

The Feasibility of Implementing
a
Photographic Silver Recovery Program
for the
Ball State University Art Department

An Honors Thesis (ID 499)

by

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A VALUABLE, IMPORTANT RESOURCE--SILVER

Silver is the valuable but diminishing natural resource which forms the photographic image on most films. Without silver photography, as it is generally used today, would not be possible. "The free world uses approximately 423 million troy ounces of silver annually in industrial products."¹ In 1973, according to the Handy and Harmon Silver Review photography was the number one silver consumer in the United States using 48 million ounces.² Since then the photographic industry in the United States alone has increased its consumption to 60 million troy ounces. That was an increase of 9.7 million ounces from the previous year.³

Although silver is a very profitable and useful commodity new mine production is in the vicinity of 265 million troy ounces. This leaves a 145 million ounce deficit or one third of the consumption that must be made up in another way.⁴ A great deal of the silver used in photographic processes can be recovered, refined and used again. Unfortunately scrap recovery is down more than eight percent.⁵

¹ Recovering Silver from Photographic Materials (Rochester, NY: Eastman Kodak Company, 1979), p. 2.

² Kenneth Poli, "Critical Focus--Will Silver Hoarders Kill Photography," Modern Photography, 75, No. 3 (1974), 12.

³ Ibid.

⁴ Recovering Silver.

⁵ Poli.

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Since the domestic production is up less than three percent imports must jump 342% to keep up the demand.⁶ This points to a need for greater and more efficient use of recovery systems.

THE IMPORTANCE OF SILVER RECOVERY

At the current market price of \$12.23 a troy ounce⁷ there is money to be made from recovered silver. Since 1967, when Congressional restraints on the price were dropped, silver has moved upward from a low of \$.90 a troy ounce to the current price.⁸ This twelvefold increase in value has made it profitable for even smaller film users to start their own silver recovery programs.

Thus the importance of silver recovery lies not only in the money available but in the recycling of an important, diminishing natural resource. There are several ways of recycling this resource and each has advantages and disadvantages that are important to consider when outlining a recovery program.

SOURCES OF SILVER

When considering a silver recovery program the first thing to do is determine where your hidden silver is and how much you have. Recoverable silver enters as part of a

⁶ Ibid.

⁷ Thompson McKinnon Securities, INC., April Silver Futures (Muncie, IN: 6 April 1981).

⁸ A. David Charlton, "The Silver Lining," Kodak Bulletin for the Graphic Arts/36 Special Issue: Silver Recovery, 1979, p. 1.

sensitized product--usually film. This film contains an emulsion that uses an insoluble, light-sensitive silver halide as the initial means of forming the latent image.⁹ Absorbing light during exposure converts some of the halides into a developable form. Development then changes the exposed silver halide to metallic silver, which forms the final image on black-and-white products. A thiosulfate compound completes the process by fixing the image. In the fixing bath, the insoluble unexposed silver halide reacts with the thiosulfate to form a soluble silver thiosulfate complex, which is removed from the emulsion in the fixing bath and succeeding wash. Through this basic process silver leaves in two ways: in used fixer solution and in used film. At this point there are two options available--waste the silver by pouring fixer down the drain and throwing scrap film away or recover it!

DETERMINING RECOVERABLE SILVER

How much silver there is available for recovery purposes depends on the type of work you are doing. A lot of negative work with a high percentage of the film exposed will result in most of the silver being retained in the film as the black area and a small amount will be found in the fixer. Conversely, a lot of positive film work with a small percentage of exposed area will yield a batch of fixer with

⁹ Recovering Silver, p. 4.

most of the silver dissolved in it and only a small amount will be left in the film image. An easy rule of thumb is that

"with a high percentage of exposed area (negative), recovery from fixer will be less, but you can expect to get a higher price per pound from your scrap film and vice versa."¹⁰

Type of film also makes a difference. X-ray films, for example, have the highest yield of silver as they are coated on both sides of the base with emulsion. Therefore, silver recovery from both x-ray film and fixer would be proportionally quite high due to the high silver content.

Graphic arts film has a single, thin layer of emulsion. This means there is less silver than x-ray film; thus, there is less silver to be recovered.

Color film and prints present another consideration. Although they have three layers of silver-bearing emulsion and are processed in the same way, a dye must be formed at the sites of the developed silver. At a later stage all the silver is removed from the film or paper. For this reason all the silver, nearly 100%,¹¹ is in the fix solution and scrap processed color film or papers have no silver value.¹²

Black-and-white reversal processing differs slightly in that this method uses a dichromate bleach, which acts as a silver solvent rather than a rehalogenating bleach as

¹⁰ Charlton.

¹¹ Recovering Silver, p. 5.

¹² Charlton.

in color processes.¹³ Most of the silver in this process is removed in the bleach, where it is present as silver ion, rather than in the fixing bath as a silver thiosulfate complex. A different technique is required for recovery of silver from dichromate bleaches than those used for fixes and bleach-fixes.

To be recovered then, silver may be in any of four basic forms; an insoluble silver halide, a soluble silver thiosulfate complex, a silver ion and elemental silver. The type of process and the stage at which the silver is recovered determines the form it is in.

Silver in scrap film and paper can also be recovered; although, solid wastes are more difficult to handle and the silver is harder to separate from the base material than it is from a fixing bath. This recovered silver is also in the form of elemental silver. For these reasons the recovery is more complex and is generally done by a specialist who buys discarded silver-containing materials.

RECOVERY METHODS--SCRAP

Two methods are used by the commercial recovery specialists, once the scrap is collected, to separate silver from the scrap. The most common is to burn the film or paper leaving a silver-rich ash from which the silver can be recovered. The second technique is to chemically remove the silver from the waste and then recover the silver from

¹³ Recovering Silver.

the wash water used to remove the chemical and the emulsion. This is a more complex process and is usually used when the base is to be recovered in addition to the silver.

Just about any unit that does its own film work, be it a printing plant, industrial plant or an educational photography lab, can make extra money by reclaiming the silver that exists in the fixer solution and the scrap film.

RECOVERY METHODS--SOLUTION

Two recovery methods are in popular use to remove silver from used fixer. The metallic replacement cartridge is one and the other is the electrolytic recovery unit.

The metallic replacement cartridge looks like a plastic five-gallon bucket with tubes sticking out the top--which is exactly what it is. The bucket is filled with steel wool or a wire screen material when new that does the job of silver recovery.

The cartridge operates on the principle of metal ion exchange, which states that the more active metal in the electromotive series of elements will replace a less active metal in solution.¹⁴ This means that when silver-rich fixer solution is circulated through the cartridge the iron in the steel wool or wire screen filler material will replace the silver ion solution. The silver then drops to the bottom of the cartridge as an impure metallic silver sludge. The iron ion, now in the solution, is carried out of the cartridge

¹⁴ Kodak Bulletin for the Graphic Arts/36, p. 4.

and down the drain.

After a specified period of use the steel wool is used up and the cartridge must be replaced. Tests have indicated that when approximately 85% of the filler material is used, the cartridge will start to pass silver in a concentration high enough to be cost efficient. Therefore the cartridge is considered exhausted before the filler is completely used up.

Cartridges work best when there is a continuous flow of solution passing through the filler material. Whether you use steel wool or a wire screen depends on the flow rate and dwell time of the fixer solution in the cartridge. The steel wool filler has a greater surface area than the screen and will work faster. If the flow rate is low either type of filler will work efficiently. However, if the rate is high a steel wool cartridge or two screens connected in a series is preferred for greatest efficiency. The primary advantage of having a wire screen is that more pounds of iron can be put into the cartridge and it does not have to be changed as often.

If a cartridge is used just once a week the filler material oxidizes, forming rust. Rust cannot enter into the chemical reaction, so the capacity of the cartridge is reduced. Regular, continuous use adds to the efficiency of the metallic replacement cartridge.

The cost of metallic replacement cartridges range

from \$30 to \$50.¹⁵ There are a few cartridges available which can be recharged with filler material by the user, but most units are factory sealed and must be totally replaced each time they are exhausted.

The electrolytic recovery unit is more complex than the metallic replacement cartridge, both in design and operation. The electrolytic units pass an electric current through the silver-rich fixer solution which causes the silver to plate out of the solution onto a cathode in the form of nearly pure metallic silver. The capacity of a unit is determined by its current density, which is the amount of direct current measured in amperes related to the surface area of the cathode.

Therefore, recovery capacity depends on the amount of current and the size of the cathode. A small cathode working with a high current could have the same plating capacity as a large cathode working with a low current. However, a large cathode working with a higher current would have a greater plating capacity.

Tank capacity is another consideration. Units are available with tank capacities from two gallons to 40 or more gallons. The smaller tanks usually have less plating capacity due to smaller cathodes. These units, though, may be the best match for limited operations using small amounts of fixer and processing smaller amounts of film. As with the metallic replacement cartridge, the electrolytic

¹⁵ Recovering Silver, p. 8.

recovery unit should be matched to the potential silver yield from your process.

An important consideration in design for electrolytic units is the method of agitation. The solution must be constantly agitated as it passes the cathode for optimum efficiency. If the solution is not constantly changing at its interface with the cathode, a barrier of de-silvered solution will build up and prevent the silver in the remaining solution from plating.

Three methods of agitation are commonly used: the cathode can be rotated, the anode can be rotated or both can be stationary while the solution is pumped past the cathode.

Rotating the cathode provides excellent agitation at the interface between the cathode and the solution. However, as the mass increases on the cathode, from 25 to 35 pounds of silver flake, an increasing load may be put on the motor and the bearings causing possible failure due to excessive wear.

There is no build-up of silver flake on the rotating part with the rotating anode, so the extra strain on the motor and bearings does not exist. Because the rotating anode only stirs the solution around in the unit it does not provide as efficient agitation as the rotating cathode.

Keeping both the cathode and the anode stationary and pumping the solution through the recovery unit eliminates the need for a drive motor on either unit. Instead, there is a need for a high-capacity pump and a motor to operate it. Good agitation can be accomplished provided you have

adequate pump capacity. This, however, adds to the cost and maintenance of the unit.

In addition to the method of agitation is the importance of the design of the cathode. One popular design is simply a flat plate which is inserted into the solution. The flat plate represents considerable surface area as both sides are exposed to the solution. Therefore a high current is necessary to provide effective recovery.

A cathode composed of four or more disks mounted on a single shaft is an earlier design variation. This design requires movement of the solution over the disks which is accomplished by rotating the shaft. Disks have a greater agitation at the circumference so the silver will plate more heavily there.

Currently, the most popular cathode design is a rotating cylinder. The cathode is a thin, flexible metal, exposing both sides (inside and outside) to the solution. The same recovery efficiency is possible with less current than the two previously described designs.

Prices for electrolytic units are based on capacity and controls. The price range starts at \$150 and can cost \$15,000¹⁶ and there are real differences between the units to justify the price range. One of the major differences is sophistication of the current control.

Control of the current by which the silver is plated on the cathode is important. If too little current is used

¹⁶ Ibid., p. 12.

less of the silver in the solution will be plated and some may be lost down the drain. If too much current is used, or if the unit is left on too long, chemical compounds will break down and sulfides from the fixer solution will plate out also. This will lower the purity of the solution, consequently lowering the resale value. In addition, plating efficiency will decrease.

Inexpensive units which have only an "on-off" switch as the current control are fine, if your process is fine-tuned, your work load is constant and you know how long it takes to get the silver out of your solution. A switch and a reliable person to operate it will be all you need in this case.

As the capacity and flexibility of the controls increases so does the cost. Some expensive units have a variable current control and often a meter to indicate the current flow in the solution. Others have built-in timers or are connected to the processor so that they operate only when the processor does.

The high-priced units may have a sensor-probe that will automatically adjust the amount of current relative to the silver concentration when inserted in the fixer solution. When the silver concentration reaches a minimum level the probe will either shut the unit down or place it on "stand-by." Another method of control is a time-unit counter that relates plating time to volume of film processed.

CHOOSING A RECOVERY METHOD

Only two recovery methods for fixer have been discussed in this paper because they are the most practical methods for the smaller volumes used by graphic arts plants or educational laboratories. Although an equipment sales representative can give you detailed information regarding your specific program and needs, the final decision should be up to you. How much solution you use, the amount of time and effort you want to devote to a silver recovery program and how much capital you can afford to invest in a recovery unit are the most important considerations. In comparing the features of metallic replacement cartridges with the electrolytic recovery units the key is to look for one that will provide the greatest return on your investment.

Comparing the advantages and disadvantages of the two recovery systems is important when deciding on a unit for your plant or lab. Table 1 can be helpful in your considerations when choosing a recovery unit.¹⁷

Although the capital expenditure for the electrolytic recovery system is much larger, remember the metallic replacement cartridge must be replaced--each time--at a cost of \$30 to \$50. For example, a five-gallon six cartridge would be exhausted after processing 220 gallons of fixer.¹⁸

With the electrolytic recovery system the reduction

¹⁷ Ibid., p. 15.

¹⁸ Kodak Bulletin for the Graphic Arts/36, p. 5.

TABLE 1--ADVANTAGES AND DISADVANTAGES

<u>Metallic Replacement</u>	<u>Electrolytic</u>
*Initial capital expenditure is approximately \$30 to \$50.	*Capital expenditure can run \$150 to \$15,000.
*Installation is easy, requiring only a simple plumbing connection.	*Electrical as well as plumbing connections are required.
*Yields a silver sludge that varies in silver content, resulting in higher shipping and refining costs.	*Yields silver with a high degree of purity.
*Can reduce silver concentration to less than 1 mg/L in a single pass.	*A reduction in silver concentration to 500 mg/L in a single pass may be the best that can be achieved.
*Does not permit reuse of fixer.	*Permits reuse of fixer for some processes.
*Requires little monitoring and uses simple analytical procedures.	*Requires frequent monitoring for maximum efficiency.
*Can be used for recovery of silver from wash water.	*Is not suitable for silver recovery from wash water.
*Can be used with regenerating bleach-fix systems.	*Not all equipment is suitable for use in bleach-fix regeneration.
*Cannot be used in a continuous circulating system.	*When incorporated with a continuous circulating system more silver is available for recovery. Less silver is carried into the following wash.

Source: Recovering Silver from Photographic Materials, Eastman Kodak Company, 1979.

in silver to 500 mg/L can be improved by making more than one pass or following it up with a metallic replacement cartridge.

As mentioned above, personal preferences and the time you want to put into your program determines the system you use. Both have advantages and disadvantages inherent which can sometimes be overcome.

SCRAP FILM AND PAPER

Concerning scrap film and paper the best option available to the small laboratory is to sell them to a dealer or broker. They buy your scrap by weight, estimating the amount of recoverable silver per pound. If the scrap is "clean," meaning that the masking paper and stripping tape have been removed and there is little or no miscellaneous trash, you should expect a higher price. Also, a high percentage of negative materials, which are silver-rich, as opposed to film positives, should bring a higher price when you sell your scrap.¹⁹

The dealer or broker estimates the value of the silver in your scrap by observation and you can expect the estimated prices to vary with the estimator. This makes it very important to get as many bids as possible, then take the best offer.²⁰

¹⁹ Ibid., p. 7.

²⁰ Ibid.

SELLING THE RECOVERED SILVER

Once the silver is recovered, you must find a buyer who will pay an acceptable price. Since the objective is to buy reclaimed silver and sell it at a profit, competition is keen among reclaimers.

In the two systems discussed, two forms of silver have been considered for reclaiming--sludge that comes from metallic replacement cartridges and flake that comes from electrolytic recovery units.

The amount of silver in an exhausted metallic replacement cartridge sent to a dealer is unknown. For this reason, payment usually occurs several weeks after delivery to a refiner for the amount of silver determined by an assay and at a specified market price.

Silver flake is 90 to 95 percent pure²¹ and is usually purchased on a percentage of the market price. In most cases, the dealer weighs the silver flake in the customers presence and makes an immediate payment at a specified price. Generally, the price quote will be lower than the 90 to 95 percent purity of the reclaimed silver. In some instances, it may be better to have the silver assayed and wait for payment based on a verified purity.

²¹ Charlton.

PRICING AND TROY OUNCES

Always check the prices quoted to you. The price can be from one of two sources: the New York Commodities Exchange spot price or that of a major company dealing in precious metals. It is best to get your quote in writing.

Market prices are quoted in troy ounces and this can get confusing. The troy ounce has a metric equivalent of 31.10 grams, while the avoirdupois ounce has a metric equivalent of 28.35 grams. In other words, there are 14.583 troy ounces in an avoirdupois pound and 16 ounces in the same pound. This means that the troy ounce is about eight percent heavier than the avoirdupois ounce.²² It is important that you understand how the buyer is weighing your silver and quoting payment--keep the transactions in troy ounces.

Again, before selling your silver, in any form, get several estimates and take the best one.

BALL STATE UNIVERSITY ART DEPARTMENT

The Ball State University art department provides course work for approximately 625 students each year. The department also offers a variety of studio, history, education, interior design and visual communication courses. Among these course offerings are four photography courses and four other courses concerned with the photographic process

²² Ibid.

which are, graphic design and the advanced design group-- courses 1, 2 and 3.²³ In addition to the courses listed in the undergraduate catalog for 1978-80, there are several other courses which use a photographic process of one kind or another.

Approximately 40 students take photography courses each quarter. For four quarters that makes a total of 160 students involved in the photographic process a year. Professors who have been involved with the photography courses estimate that each student uses one gallon of fixer per quarter. At such a conservative estimate, the total number of gallons of fixer which go down the drain each year in the art department is approximately 160.

RECOVERY OF THE ART DEPARTMENTS SILVER

Recovery of the silver for the art department would be relatively easy. A holding tank would need to be placed in a central location or a small holding tank could be placed in each darkroom. The students would need to be instructed to pour their used fixer into the holding tanks. The person in charge of the recovery program would need to monitor these tanks and empty them on a regular basis, depending on the tank capacity. To empty them he or she would run the contents through a recovery unit and then place them back in their respective positions. With this type of program

²³ Undergraduate Catalog (Muncie, IN: Ball State University, 1978-80), pp. 122-124.

the recovery unit would need to be run only when there was enough fixer available to make it cost efficient. A program such as this would be possible for both metallic replacement and electrolytic plating systems.

Basing the economic gain for the departments program on a standard of at least $\frac{1}{2}$ a troy ounce of silver concentration per gallon of fixer²⁴ with the current price of silver at \$12.23, a profit is attainable in a relatively short time.. The initial capital expenditure and the cost of recovering and refining the silver will of course be deducted from this profit. Using the above estimate of 160 gallons of fixer; multiplying it by $\frac{1}{2}$ a troy ounce of silver gives a potential yield of 80 troy ounces of silver. At approximately \$12 per troy ounce the net profit for one year could be as much as \$960. This is, of course, a rough estimate before deducting costs or allowing for error.

SAMPLE PROGRAMS

Earlier it was mentioned that one of the drawbacks to metallic replacement units is the fact that a continuous flow of solution must pass through the filler material. If the filler material is allowed to oxidize efficiency is greatly reduced.

To use a metallic replacement cartridge system a holding tank capable of containing a minimum of 200 gallons

²⁴ Recovering Silver, p. 6.

would be necessary. The full holding tank would then be run through the system once a year and the sludge sent to a refiner for processing. The refiner would then pay the department for the sludge, after it was assayed, at considerably less than market value due to his costs of refining and shipping.

There are a few disadvantages to this program for the art department. First, obtaining a holding tank or two with the necessary capacity and then finding a place to keep it would be difficult. Second, evaporation of solution over a years time would drop the amount of silver obtainable. Third, the amount of time necessary to run the solution through the cartridge would be considerable. Fourth, the outlay every year would be between \$30 and \$50. With time and inflation this cost is sure to increase. Fifth, the low purity of the sludge coupled with the refining and transportation costs would lower your return.

The second program uses an electrolytic recovery unit. With this system a large holding tank is not necessary. As the anode and cathode do not oxidize you can run solution through the system and let it sit as long as wanted or you can flake off the silver between runs. Since the flake is usually 90 to 95 percent pure you can get a much better price. A refiner will pay you a percentage of the market price, usually on the spot, for your silver flake.

Disadvantages for the electrolytic recovery system are

1) the initial cost, which can run from \$150 to \$15,000 and 2) the frequent monitoring required for maximum efficiency. The cost of the electrolytic unit is only a minor setback. Instead of constantly outlaying cash for your program, an electrolytic unit will eventually pay for itself. The amount of monitoring necessary would not be much more than is required for the program using the metallic replacement cartridges.

RECOMMENDED PROGRAM

I recommend a photographic silver recovery program for the Ball State University art department using an electrolytic recovery unit. Since the department would be utilizing a holding tank to collect enough solution to be delivered, a recirculating electrolytic unit with a basic current control consisting of an "on-off" switch is a good choice. For \$500, maximum, a very good unit can be purchased that will more than meet the present needs of the art department. The cost of installation could run a couple hundred dollars, depending on where it is put and who does it. The only expenditure that will be variable will be the wage of the person monitoring the unit. With the recirculating unit there will be additional monitoring in order to provide the most efficient use. There will not be a transporting cost nor a refining fee as the refiner will come out to get your flake and pay on-the-spot leaving himself a profit margin. Do get estimates from several sources before deciding on anything!

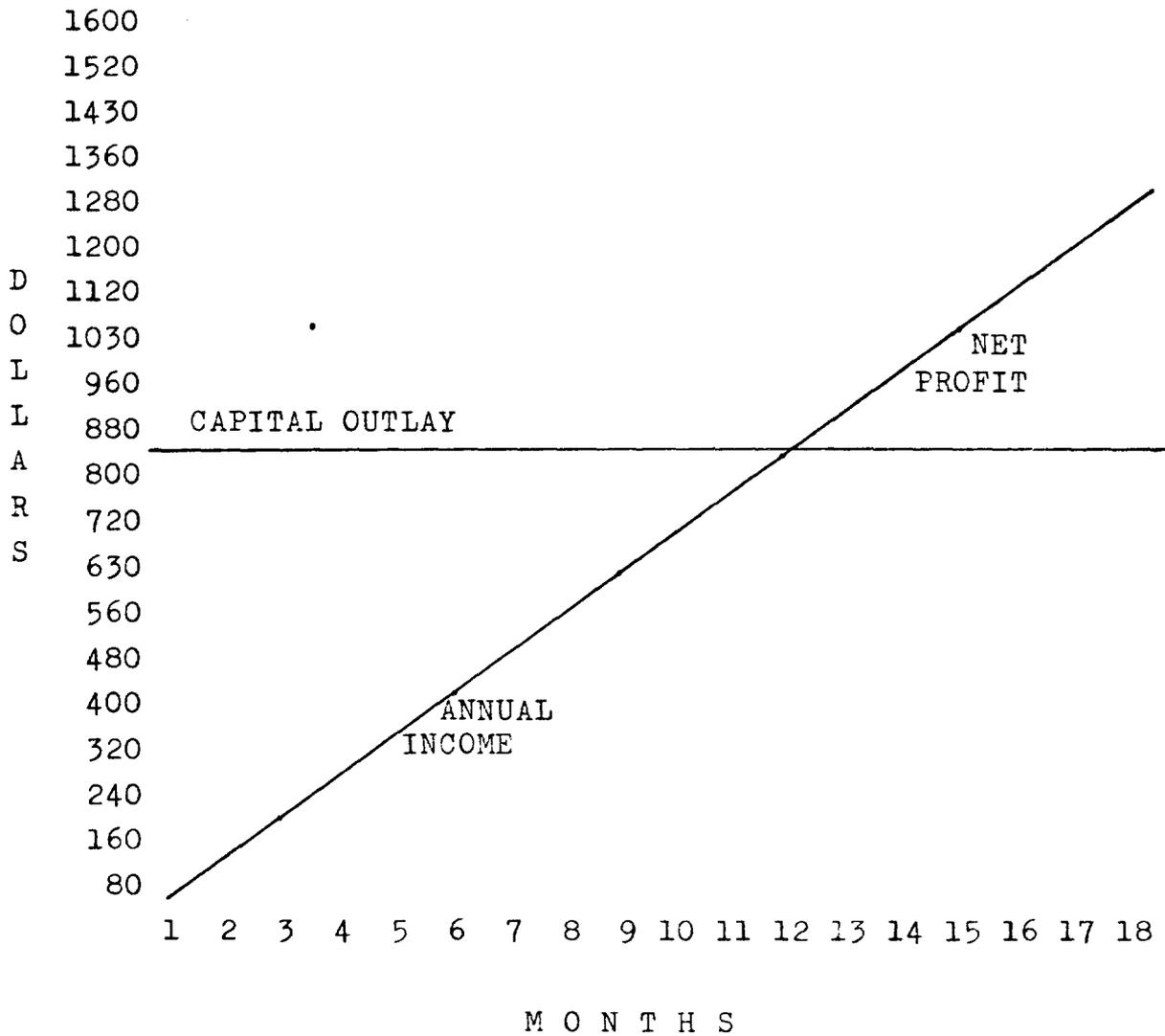
BREAKEVEN POINT

Using this program with projected costs and a net profit of \$800 per year, the art departments electrolytic recovery unit can pay for itself in three years, at the outside, most likely sooner. Table 2--a breakeven point chart will show an estimated breakeven point.

CONCLUSION

In short, I feel very strongly about implementing this program. The positive aspects of this program far outweigh the negative. A little bit of time and effort on the part of the art department can reap monetary benefits that are much needed, especially now that government spending and endowments for the arts are being cut from the national budget. This program should very definitely and seriously be looked into and considered for the very real present. Do it now before it becomes more costly!

TABLE 2--BREAKEVEN CHART



Note: CAPITAL OUTLAY includes necessary materials and equipment expenditures, and wages for one year.

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