CHAPTER I

INTRODUCTION

For many years, attention has been given to recovery, purification and reuse of Silver in the photographic processing Industry.[1] There are many reasons why the effort to recover silver from photographic processing solution will be an interesting conservation of a valuable resource. Figure 1.1, shows graphically the silver price history, together with the trends of production and consumption during the entire ninety-year period,[2] Silver production historically has exceeded industrial consumption by very substantial amounts. The situation at present is just the opposite. The rapid technological and economic expansion which took place in the industrialized countries of the world after World War II resulted in a substantial increase in silver consumption with little offsetting increase in production. World industrial consumption over the past ten years has increased at an average annual rate of about 6 percent while new production over the past ten years increased at an average rate of only about 1 percent per year in 1973. It was estimated that the total world consumption of silver was approximately 480,000,000 troy ounces, approximately 50% of the silver used.[3] This would leave a deficit of 240,000,000 troy ounces. This deficit is the supply

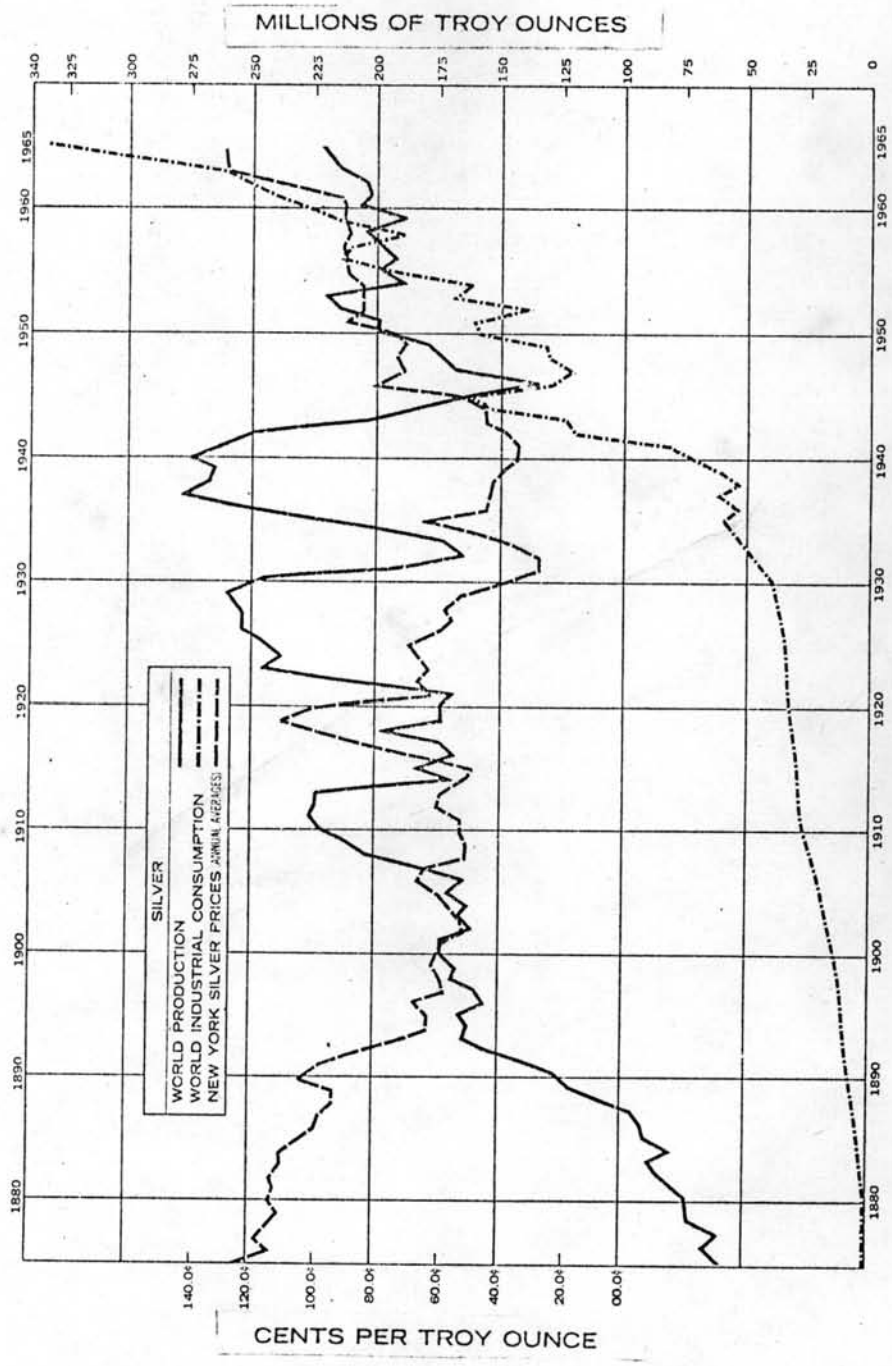


FIG. **1.1** Silver: Production, Consumption, Prices.

problem in the years ahead which can be filled from secondary sources. There are several regularly recurring sources of secondary silver, the major sources which make up the deficit of silver are demonetized coinage (which contains a large quantity of previously mined silver.) Another source which grow important is to be found in the wide variety of industrial scrap and salvaged industrial wastes.

Table 1.1 Breakdown of Industrial Consumption of Silver By Major Categories.

Category	Percent of Total
Photography	32
Electrical and electronic (including batteries)	31
Silverware and jewelry	17
Brazing alloys and solders	13
All other	7
Total	100

The ratio in table 1.1 have been derived by the U.S. Department of Commerce in June, 1965.[2]

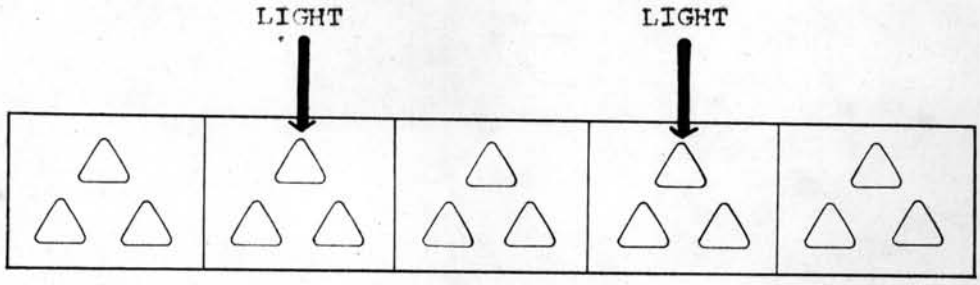
From Table 1.1 shows that photographic industry is estimated to consume 32 percent of the total silver used by industry. Then silver recovery in the photographic solution waste represents a significant means for conserving silver as a natural resource.

It is also a significant potential source of revenue for users of photographic products.

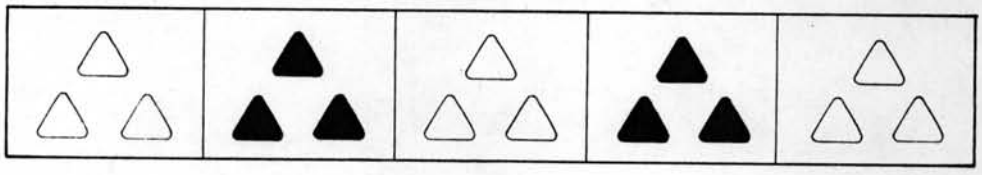
Another reason is that the practice leads to a cleaner environment as silver is classified as a water pollutant. There are a number of articles in the literature that show the excellent bactericidal properties of the free silver ion.[4]

From 1962 to 1972, silver prices fluctuated between $0.90 and $2.56 per troy ounce. However, during 1974 silver prices soared to a record high of $ 6.70 per troy ounce.[5] At the present time (1979). The silver price is $ 17.60 per troy ounce. This high price of silver increases the economic incentive for recovery and makes recovery of silver from more dilute solutions economical.

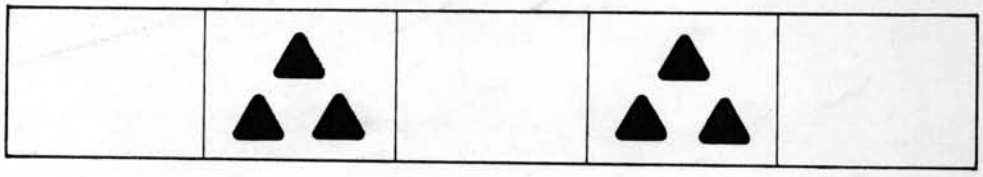
There are two main sources of recoverable silver in the photographic processing industry. One source is various exhausted processing solution; the other source is expended processed films, paper and printing plates. Figure 1.2 Shows the Black and white film process where as much as 80 % of silver in the emulsion of film may be removed and may remain in solution in the fixing bath, the remainder of the silver stays on the film to form the image. These figures can vary, of course, depending on the type of film used, its application and the amount of exposure and development it receives.[6] Fig 1.3, Shows the Color Film Process, the final image consists of dyes. Essentially all of silver originally in the product film is removed by the fixing bath,[6] these result represents a significant means for recovery silver in exhausted processing solution.



(a) Exposed Film.



(b) After First Development.



(c) After Fixing.

△ = Silver halide

▲ = Metalic Silver

Figure 1.2 Black and White Film Process.

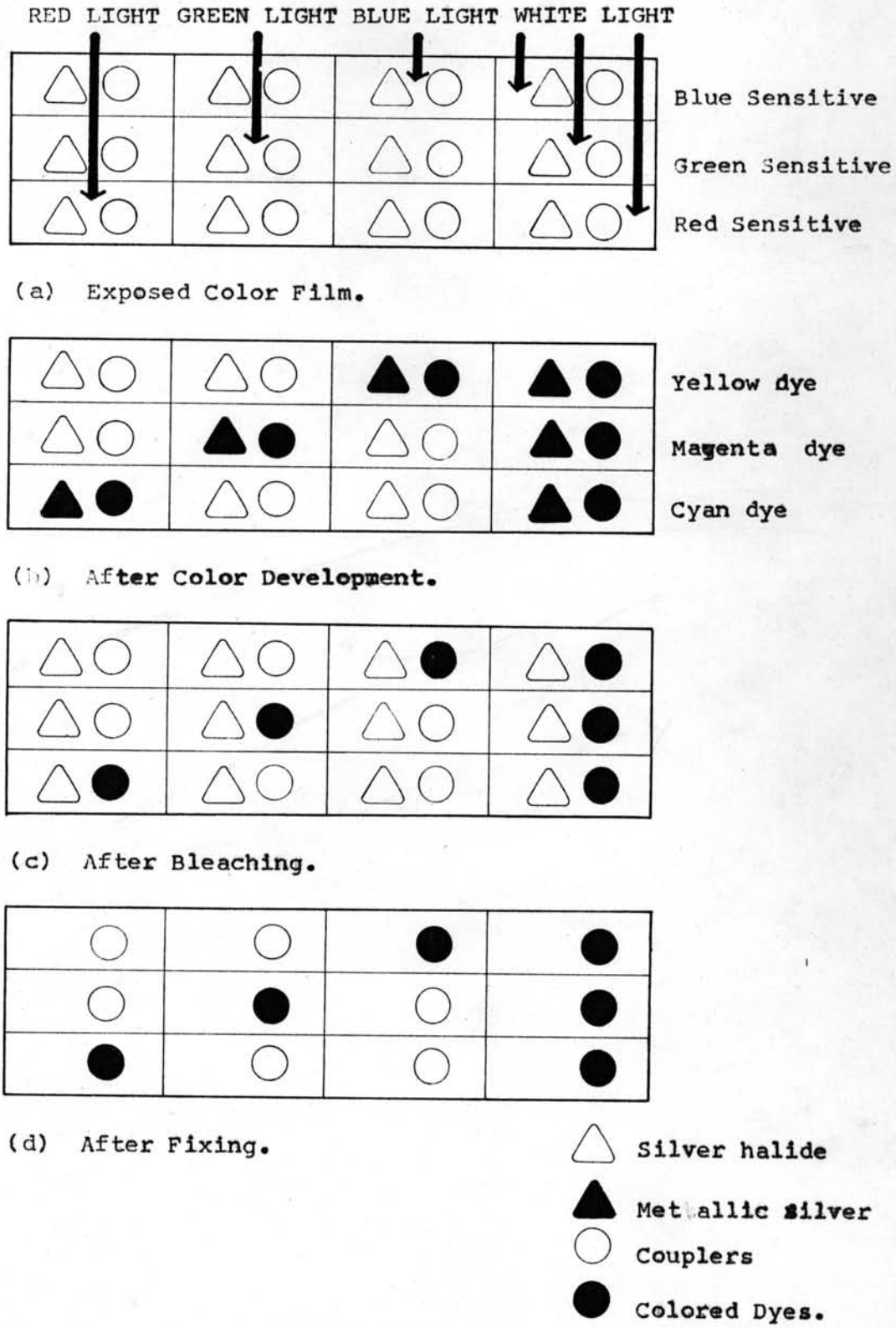


Figure 1.3 Color Film Process.

The recovery of silver from exhausted processing solution has been extensively investigated for many years. Most of the methods developed are based on the fact that silver is far removed in the electromotive series from the other metallic ions in the fixing bath. The following methods can be used.

1. Precipitation with sodium or potassium sulfide
2. Precipitation with sodium hydrosulfide
3. Precipitation with sodium borohydride
4. Replacement by zinc
5. Replacement by iron
6. Recovery by ion exchange resins
7. Electrolytic methods

The precipitation method can be operated with a relatively inexpensive installation, but the dis advantages[7] are

1. Difficulty of handling and refining the resulting silver sludge. Decantation is slow and filtration requires an expenditure for equipment.

2. Hazardous process because of possible accidental acidification and liberation of hydrogen sulfide.

3. Setting time is very long. This requires holding tank of a size commensurate with several days out put of fixer. Not particularly suited to very large installation.

4. Requirement of the storage of chemicals which can potentially contaminate the photographic process.

5. Desilvered fixing bath is usually unsuitable for reuse in photographic process.

In general, the electrolytic recovery method is preferred because of the clean installation, purity of silver produced and is best for large installations. This method consists of passing an electric current through the photographic solution waste in a specially built electrolytic cell. Then the silver ion in the solution plates out as metallic silver on the cathode.
The efficiency of an electrolytic cell depends on many factors, such as, agitation, pH, temperature, current density and chemical concentration.[8] To determine the optimum condition, it is necessary to study the effect of these factors. This is the objective of this thesis. The outline of this thesis is as follows.

1. Determine silver concentration in photographic solution waste from difference sources by the Atomic Absorption Technique.

2. Build an Electrolytic cell to recover silver.

3. Study effect of agitation, pH, current density, chemical concentration up on current Efficiency to find out optimum condition.

4. Study economic of electrolytic cells of various sizes.

The foreign trade statistics of sensitised material which was published by the Department of Customs, Bangkok, is summarised in Table 1.2. The data covers imports for the whole country. It shows that, a lot of money have been used for importing sensitised material per year.

Table 1.2 Cost of sensitised material imported for the whole country.

Type of sensitised material	Cost per year (Bath)		
	1976	1977	1978
Plates, sensitised, unexposed (For X-ray and other)	60,570,576.-	83,884,558.-	84,503,690.-
Film in rolls, sensitised, unexposed (For cinematograph, X-ray and other)	58,363,218.-	101,391,853.-	103,471,962.-
Sensitised plates and film, exposed but not developed	91,454.-	6,646,713.-	7,283,181.-
Sensitised paper, paper board and cloth	116,718.-	72,510,690.-	84,846,520.-
Total cost per year (Bath)	119,141,966.-	264,433,814.-	280,105,353.-

When these sensitised material pass through the fixing bath, a lot of silver will dissolve in the used fixing solution. The total cost of the silver is proportional to the total cost of sensitised material, and averages about 4.98 - 6.60 percent of the sensitised material, (Appendix III). Thus, if all the silver in the photographic waste solution can be recovered, not less than fourteen millions baht will be saved annually. More over recovery of silver will reduce environmental polution. A research program leading to the recovery of silver is, therefore, useful and beneficial