United States Patent

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[54] **SILVER RECOVERY PROCESS**
9 Claims, No Drawings

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[50] **Field of Search** 75/83, 63, 118

[56] **References Cited**

UNITED STATES PATENTS

2,944,886	7/1960	Fisher et al.	75/83
2,131,072	9/1938	Reid	75/83
2,218,250	10/1940	Reid	75/83
3,334,995	8/1967	Gaspar	75/118

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ABSTRACT: Silver from used manufactured organic materials such as photographic film, sensitized paper and printed circuit boards, is recovered by placing the material in an enclosed retort and subjecting the retort to a noncombustible atmosphere such as steam and then increasing the temperature of the material to a final temperature between 500° and 960° C. to vaporize the volatile constituents and carbonize the organic material to leave a silver and carbon residue. The silver is then separated from the carbon by burning the carbon in a combustible atmosphere to transform the residue into silver and ash. The silver and resulting ash may be efficiently separated by conventional flux or flotation processes.

SILVER RECOVERY PROCESS

BACKGROUND OF THE INVENTION

This invention relates to processes for recovering silver from used manufactured organic products such as printed circuit boards, photographic film and sensitized paper.

Used or damaged photographic film or sensitized paper is frequently discarded even though it is well known that such film contains certain amounts of silver. As a general rule it is estimated that used film contains up to 8 percent silver by weight. This figure will vary widely depending upon the type of the film involved and the degree of exposure of the film.

Often the cost involved in processing used film by presently known methods to recover silver does not justify the effort particularly for small quantities of film. Frequently large quantities of film cannot be economically gathered to justify large batch operation. Furthermore, the purity of the recovered silver must be quite high to be used for photographic purposes. This requires a very efficient recovery process.

Two known processes of recovering silver from used film that have been used to some degree are described in U.S. Pat. No. 2,944,886. One involved the treatment of the used film in a hypo solution of sodium thiosulfate to dissolve the silver into solution. The silver is later recovered from the hypo solution by chemical means. The hypo process is quite expensive and has been most frequently used for recovering the silver from used X-ray film. The second method, presently the most common, is described as a burning or smelting process in which the film is burned in a combustible atmosphere to form an ash. The air pollution problems associated with such a treatment and process are quite substantial requiring that the process be conducted away from populated centers. Often the film is burned in open pits billowing black smoke soot into the air. Furthermore, in the burning process a considerable amount of silver is lost in the flue gases as they escape into the atmosphere. Other processes are described in the U.S. Pat. Nos. 3,131,072 and 2,218,250. A technique using hot caustic to dissolve the gelatin from the film has been employed. However, it has been found that such a process is uneconomical.

Often printed circuit boards are manufactured utilizing silver as a conductive material in electrical circuit between components. Frequently the boards are thrown away when the electrical components malfunction or become obsolete. Presently some recovery of silver is attempted from used or damaged circuit boards by burning the boards in a combustible atmosphere. Here again, such a method presents substantial air pollution problems.

One of the principal objects of this invention is to provide an economical process for recovering silver from manufactured organic materials such as printed circuit boards and photographic film and sensitized paper.

An additional object of this invention is to provide a process that does not pollute the air.

A further object of this invention is to provide an efficient process in which a large percentage of the silver remaining in the used organic product is recovered.

These and other objects and advantages of this invention will become apparent upon the reading of the following detailed description of the preferred embodiment.

DETAILED DESCRIPTION OF A PREFERRED EMBODIMENT

Generally photographic film comprises a sensitized emulsion spread over a film base or substrate of organic material. Frequently a layer of solvent or other binder material is formed over the film substrate prior to the addition of the sensitive emulsion to adequately adhere the emulsion to the film substrate. Frequently a dyed antihalation backing is placed on the back side of the film substrate to improve resolution.

In past years a film substrate material of cellulose nitrate was widely used. In recent years, cellulose acetate has been widely used as the film substrate in motion picture films, X-ray films and the like. Recently film substrate materials have included other organic materials such as cellulose acetate, propionate, cellulose triacetate and polyester. Sometimes cellulose ester film substrate is used. The thickness of the film generally varies from three thousandths of an inch to nine thousandths of an inch. Occasionally plasticizers are added to the film substrate to give flexibility to the film. The emulsion material has silver or silver compounds distributed throughout the gelatin.

A sensitized paper generally is made by impregnating silver onto the paper by passing the paper through a silver solution bath.

Printed circuit boards generally have a substrate made of an organic material such as epoxy impregnated paper or cloth or phenolic or polyester reinforced by fiber glass. A thin layer of silver or other conductive material is then formed on the substrate. A circuit pattern or mat is positioned on the silver forming areas in which the silver is exposed and areas where the silver is covered. The exposed areas are etched away leaving a circuit pattern of silver.

To reclaim the silver or waste from organic materials, the materials are loaded onto an enclosed retort. The materials are subjected to a noncombustible atmosphere such as steam. Materials are then progressively heated to a temperature below the melting point of silver which is sufficient to volatilize and carbonize organic materials to form a silver and carbon residue. The melting point of silver is approximately 960.8° C. Subsequently, the silver and the carbon are separated.

An initial substep in the separation step includes the burning of the silver and carbon residue in a combustible atmosphere to form metallic silver ash. The ash in the metallic silver may be separated by conventional processes of fluxing or leaching.

During the heating step, it has been found that the materials begin to pyrolize when the temperature of the materials reaches approximately 350° C. It has been found that almost complete pyrolization is accomplished at temperatures above 500° C. Thus the preferred process is to heat the materials to a temperature greater than 500° C. but less than 960° C. The heating step may be accomplished by subjecting the waste materials to a superheated steam atmosphere having temperatures above 500° C. or injecting steam into the retort and then heating the retort sufficiently to bring the temperature of the base material and the steam above 500° C.

Because of the high pressure code requirements it is preferable to maintain the pressure in the retort at a pressure of less than 15 p.s.i.g.

During the pyrolization, the organic materials are broken down into volatile constituents and carbon. Depending upon the residence time utilized in accomplishing the pyrolization step, varying amounts of hydrogen, methane, carbon monoxide and carbon dioxide are formed. Some of these gas constituents may be considered as byproducts and can be used in producing heat values for producing steam or heating the retort.

During one test 207.3 grams of photographic film containing green film, heavily exposed developed film, and lightly exposed developed film was placed in a Lindberg tube furnace. The 207.3 grams of film contained approximately 4.56 grams of silver as determined using analytical procedures on samples randomly selected from the film mixture prior to pyrolysis. The furnace chamber was enclosed with an inlet for supplying water to the chamber and an outlet for conducting the gases from the chamber. The film was heated slowly from atmospheric temperature to a temperature close to 600° C. over a period of 5 hours. It was found that the film started to melt down and bubble occasionally at a temperature of approximately 300° C. It was further found that complete polarization occurred at temperatures above 500° C. Water was injected into the chamber to produce a superheated steam to provide a noncombustible atmosphere during the polarization process. After the film had been reduced to a silver and carbon residue the heating chamber was opened to the atmosphere. The

material was then oxidized at approximately 600° C. The weight of the ash including the silver after the oxidation was approximately 6 grams.

The ash residue was leached in nitric acid and boiled down. The solution and residue were then made alkaline with ammonium hydroxide. The silver was precipitated as silver sulphide with a caustic sulfide ion solution. The solution was filtered to retain the silver sulphide and the silver converted to silver nitrate solution by boiling with nitric acid. The amount of silver in the solution was calculated by a titration process known as the "Volhard" method. It was found that the ash contained 4.49 grams of silver. From this it was calculated that the silver in the ash was approximately 74.2 by weight and that the efficiency of this process was approximately 98 percent recovery of the silver from the film.

During another test approximately 200 pounds of used film, utilized in offset printing, was pyrolized to a carbon silver residue in about 5½ hours to remove all the constituents except the silver and the carbonized cellulose film base material. In this test the heat was applied by injecting superheated steam into the chamber at temperatures above 500° C.

There was no pollution problem evident from this process. No fly ash is generated from the process. All the noxious offgas products were condensed with the excess steam, or otherwise treated by burning. It should be appreciated that this process lends itself to both large and small operations.

Now having described the preferred embodiment of this invention, it is requested that a United States Letters Patent be issued to the applicant protecting his invention defined as follows:

1. A silver recovery process for recovering silver from used organic materials having silver intimately associated therewith, comprising the steps of:

a. subjecting the materials to a noncombustible atmosphere;

b. progressively increasing the temperature of the materials in the noncombustible atmosphere to a final temperature below the melting point of silver which is sufficient to carbonize the organic materials to form a silver and carbon residue; and

c. separating the silver and carbon residue.

2. A silver recovery process as defined in claim 1 wherein the noncombustible atmosphere includes superheated steam.

3. A silver recovery process as defined in claim 2 wherein the noncombustible atmosphere has a pressure less than 15 p.s.i.g.

4. A silver recovery process as defined in claim 1 wherein the temperature of the materials is progressively increased to a final temperature above 350° C. and below the melting point of silver.

5. A silver recovery process as defined in claim 1 wherein the temperature of the materials is progressively increased to heat the materials to a final temperature above 500° C. and below the melting point of silver.

6. A silver recovery process as defined in claim 1 wherein the silver and carbon residue are separated by burning the silver and carbon residue in an oxidizing atmosphere to produce a silver and ash residue and separating the silver from the ash residue.

7. A silver recovery process as defined in claim 1 wherein the organic material is printed circuit boards having conductive elements of silver therein.

8. A silver recovery process for recovering silver from used photographic materials such as film and paper, that includes the steps of:

a. subjecting the used photographic material to a noncombustible atmosphere;

b. progressively increasing the temperature of the used photographic material to a temperature below the melting point of silver which is sufficient to vaporize and carbonize the used photographic material except the silver to form a residual silver and carbon residue; and

c. separating the silver and carbon.

9. A silver recovery process as defined in claim 8 wherein the temperature of the used photographic material is progressively increased to a temperature above 500° C. and below the melting point of silver.

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