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(71) Applicant: **KODAK LIMITED**
Patent Department,
Headstone Drive
Harrow, Middlesex HA1 4TY(GB)
(84) **GB**

(71) Applicant: **EASTMAN KODAK COMPANY**
343 State Street
Rochester New York 14650-2201(US)
(84) **BE CH DE FR IT LI NL**

(72) Inventor: **Sewell, Andrew James, c/o KODAK LIMITED**
Patent Department,
Headstone Drive
Harrow, Middlesex, HA1 4TY(GB)

(74) Representative: **Baron, Paul Alexander**
Clifford et al
Kodak Limited
Patent Department
Headstone Drive
Harrow Middlesex HA1 4TY (GB)

(54) Method and apparatus for silver recovery from photographic processing solutions.

(57) An apparatus for the treatment of photographic effluent solutions comprising a tank (1) for holding a solution of trimercapto-s-triazine or a water-soluble salt thereof; at least one effluent tank (2) for holding overflow from a post-development photographic processing solution; a reaction and precipitate-conditioning vessel (4); means for determining when the or each effluent tank is filled to a predetermined extent; means (3) for delivering the contents of an effluent tank and an appropriate amount of the trimercapto-s-triazine solution to the reaction and precipitate-conditioning vessel (4); and means for separating the insoluble silver compound from the treated solution (6,7,8) after precipitation of an insoluble silver compound.

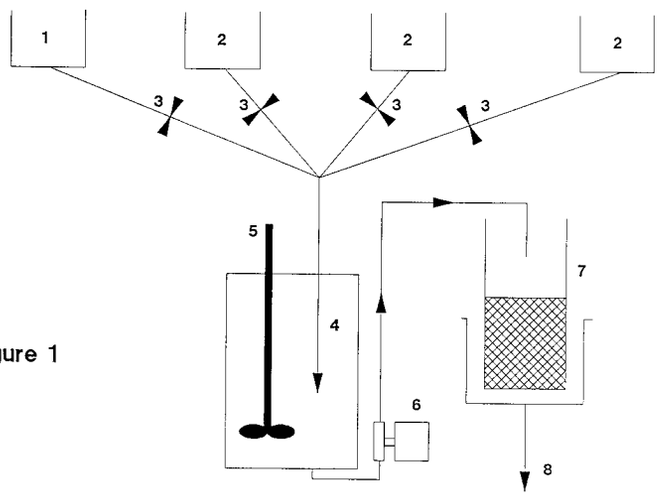

Figure 1

EP 0 596 549 A1

This invention relates to a method and apparatus for silver recovery from photographic processing solutions or effluent or overflow solutions therefrom.

There are many ways in which silver has been recovered from photographic processing solutions and waste liquors. Some involve exchange of iron for silver using steel wool. Others involve an electrolytic step in which silver metal is recovered at the anode.

In copending PCT application EP92/01583 there is described a method and apparatus for treating effluent produced by a photographic processing apparatus which, by a multistage process, produces a liquid and a solid which can be disposed of directly to drain or landfill respectively without infringing any current environmental disposal regulations. The specification does not, however, deal with the question of silver recovery.

Clearly the recovery of silver is worthwhile from an environmental standpoint alone but, in addition, the cost of recovering silver is usually outweighed by the value of the silver so recovered.

The present invention has as its object a machine which is able to recover silver from photographic processing or effluent solutions efficiently and automatically without operator intervention.

According to the present invention there is provided an apparatus for the treatment of photographic effluent solutions comprising a tank for holding a solution of trimercapto-s-triazine or a water-soluble salt thereof; at least one effluent tank for holding overflow from a post-development photographic processing solution; a reaction and precipitate-conditioning vessel; means for determining when the or each effluent tank is filled to a predetermined extent; means for delivering the contents of an effluent tank and an appropriate amount of the trimercapto-s-triazine solution to the reaction and precipitate-conditioning vessel; and means for separating the insoluble silver compound from the treated solution after precipitation of an insoluble silver compound.

The post development processing solutions may, for example, be bleach and/or bleach-fix and/or fixer and/or stabiliser solutions and/or wash waters.

The present invention also provides a method of treating silver-containing photographic effluent solutions contained in an effluent tank which comprises reacting a batch of the effluent solution with an appropriate amount of a solution of trimercapto-s-triazine or a water-soluble salt thereof, precipitating an insoluble silver compound thereby, allowing the precipitate to be conditioned by holding it for sufficient time in the conditioning tank and separating the solid and liquid phases in an apparatus as described above. The process is preferably triggered in response to a signal from an effluent tank level determining means indicating that the next batch of predetermined volume is ready to be processed.

In a preferred embodiment, the apparatus is controlled by a microprocessor.

The advantage of the present invention is that it allows easy automated silver recovery at a level of silver of 2ppm silver or below in the solution, little operator involvement and minimal power consumption.

The trimercapto-s-triazine compound may be an alkali metal salt thereof, for example the trisodium or tripotassium salt. As used below the term trimercapto-s-triazine will include both the compound itself and salts thereof. These compounds are available from DEGUSSA. The amount of trimercapto-s-triazine used will be based on the volume of solution to be treated and its origin (ie whether from a film or paper process) as its silver content will be known with sufficient accuracy. In this case it is convenient to have two effluent tanks, one from a film processor and the other from a paper processor. A third tank containing overflow from the stabiliser can also be used. In one embodiment of the present invention known volumes from each of the effluent tanks may be combined for silver recovery.

Alternatively, instead of calculating the amount of silver present, the silver content of the effluent can be determined by known means, for example by measuring its pAg with an suitable electrode.

When using the trisodium salt of tricmercapto-s-triazine (TMT) from 1 to 3 moles can be added per 3 moles of silver. A preferred amount of TMT is 1.25 to 1.5 moles per 3 moles of silver.

In one embodiment of the present invention the reaction and precipitate-conditioning vessel may be replaced by separate reaction and precipitate-conditioning vessels. This allows each vessel to be optimised for its purpose. The vessel where the precipitation takes place is preferably fitted with a stirrer.

In a combined vessel the solutions are run into it to react and precipitate the insoluble silver salt and remain there for the silver salt to settle out. It is believed that during this conditioning period the finer particles of the precipitate dissolve and re-precipitate onto the the larger particles thus reducing the number of small particles present. Clearly this aids separation of the solid and liquid phases. In the case of separate vessels, each can be optimised for its own function.

The effluent tank(s) are preferably fed from a larger collection tank fed by overflow from the processing tanks. This allows the effluent tank(s) to be filled with a fixed volume of liquid as soon as they are emptied. It is preferred in such a case that

means are provided for transferring a predetermined volume of effluent from the collection tank to an effluent tank which is sufficient to substantially completely fill it. The effluent tank(s) will then be able to deliver the next batch of effluent of known volume as soon as the reaction vessel is free to process it. The collection tank may have a volume of 15-20 litres, while the smaller tanks may have a volume of 0.2 to 3 litres, preferably 0.5 to 1.5 litres.

After a predetermined number of treatments the contents of the sedimentation tank is transferred to a filter to separate the liquid and solid phases prior to disposal and silver recovery. The liquid phase may optionally undergo further treatment or be reused in a processing solution.

If the liquid phase is to be processed further it could be passed to an apparatus as described in PCT Specification EP92/01583 where it could be combined with developer effluent.

Although the apparatus and method are described below with particular reference to minilabs, the present apparatus may also be designed on a larger scale to deal with effluent from a photofinishing laboratory.

The invention will now be described with reference to the accompanying drawings in which:

Figures 1 and 2 are diagrammatic representations of apparatus according to the present invention.

In Figure 1 the tank holding trimercapto-s-triazine solution (1) and effluent tanks (2) are arranged to deliver their contents flowing under gravity via valves (3) into combined reaction and precipitate-conditioning vessel (4) in which a stirrer (5) is provided. Typically in the minilab environment, the effluent tanks will contain overflow from the film fixer, paper fixer and wash water. When one of the tanks (2) is filled to a predetermined level its contents together with the appropriate amount of trimercapto-s-triazine solution from tank (1) is also added. Each tank (2) can be fed from a different source whose average silver content is known, hence the amount of trimercapto-s-triazine can be calculated. Tank (4) can have a volume in the range 10-20 litres, preferably 12-15 litres. When ready the precipitate and liquid are pumped by pump (6) into a filter bag (7) through which the liquid will pass and exit via outlet (8).

When attached to a minilab processing 50 customer orders per day, then a total of 12 litres of silver-bearing solution will need to be treated. The residence time in tank (4) will be approaching 2 days. The residence time can vary from from 1-5 hours, preferably 2-3 hours but has no upper limit.

In normal operation, after a predetermined number of treatment cycles, the conditioning tank (4) contents will be separated. When microprocessor controlled the calculation is made by the system software and, when required, the pump (6) will be activated thus transferring the contents of tank (4) into the filter bag (7). The preferred filter bags have mesh apertures of 0.2 to 2 μm, preferably 0.5 to 1.0 μm. The separation may take place under the influence of gravity over a period of several hours. After several cycles the filter bag will be changed and the separated solid sent for silver recovery by a refiner.

The apparatus will remove silver leaving no more than 2 ppm silver in the liquid phase.

In figure 2 tanks (1) and (2) carry out the same functions as above, as do pump (6), filter bag (7) and outlet (8). A separate reaction vessel (9) is provided together with a recirculating pump (10) which is active during the precipitation step. The fully reacted mixture will then pass to conditioning tank (4) so that the small particles will dissolve and reprecipitate on the larger grains. Separation of the solid and liquid phases will be carried out as described above in relation to Figure 1.

Claims

1. An apparatus for the treatment of photographic effluent solutions comprising a tank (1) for holding a solution of trimercapto-s-triazine or a water-soluble salt thereof; at least one effluent tank (2) for holding overflow from a post-development photographic processing solution; a reaction and precipitate-conditioning vessel (4); means for determining when the or each effluent tank is filled to a predetermined extent; means (3) for delivering the contents of an effluent tank and an appropriate amount of the trimercapto-s-triazine solution to the reaction and precipitate-conditioning vessel (4); and means for separating the insoluble silver compound from the treated solution (6,7,8) after precipitation of an insoluble silver compound.

2. An apparatus as claimed in claim 1 in which the means for separating the insoluble silver compound from the treated solution is a filter.

3. An apparatus as claimed in claim 1 or 2 in which the reaction and precipitate-conditioning vessel (4) is replaced by separate reaction and precipitate-conditioning vessels (9,4).

4. An apparatus as claimed in claim 3 in which the precipitate is allowed to settle in the precipitate-conditioning vessel (4) and the separation is achieved by removing the supernatant liquid from the settled solid.

5. An apparatus as claimed in any of claims 1 to 4 in which the effluent tank(s) are fed from a

larger collection tank fed by overflow from the processing tanks.

6. An apparatus as claimed in claim 5 in which means are provided for transferring a predetermined volume of effluent from the collection tank to an effluent tank which is sufficient to substantially completely fill said effluent tank.

7. An apparatus as claimed in any of claims 1 to 6 which is controlled by a microprocessor.

8. An apparatus as claimed in any of claims 1 to 7 in which the filter has an aperture size of from 0.2 to 2 μm.

9. An apparatus as claimed in any of claims 1 to 8 in which the separated liquid phase receives further treatment prior to disposal or is recycled for use in a photographic processing solution.

10. An apparatus as claimed in any of claims 1 to 9 which is designed for use with a minilab processing apparatus.

11. An apparatus as claimed in any of claims 1 to 9 which is designed for use with a large scale processing apparatus.

12. A method of treating silver-containing photographic effluent solutions contained in an effluent tank (2) which comprises reacting a batch of the effluent solution with an appropriate amount of a solution of trimercapto-s-triazine or a water-soluble salt thereof, precipitating an insoluble silver compound thereby, allowing the precipitate to be conditioned by holding it for sufficient time in the conditioning tank (4) and separating the solid and liquid phases in an apparatus as claimed in any of claims 1 to 11.

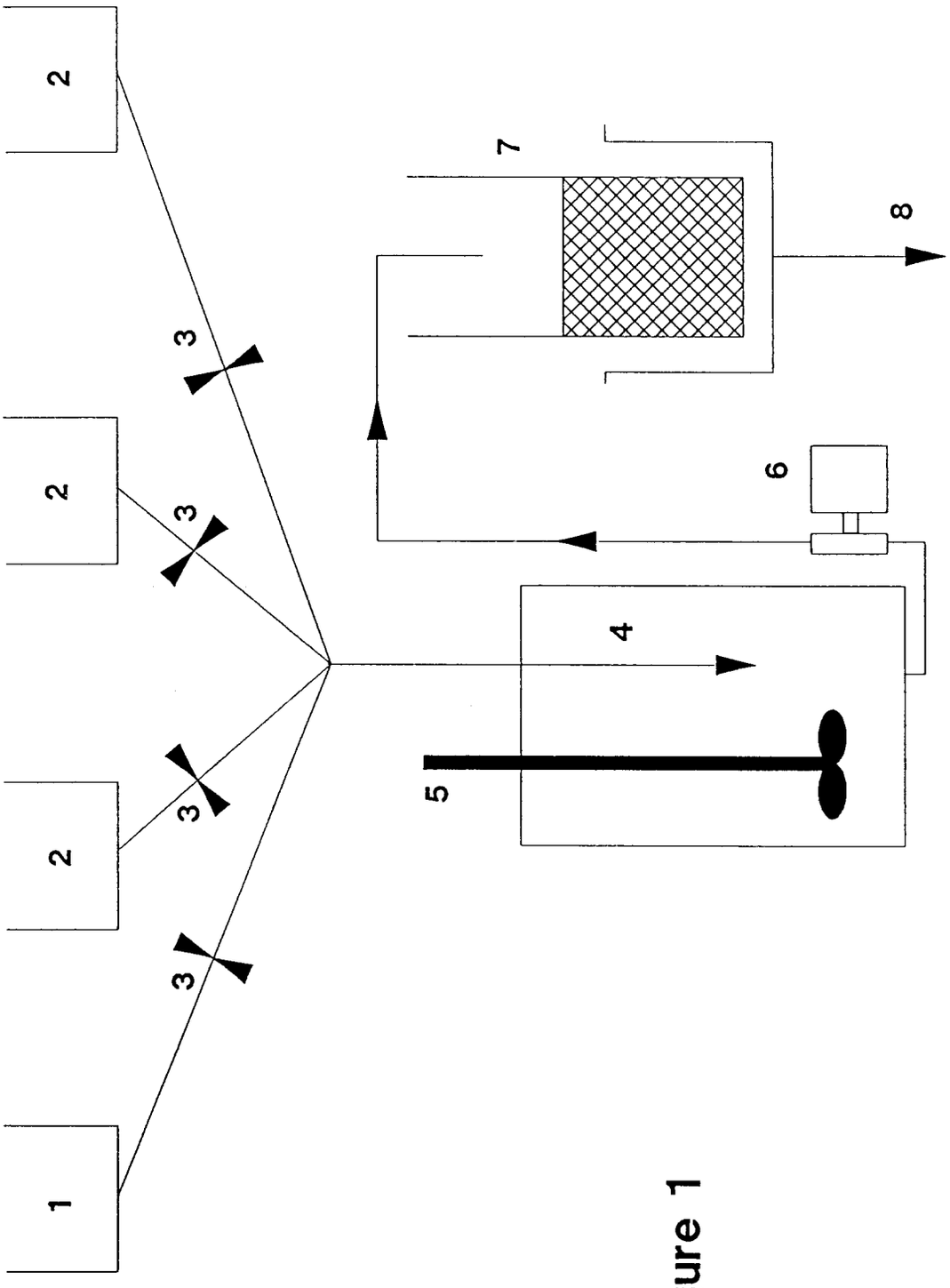

Figure 1

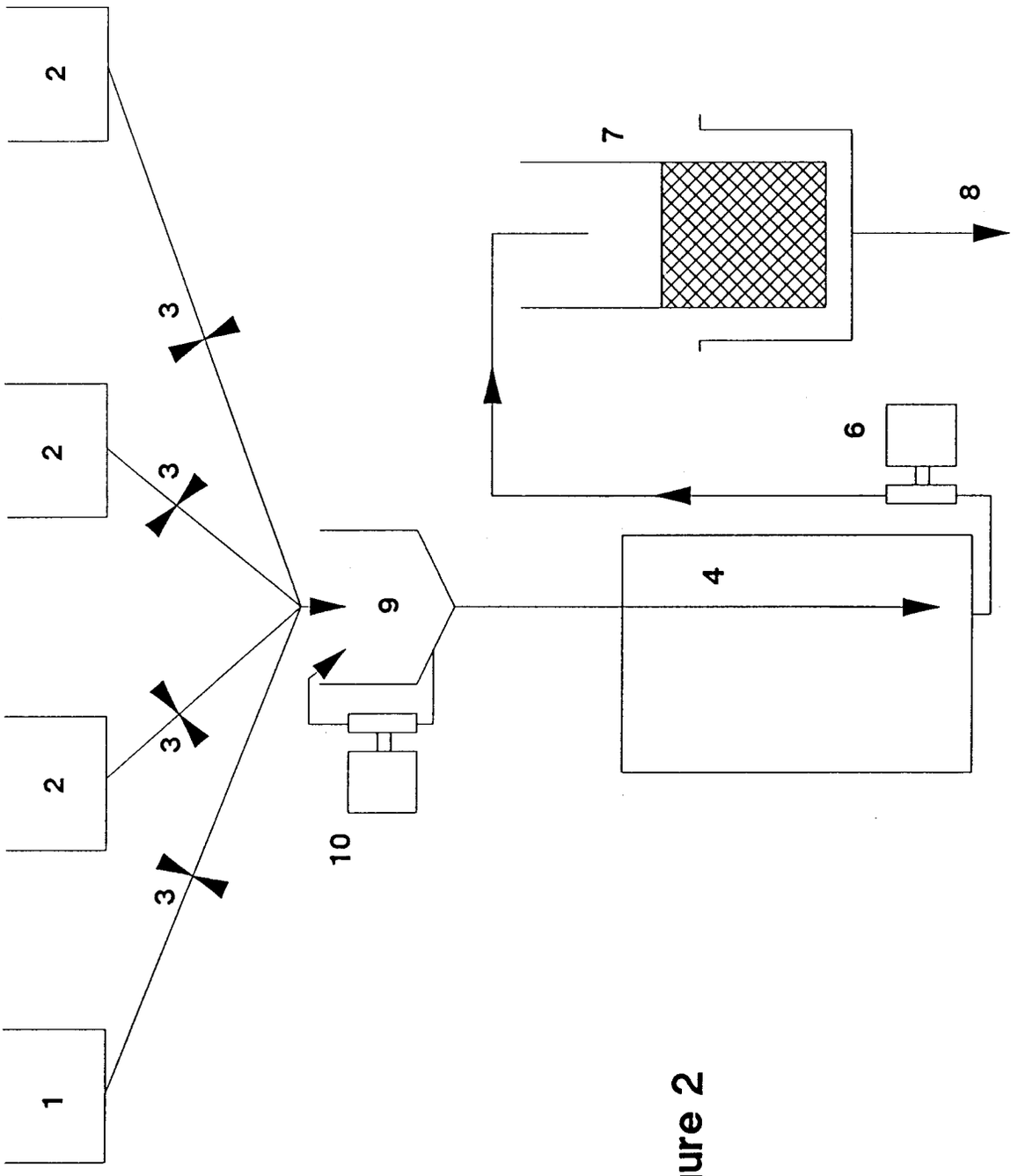

Figure 2

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 20 2671

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X Y	FR-A-2 149 546 (SANKYO KASEI COMPANY LTD.) * PAGE 1, LINE 1 - PAGE 5, LINE 2; PAGE 7, LINE 5 - PAGE 9, LINE 21; EXAMPLE 2; CLAIMS 1, 2, 4 - 6 * ---	1,12 3-5,7	G03C5/395 G03D3/06
X Y	FR-A-2 534 900 (REHMANN PROCESSENGINEERING) * ABSTRACT; PAGE 1, LINE 1 - PAGE 6, LINE 24; PAGE 7, LINE 23 - PAGE 9, LINE 25; PAGE 10, LINES 11 - 28; PAGE 11, LINE 29 - PAGE 12, LINE 10; PAGE 13, LINE 6 - PAGE 14, LINE 2, LINE 23 - PAGE 19, LINE 5; CLAIMS 1,10; FIG. 1, 2, 4 * ---	1,2,6, 8-12 3-5,7	
P,X, L D,Y A	WO-A-93 02391 (KODAK LTD.) * ABSTRACT; PAGE 1, LINE 1 - PAGE 7, LINE 8; PAGE 9, LINE 16 - PAGE 10, LINE 24; CLAIMS 1, 2, 5; FIG. 1 * ---	1,2,6-11 3-5 12	
A	EP-A-0 424 820 (FUJI PHOTHO FILM CO., LTD.) ---		TECHNICAL FIELDS SEARCHED (Int.Cl.5) G03C G03D
A	GB-A-1 411 985 (ILFORD LTD.) -----		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	1 March 1994	Fischer, W

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

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