concentration of silver/cadmium, and pump pressure to determine the percentage of silver recovered. (see appendix, table 3, for experimental values and randomization).
RESULTS AND DISCUSSION

After preparing the CROVEX® Filter Cartridge for the initial tests of proper operation and a check for leaks it was found that the cartridge needed a seasoning period. The seasoning period consisted of 2 days of operation with 100 gallons of effluent processed. The percentage of silver recovered initially was low (less than 50%). After the two initial seasoning days, the cartridge efficiency increased to +90%.

The seasoning period may be due to dirt and oil on the steel wool surface. Once the surface is cleaned of the oils, the effluent can be in contact with the steel wool allowing the recovery of silver. A second reason for the seasoning may be due to the etching of the surface by the effluent. Once the etching of the old surface occurs, the recovery of silver may proceed faster.

The \(2^3\) factorial experiment was run after processing +1000 gallons (167 cycles) of effluent. Two experiments for silver recovery were run. The first experiment had losses due to improper dilutions. Data was kept for a secondary check. The second experiment was successful with only one data point out of limits. Results as follows:
**TABLE 2**

**TWO-LEVEL FACTORIALS-RANDOMIZED DESIGN**

<table>
<thead>
<tr>
<th>ORDER</th>
<th>TRIAL</th>
<th>CONC. Ag (out)*</th>
<th>1st Experiment</th>
<th>% Rec.</th>
<th>2nd Experiment</th>
<th>% Rec.</th>
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<tr>
<td>1</td>
<td>9</td>
<td>22.1 ppm</td>
<td>90%</td>
<td></td>
<td>25.6 ppm</td>
<td>88.4%</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>26.8</td>
<td>92.3</td>
<td></td>
<td>31.7</td>
<td>90.8</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>17.9</td>
<td>90.1</td>
<td></td>
<td>18.3</td>
<td>79.2</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>16.9</td>
<td>80.8</td>
<td></td>
<td>16.9</td>
<td>80.8</td>
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<tr>
<td>5</td>
<td>8</td>
<td>33.6</td>
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<td>89.8</td>
</tr>
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<td>9</td>
<td>31.8</td>
<td>85.5</td>
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<tr>
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<td>-</td>
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<td>93.5</td>
<td></td>
<td>18.3</td>
<td>91.7</td>
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* Corrected for noise in spectrophotometer

When the results are converted to percentage recovered of silver and placed in a three dimensional form, along residence time at 240 seconds, low silver concentration of 88 ppm, and high pump pressure of 5 psi give a +96% silver recovery (see Appendix, Figure 7).

When the percentage of recovered silver is compared between high and low pump pressures, it is found that the pressure has no statistical significance. (see Appendix, Table 4) Some pressure is needed for the mixing action
although it need not be 5 psi. Having a pump pressure below 5 psi may cause pumping times so long that the unit may not be able to handle a processor's effluent.

When the residence time is compared against the concentration, long residence times are shown to produce more efficient systems. The residence times, just like the pressure, is limited in range by a processor's effluent flow rate. Graphically it is shown that a leveling off of recovery percentage of silver occurs with residence time. A residence time of 1½ minutes is adequate for 90% removal yet 4 minutes are preferred for +96% removal of silver. (see Appendix, figure 8)

Using a residence time of 4 minutes and pressure of 5 psi, 60 gallons of +7,000 ppm silver laden fixer was placed through the cartridge unit. The cartridge removed +92% of the silver. Using the above parameters show that removal of silver is worked on a percentage and not on a single maximum quantity.

Using the parameters of 4 minutes residence time and 5 psi with 60 gallons of 500 ppm cadmium solution, the cartridge removed +92% of the cadmium. The cartridge is capable of removing cadmium as expected.

When low concentrations of silver (50 ppm or less) fixer were tested for cartridge efficiency, percentage removal approached +98%. Removal of 100% of the silver/cadmium may not be possible because of solid silver/cadmium particulates that are not removed by metallic exchange. This was not tested
for in this experiment.

CONCLUSION

By following the outlined parameters (above) of a residence time of 4 minutes, pump pressure of 5 psi, a pH averaging 6-8, temperature average of 70° F, it is feasible to achieve a +98% level of recovery of silver and cadmium using a CROVEX® Filter Cartridge System from photographic processing effluent.

The Kodak Survey results given in the introduction of this thesis (Table 1) indicate that this system could be used to help meet the tightening city sewer codes for small photographic facilities with a small capital outlay.

An example of using the CROVEX® cartridge and the stated parameters would be the following: a processor with wash flow rate of 1½ gallons per minute, fixer replenishment rate of 100 CC (3.4 ounces) per minute at a 1000 ppm of silver level, diluted in 4 minutes to 6 gallons of total effluent at 20 ppm of silver prior to removal. Readings from the graph (Figure 8a) for 20 ppm silver "in" yields 0.4 ppm "out" (98% efficiency). If the effluent is diluted one time after recovery, the effluent will meet the code for a level of silver less than 0.25 ppm.
By following the parameters given it is possible to use the cartridge system to meet the tightening sewer codes. As time goes on, stricter sewer codes will be enforced, which indicates a study of the use of two cartridges in series would be beneficial in extending the efficiency of the unit.
REFERENCES


3. Ibid., p. 37.


5. Ibid., p. 95.


10. Ibid., p. 134.


14. Ibid.


24. Ibid., p. 19

25. Ibid., p. 5.

26. Larry Friar, Du Pont Co., personal communication.

27. Ibid.


30. Levenson, G.I.P., p. 34.
CROVEX® SILVER RECOVERY CARTRIDGE

\( (2)^3 \) FACTORIAL

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<th>RANGE</th>
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TWO-LEVEL FACTORIAL DESIGN

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</tr>
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TWO-LEVEL FACTORIALS-RANDOMIZED DESIGN

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<td>11</td>
<td>9</td>
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<td>220</td>
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</table>

Table 3: \((2)^3\) Factorial Designed Experiment
<table>
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<tr>
<th>TREATMENT</th>
<th>RESPONSE</th>
<th>SUM OF SQUARES</th>
<th>MEAN SQUARE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>80.8, 79.9</td>
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<td></td>
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<tr>
<td>A</td>
<td>95.3, 95.3</td>
<td>169.24</td>
<td>56.41 **</td>
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<tr>
<td>B</td>
<td>92.3, 90.8</td>
<td>11.92</td>
<td>3.97</td>
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<tr>
<td>AB</td>
<td>91.7, 93.5</td>
<td>96.3</td>
<td>32.10 **</td>
</tr>
<tr>
<td>C</td>
<td>80.1, 78.2</td>
<td>7.13</td>
<td>2.38</td>
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<tr>
<td>AC</td>
<td>96.5, 96.4</td>
<td>3.51</td>
<td></td>
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<tr>
<td>BC</td>
<td>85.8, 87.4</td>
<td>7.02</td>
<td>3.99</td>
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<tr>
<td>ABC</td>
<td>90.4, 89.7</td>
<td>1.32</td>
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</table>

** F - TEST: F 2,3,0.09 = 9.5521

** Significant Terms

Table 4: Yates analysis of experiment

Contrasts

For A (Residence Time):
\[
\frac{1}{8}(95.30 + 92.60 + 96.40 + 90.05 - 80.35 - 91.55 - 79.15 - 86.60) = +4.587 \text{ average}
\]

For B (Silver Concentration):
\[
\frac{1}{8}(91.55 + 92.60 + 86.60 + 90.05 - 80.35 - 95.30 - 79.15 - 96.40) = +1.6 \text{ average}
\]

For AB (Interaction)
\[
\frac{1}{8}(92.60 + 90.05 - 91.55 - 86.60) - (95.30 + 96.40 - 80.35 - 79.15) = -3.46 \text{ average}
\]

Table 5: Contrasts for significant factors
REGRESSION ANALYSIS

The regression equation is:

\[ Y = 64.1 + 0.139 \, X_1 + 0.0674 \, X_2 - 0.0004 \, X_3 \]

(at 3 to 5 psi)

R-squared = 94.2%
R-squared = 89.9%, adjusted for d.f.

\[ X_1 = \text{residence time} \]
\[ X_2 = \text{silver concentration} \]
\[ X_3 = (X_1) \times (X_2) \]
Figure 7: Three dimensional diagram of percentage of silver recovered with factors.
Figure 8a, b: Silver level going in cartridge vs. silver level out of cartridge.
VITA

I was born on October 17, 1959 in Cleveland, Ohio. I lived in Seven Hills, a suburb of Cleveland, where I attended public school. I graduated from senior high school in June 1977. I was granted a two year scholarship to attend Cuyahoga Community College in Cleveland for an Associate of Printing Management degree. While in high school and first two years of college, I worked for The City Blue Printing Co. in Cleveland, Ohio as a process cameraman. I graduated with an Associate degree in Printing Management in June, 1979. In the fall of 1979 I enrolled in the first year of the Photographic Science and Instrumentation program at Rochester Institute of Technology. I worked for Monroe Reprographic Inc. of Rochester as a cameraman my first two years in Rochester. In the summer prior to my senior year I worked for the E. I. DuPont de Nemours Company's Rochester Plant in the Test Methods Group. The DuPont Co. allowed me to work during my senior year on projects as well as this thesis. In the spring of 1982 I accepted a job offer with the Du Pont Co., as a Technical Service Representative in Wilmington, Delaware. After graduation, on June 1, 1982, I will have started my job with DuPont.