THE PUREFLOW PF-16
SILVER ECOVERY SYSTEM

A PRACTICAL EVALUATION

By
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BACKGROUND

Metallic replacement technology has been around for an impressive amount of time with references dating back to the beginning of the Fourth Century. It was eventually understood that a metal with a more positive oxidation potential would pass into solution to replace a metal with a less positive potential. Now, jump ahead a few thousand years to the advent of photography in 1854 when metallic replacement was first suggested for removal of silver from photographic fixers using copper, zinc, or even mercury. The use of steel wool in closed containers, used in series, was first proposed in 1937 as a means of removing silver from photographic solutions. By 1959 a patent was granted for a steel wool silver recovery system, but there was little interest because silver was plentiful and its discharge largely unregulated. Although silver recovery is now practiced almost universally, metallic replacement technology has changed little since 1959.

The current devices go by many names: MRC (Metallic Replacement Cartridge), SRC (Silver Recovery Cartridge), CRC (Chemical Recovery Cartridge), Silver Cans, and Silver Buckets. One manufacturer even uses the term “ion exchange” although that term implies an entirely different technology for silver removal. For the remainder of this discussion, the term SRC will be used as it specifically refers to silver.

SRCs may be used to remove silver from X-ray fixers, graphic arts fixers, silver bearing wash waters, and from the combined silver bearing overflows generated by today’s photofinishing processes. SRCs have limited usage as primary recovery in large wholesale photofinishing labs. The vast majority of SRCs are used in mini-labs.

MINI-LAB USAGE

SRCs are well suited for silver recovery in mini-labs. Their small size is beneficial in limited mini-lab floor space. Because they work best at slow flow rates, the relatively small volume of silver bearing solution can be pumped through the SRC effectively, but still keep up with the overflow being generated. They have a fairly long life and are relatively inexpensive. Additionally, an SRC system is a passive, continuous system requiring little operator intervention.

All is not ideal however. There are well-known and well-documented shortcomings involved in using SRC systems. Perhaps the two most serious concerns are channeling and clogged drains. Yet another problem is developer intolerance. As more manufacturers design their equipment with a combined developer and silver bearing overflow, this issue will become more significant.

When silver bearing solution moves up through the bed of steel wool, it is possible for some of it to move non-uniformly, in a specific path, to the discharge point. The steel wool along this path, or channel, becomes spent and provides a way for subsequent

solution to reach the discharge untreated. When channeling occurs, the SRC must be removed regardless of its service time. The real danger is that channeling occurs unpredictably and will often go unnoticed for long periods of time. Channeling is often the reason for silver discharge violations. While improvements to SRC design have been made over the years, channeling remains a concern.

The term “metallic replacement” is quite descriptive. As one metal (silver) is collected, another metal (iron) is released. The iron is oxidized by the photographic solutions and forms iron oxide, commonly known as rust. The rust coming from SRCs can wreak havoc with drain lines. Even four-inch drain pipes can become completely choked off. Often, in a mini-lab environment, the effluent from the SRC system is the only flow to the drain for most of the day and there is little water-flow to provide a flushing effect. The problem is so prevalent that some SRC manufacturers sell additional equipment to “blast” the drains on a regular basis in an attempt to mitigate the clogging problem. Drain backups and expensive drain cleanings are common in most mini-labs using SRCs.

The presence of developers in the feed stream will seriously compromise the ability of the SRC to remove silver down to the levels required to meet most discharge limits. Developer in the cartridge causes complex chemical changes, but one easily understood factor is the pH change. SRCs are most effective at a pH between 5 and 6. Developers are in the 10-11 pH range. Developers will raise the pH and degrade performance. Although there are trace amounts of silver present, developers are considered to be non silver bearing and can be directly discharged. There are times, however, when developer becomes contaminated with silver bearing solution and should be treated. Also, some newer mini-lab equipment is not configured to segregate developer overflow.

THE PUREFLOW PF-16 SILVER RECOVERY CARTRIDGE

ECS Refining manufactures the patented PF-16 SRC that is unique among metallic replacement cartridges. Like all other SRCs it uses a bed of steel wool as the metal exchange media, but what makes the PF-16 different is the addition of a chemical inside the cartridge.

ECS claims that the PF-16 overcomes problems such as developer intolerance, channeling, and drain clogging. Claims are also made for longer cartridge life, lower silver levels, and overall cost savings as compared to other cartridges.

The test results for silver are impressive. Four sites were tested: Two with Kodak chemistry and two with Fuji chemistry. All sites used the standard two cartridges in series. Two sites had high replenishment rates (lower silver input) and two had low replenishment rates (higher silver input). Input silver concentrations ranged from 1500 mg/l to 2800 mg/l. In each case**, the input flow included developer**. Despite the input variances, each site had the same average output of 0.09 mg/l. Silver at or near this level will meet the most stringent discharge limits.

Manufacturer’s claims should *always* be questioned; especially claims requiring subjective opinion by the user in order to validate. Fortunately, the PF-16 is not new. In fact, it has been in use for three years and is currently being used in over 2,000 locations. It has a track record.

THE SURVEY

Manufacturer's claims are one thing, but if you want to get the "real story", talk to users. With that in mind, a user survey was conducted. Respondents included owners and operators of single site mini-labs as well as representatives of large, multi-site users. Nearly all 2,000 users were represented.

The attached survey results (Figure 1) require some clarification. Those using the PF-16 over three years had participated in beta testing. Each respondent had previously used conventional SRCs before switching to the PF-16. If ECS's conventional cartridge had been used previously, it has been noted. The word "other" was used if the previous SRC was not from ECS. The "other" group includes three different manufacturers. If any response went beyond a simple yes or no, when it was more emphatic, it has been noted. ECS recommends a thorough drain cleaning prior to using the PF-16 so that previous blockage is not an issue. One large multi-site user had not performed the recommended cleaning. Those not treating developers simply left their plumbing "as is" when switching to the PF-16 system.

THE RESULTS

The first requirement of an SRC is to recover silver and remove it to a level that will enable the site to meet its discharge limit and avoid violations. The PF-16 appears to do this extremely well. Most all respondents had no violations, and those who did cited reasons other than SRC performance as the cause. Not a single respondent felt that the PF-16 did not adequately remove silver and that include those sites putting developer through the system. One user who routinely tests silver output reported, "I've had more non-detects than ever since using the PF-16." The large number of users having no silver violations attributable to the recovery system lends strong credence to the claims that silver discharge levels are very low and channeling issues are largely eliminated.

Surprisingly, no survey topic evoked more enthusiastic response than that of cleaner drains. Apparently this is a big issue with users, and they voiced their opinions freely. Developer tolerance and extra-low silver levels are not "in your face" issues, but a clogged drain means shutting down, lost business, calling the plumber, and most likely, mopping. Some of the subjective comments:

- "I used to clean my drains every 90 days or so."
- "I was cleaning every six months. I got tired of calling a plumber so I bought a snake. I haven't had to clean with the PF-16."
- "I was cleaning every 10 months before."
- "I was cleaning every three months before."
- "I was cleaning every six months, but not now."
- "It was a mess before. I had to call a plumber."
- "I had 10-15 damage claims per year from neighboring retailers, but only three since using PF-16."

The claim of cleaner drains appears to be substantiated by these testimonies.

Survey respondents also seem to generally confirm the ECS claim that PF-16 lasts longer than other cartridges. The predominant response was that the PF-16 is changed less frequently than the conventional cartridges. It is important to note that the large, multi-site users, who have good data on change frequency, report fewer changes.

ECS claims that the PF-16 saves money. Often the survey respondent was not in a position (or willing) to provide a dollar or percentage answer to this question but to the extent that there were fewer cartridge changes, fewer drain cleanings, and overall less involvement with the recovery system, the response was predominantly “yes” it did save money.

When asked if the PF-16 performs as advertised, the overwhelming response was “yes.”

Perhaps the most pertinent question and the question that encompasses the other subjective questions is the last: “Would you go back to your previous product even if it were less expensive?” The response was a unanimous “no”, with a few emphatic “no” answers thrown in. Users feel that the PF-16 delivers on its claims and is a marked improvement over conventional SRCs.

WHAT MAKES THE PF-16 DIFFERENT?

Like all other SRCs, the PF-16 contains a bed of steel wool necessary for the metallic replacement reaction to occur. The difference is the addition of a small amount of a chemical to each cartridge. That chemical is tetramethylthiruram disulfide, which is also known as thiram. Thiram is used in many applications. It is used as a fungicide in agriculture, in the treatment of human scabies, as a sun screen, as a bactericide applied directly to the skin or incorporated into soaps, in the pharmaceutical Antabuse for the treatment of alcoholics, as an accelerator in the manufacture of rubber products with human food approval, and now, to improve the effectiveness of silver recovery in metallic replacement cartridges.

The chemical reactions caused by thiram to improve the performance of an SRC are complex and will not be discussed here. In simple terms, thiram serves to keep the surface of the steel wool fibers clean, which dramatically reduces the chances of channeling and extends the useful life of the cartridge. Iron oxide, which would normally exit the cartridge as rust, is precipitated and bound by thiram. This substantially reduces the amount of rust entering the drains.

THIRAM

A small amount of thiram, as a white powder, is encapsulated in an permeable inner container inside the cartridge itself. A release of thiram would occur only if the cartridge was broken open and the inner container ruptured. This has never occurred and is not likely to ever occur. Should there be a spill of thiram, using normal PPE—including gloves, goggles, and apron—the user would collect the powder and avoid any air born dust. The powder should be contained, and ECS contacted for disposal information. Once the cartridge has been wetted, exposure to the dry powder is not possible.

Unlike other SRCs, the PF-16 comes with a Material Safety Data Sheet (MSDS). Responsible users of any chemical product should carefully review the MSDS and be aware of any potential safety, health, or environmental issues. In reviewing the MSDS supplied with the PF-16 SRC, in Section VI, Ecological Data, one notices a very high aquatic toxicity. This means that thiram is quite toxic to many fish and aquatic species. A responsible user would want to know if, by using the PF-16, they are harming the environment in any way. The answer is no, for a number of reasons.

There is only a small amount of thiram inside the cartridge, and virtually all of it is reacted, and therefore not present in the discharge. Multiple tests for thiram at the cartridge discharge have been performed. Three tests were conducted with a detection limit of 25 ppb (parts per *billion)*. All three results were below detection limit (BDL). Using a much more sensitive analytical method with a detection limit of *0.5 ppb*, two more tests were performed. These results also came back as BDL. Knowing that any thiram present will be at a concentration less than 0.5 ppb, let's assume that it is at 0.4 ppb. 0.4 ppb is the same as .0004 mg/l or ppm (parts per million). The most sensitive aquatic species listed on the MSDS has an LC_{50} of 0.13 mg/l. The thiram level would be 325-times lower than the LC_{50}, and that is *before* dilution.

Mini-labs are indirect dischargers. This means that they discharge to a publicly owned treatment works (POTW) and not directly into a river, stream, lake, or ocean. A mini-lab's discharge joins with water that comes mostly from homes and businesses throughout the city or community, and it all ends up at the POTW. Most cities have large POTWs capable of treating 100 mgd (million gallons per day). A very small POTW may treat only 1 mgd. We will assume that a typical mini-lab discharges to a small, 1 mgd POTW. The PF-16 system flows at a rate of 1 gallon/hour. If it runs for 12 hours in a day, it would discharge 12 gallons. Those 12 gallons mix with the 1 million gallons at the POTW for a dilution factor of 83,333. So our worst-case assumption of a thiram discharge of 0.4 ppb now becomes 0.0000048 ppb, or 0.0048 *parts per trillion,* before it reaches a body of water where aquatic life could be present.

Thiram has never been detected at the exit of a PF-16 system. Additionally, the dilution factor, even at a small POTW, provides reassurance to PF-16 users that no harm is being done to the environment.

CONCLUSIONS

- The ECS PF-16 silver recovery cartridge utilizes a hybrid technology as compared to conventional SRCs and represents a significant improvement over previous designs.

- Silver discharge levels are very low with an average less than 0.1 mg/l. Over a three year period, no silver violation has been attributed to system performance.

- User comments largely support the manufacturer's claims of longer cartridge life, cleaner drains, and lower costs.

- Unanimously, survey respondents stated that they would not want to return to conventional silver recovery cartridges.

- Despite high aquatic toxicity, thiram has never been detected (MDL, 0.5 ppb) in the PF-16 effluent, and by virtue of dilution at the POTW, poses no threat to aquatic species downstream.

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Pureflow 16 User Questionaire Summary

	User 1	User 2	User 3	User 4	User 5	User 6	User 7	User 8	User 9	User 10	User 11	User 12	User 13
How long have you been using PF-16? (years)	1-2	5	4	2	1	1.5	1.5	1.5	2	3-4	3	1	2
What were you using before?	Other	ECS	Other	ECS	ECS	ECS	ECS	ECS	ECS	ECS	ECS	Other	Other
Do you change cartridges more or less frequently since switching to PF-16?	Less	Less	Much Less	Don't Know	Much Less	Less	Less	Less	About Same	Less	Less	Less	Less
Do you put developer through the PF-16?	No	Yes	Yes	No	No	No	No	No	No	No	No	Yes/No[1]	Yes/No[4]
Have your drains been cleaner since using the PF-16?	Yes	Yes	Yes	Same	Much Cleaner	Yes	Yes	Yes	Yes	Yes	Yes	Yes	About Same
Does the PF-16 perform as advertised?	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Thought So	Yes	Yes
Does the PF-16 save you money?	Yes	Yes	Yes	Not Sure	Yes	Yes	Yes	Didn't Know	Yes	Yes	Yes	Yes	Not Sure Yet
Have you had any silver violations while using the PF-16?	No	No	No	No	No	Yes [3]	No	No	No	No	No	Yes [2]	Yes[5]
Have there been any other environmental issues of any kind?	No	No	No	No	No	No	No	No	No	No	No	No	No
Would you go back to your previous product even if it were less expensive?	No	No	No!!	No	No	No!!	No	No	No	No!!	No	No	No

1. Multi-site user.
2. User attributes only violation to human error, not system performance.
3. "I used the cartridge beyond the recommended change time. It was my own fault. Everything was OK after the change"
4. Multi-site user. Reommendation is to put develeloper through but not all sites are doing it.
5. Respondant attributes violations to human error and using cartridge too long.