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B 2640 Mortsel(BE)**(54) **A method for processing an imagewise exposed silver halide photographic material.**

(57) A method for processing imagewise exposed photographic silver halide material by conveying said material in succession through at least a developing, a fixing and a rinsing station, wherein

- said fixing station comprises two distinct tanks, the fixing of the photographic material occurring completely or almost so in the first tank,
- a replenishment arrangement for replenishing fixer carried-over by the photographic material from the first to the second tank,
- the silver content of fixer in the first tank is kept below a certain maximum level by electrolytic silver recovery,
- said photographic material is squeezed at its cross-over from said first to the second tank to limit carry-over of fixer to said second tank,
- fixer is caused to overflow from said second into said first tank thereby to produce a counterflow of fixer,
- fixer is caused to overflow from said first tank and is pumped to said second tank, and
- the silver content in the second tank of said fixing station is kept below 0.05 Ag<sup>+</sup>/l.

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## BACKGROUND OF THE INVENTION

## Field of the invention.

The present invention relates to a method for processing an imagewise exposed photographic silver halide material.

## Description of the prior art.

The processing of conventional photographic silver halide material comprises among others the steps of developing, fixing and rinsing.

The purpose of fixing is to remove silver halide from the film.

This silver halide can be the non developed halide in a black-and-white material or all halide in a colour material when the image is built up by dyes.

Film processing can be done in a very small processing device like a minilab or a small micro-film processor but in a huge processing machine as well like a film processor for motion picture print film running at a film speed of 15,000 m/h and more.

The present invention relates in particular to the processing of motion picture print film but its scope extends to smaller scale photographic film or paper-processing devices as well.

As a consequence of its fixing film is continuously bringing silver into the fixer. This silver is actually the only harmful and toxic chemical in the fixer, and although due to the presence of sulphide in waste waters and the insolubility of silver sulphide the risk for  $\text{Ag}^+$  in the waste water is rather limited and the concentration of silver in the effluent water is in most countries limited. Therefore, the silver and the fixer are recovered in order to keep the silver concentration in the fixer as low as possible because by carry-over from the fixer into the rinsing station following the fixing, silver ions are constantly transported to the rinsing water that finally ends up in the drain.

Once silver is in the rinsing water it can only be recovered by the use of ion-exchange resins which are very costly and for many people not easy to monitor, or by the use of metal replacement compositions mainly comprising steel wool, but which involves another pollution, viz. Fe-ions in the effluents.

For these reasons the carry-over of silver into the rinsing water has to be kept as low as possible and this has to be done in two ways : reducing the volume of fixer carry-over and reducing the silver concentration in the carried-over fixer.

## SUMMARY OF THE INVENTION

## Object of the invention.

It is the object of the invention to provide a method that reduces considerably the amount of silver in the fixer that is carried over to the rinsing water.

## Statement of the invention.

A method for processing imagewise exposed photographic silver halide material by conveying it in succession through at least a developing, a fixing and a rinsing station, wherein :

- said fixing station comprises at least two distinct tanks, the fixing of the photographic material occurring for at least 80 % in the first tank,
- the silver content of fixer in the first tank is kept below a certain maximum level by electrolytic silver recovery,
- said photographic material is squeezed at its cross-over from said first to the second tank to limit carry-over of fixer to said second tank,
- fixer is caused to overflow from said second into said first tank thereby to produce a counterflow of fixing liquid,
- fixer is caused to overflow from said first tank and is then pumped to said second or last tank if there are more than two tanks, and
- the silver content in the last tank of said fixing station is kept below 0.05 g of  $\text{Ag}^+/\text{l}$ .

Keeping the silver content in the last tank of the fixing station below 0.05 g of  $\text{Ag}^+/\text{l}$  can be achieved by electrolytic silver recovery of fixer in the first tank only, but also by electrolytic silver recovery in the first as well as in the last tank.

The method according to the present invention does not remove all of the silver from the effluent water. This means that at those instances where environment considerations are less stringent, the rinsing water may directly flow to the sewer. However, when more stringent regulations control effluent water, it is required to remove silver from the rinsing water to a degree up to, e.g., 1 ppm by means of ion-exchange resins. The fact that these ion exchange resin devices now have to remove much less silver from the rinsing than the usual devices, results in their operation to become easier, less costly, and their capacity to become smaller, which leads to important savings in installation costs.

Preferred embodiments of the method according to the invention are as follows.

The capacity of the first tank of the fixing station is such that the photographic material is

fixed for 100 % in said first tank.

The liquid contents of the last tank of the fixing station is considerably smaller than that of the first tank, and suitably even less than one third of that of the first tank.

Silver is recovered from fixer overflowing said first tank.

The silver recovery of fixer overflowing said first tank is done in a buffer tank.

A replenishment arrangement is provided for replenishing fixer carried off by the photographic material from the fixing station.

The invention includes also a modified method for attaining the claimed object.

According to the invention, a method for processing imagewise exposed photographic silver halide material by conveying it in succession through at least a developing, a fixing and a rinsing station, is characterised in that

- said fixing station comprises at least two distinct tanks, the fixing of the photographic material occurring for at least 80 % in the first tank,
- the silver content of fixer in the first tank is kept below a certain maximum level by electrolytic silver recovery,
- the photographic material is squeezed at its cross-over from the first to the next tank to limit carry-over of fixer to the next tank,
- the silver content of fixer in the last tank is kept below a level of 0.05 g/l by electrolytic silver recovery, and
- concentrated fixer chemicals are added to the first tank to keep the concentration of the fixer at an operative level.

Suitably, said concentrated fixer chemicals are added in solid form.

As described hereinbefore, the present invention is intended in particular for use in the motion picture field. Film processing in this field comprises more than the usual developing, fixing and rinsing steps. Referring e.g. to the regular so-called ECP II process, this system comprises the successive operations of conveying a film through a bath for removal of the back layer of the film, a (colour) development bath, a stop bath, a rinsing bath, a first fixing bath, a rinsing bath, a bleach bath, a rinsing bath, a sound-track development, a rinsing bath, a second fixing bath, a final rinsing bath, a stabilisation bath, and lastly a drier.

The method according to the invention can be used for the two fixing operations of the described process.

It will be understood, however, that application of the method according to the invention is not limited to this particular process.

## BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be described hereinafter by way of example with reference to the accompanying drawings wherein :

Fig.1 is a diagrammatic illustration of a first embodiment for performing the method according to the invention,

Fig.2 is a diagrammatic illustration of a second embodiment for performing the method according to the invention, and

Fig.3 is a diagrammatic illustration of a third embodiment for performing the method according to the invention.

Referring to Fig.1 there is shown a fixing station of an installation for processing an imagewise exposed photographic material. This installation may in its simplest form comprise a developing, a fixing and a rinsing station, but may as well be a more complex arrangement as described hereinbefore.

It is clear that the shown fixing station is followed by a rinsing station.

The fixing station which is generally designated by numeral 10 comprises a first tank 12 and a second one 13. The capacity of tank 13 can range between half and one third of that of tank 12. Tank 13 has an overflow opening 14 determining the liquid level 15 in said tank in normal operation. Fixer flows via overflow 14 in tank 12, as indicated generally by arrow 9. The fixer level 16 of tank 12 is determined by an overflow opening 17 disposed lower than overflow 14. Arrow 18 indicates the general transport direction of a film through the station. It will be understood that in practice a film does not follow a straight path as suggested by the arrow but, on the contrary, is conveyed over a large plurality of rollers determining a number of film loops through the fixer that are located beside and after each other to obtain the required processing time for a film in the station.

A film is entering tank 12 via a driven pressure roller pair (not shown), is squeezed by another driven roller pair upon leaving tank 12 and entering tank 13, and is squeezed by still another roller pair upon leaving tank 13 and entering the rinsing station.

Silver from the fixer in tank 12 is continuously recovered by an installation 19, which also may also comprise pump means for maintaining a continuous circulation of fixer in tank 12.

Liquid overflowing opening 17 passes through a buffer tank 20 which is coupled with a recovery installation for recovery of silver from fixer overflowing tank 12. Fixer from buffer tank 20 is pumped into tank 13 near the film outlet thereof and in that way functions to replenish said second tank. The overflow of the second tank functions as

replenisher for the first tank.

In a classical fixing station which comprises one tank only, the silver concentration is mostly kept at 0.5 - 1.0 g of  $\text{Ag}^+/\text{l}$ .

In the embodiment described hereinbefore, the silver content in the second tank can easily be kept at 0.05 g of  $\text{Ag}^+/\text{l}$  so that carry-over losses of  $\text{Ag}^+$  to the rinsing station are reduced by a factor 10 to 20.

The amount of silver to be recovered in the second tank depends on three factors : silver content of the film, silver concentration in the first tank and carry-over volume.

With a silver concentration in the film of 2 g, a silver concentration in the first tank of 1 g/l and a carry-over volume of 30 ml/m<sup>2</sup>, the amount of silver to be recovered in the second tank is 1,5 % of the total amount to be recovered. With a carry-over volume of 60 ml/m<sup>2</sup> this would be 3 %.

Fig.2 shows a fixing installation 10 wherein each of two tanks 12 and 13 comprises its own silver recovery device, viz. 21 and 22. The overflows 14 and 17 of both tanks are the same as those shown in Fig.1. The overflow of the first tank is used as replenisher for the second tank.

It will be understood that both embodiments described hereinbefore will comprise metering systems 23 and 24 for adding fixer chemicals to the system in response to the amount of processed film in order to keep the fixer concentration at a reasonably constant level.

Fig.3 illustrates an embodiment of a fixing station with two tanks 12 and 13 in which no overflow system is used. The embodiment is intended for use with a complex motion-picture film-processing system as described hereinbefore wherein the fixing station is preceded by a rinsing station and in consequence fixer in the first tank 12 is constantly diluted via carry-over of water from the preceeding rinsing tank. At the other hand, fixer is constantly removed from the first tank by carry-over to the second one. Thus, in principle the amount of liquid in both tanks remains constant. The dilution of fixer in the first tank is compensated by replenishment of fixer chemicals from a supply 25 in response to the amount of processed film. Such replenishment preferably occurs with solid chemicals.

Silver-recovery devices 26 and 27 reduce the silver content of the fixer in both tanks to the desired level.

The invention is not limited to the described embodiments.

The number of tanks for the fixing station is not limited to two, but can comprise three or even more tanks. This does not change anything to the principle of countercurrent fixing as explained with reference to Figs. 1 and 2, or to the overflow-free arrangement shown in Fig.3.

## Claims

1. A method for processing imagewise exposed photographic silver halide material by conveying said material in succession through at least a developing, a fixing and a rinsing station, wherein
  - said fixing station comprises at least two distinct tanks, the fixing of the photographic material occurring for at least 80 % in the first tank,
  - the silver content of fixer in the first tank is kept below a certain maximum level by electrolytic silver recovery,
  - said photographic material is squeezed at its cross-over from said first to the second tank to limit carry-over of fixer to said second tank,
  - fixer is caused to overflow from said second into said first tank thereby to produce a counterflow of fixer,
  - fixer is caused to overflow from said first tank and is then pumped to said second or last tank if there are more than two tanks, and
  - the silver content of fixer in the last tank of said fixing station is kept below 0.05 g of  $\text{Ag}^+/\text{l}$ .
2. A method according to claim 1, wherein the capacity of the first tank of the fixing station is such that the photographic material is fixed for 100 % in said first tank.
3. A method according to claim 1 or 2, wherein the liquid content of the last tank of the fixing station is considerably smaller than that of the first tank.
4. A method according to claim 3, wherein the liquid content of said last tank is less than one third of that of the first tank.
5. A method of processing according to claim 1, wherein silver is recovered from fixer overflowing said first tank.
6. A method of processing according to claim 5, wherein the silver recovery of fixer overflowing said first tank is done in a buffer tank.
7. A method of processing according to claim 1, wherein there is an additional silver recovery of fixer in the last tank of said fixing station.
8. A method of processing according to any of claims 1 to 7, which comprises a replenishment arrangement for replenishing fixer carried

away by the photographic material from the fixing station.

9. A method for processing imagewise exposed photographic silver halide material by conveying said material in succession through at least a developing, a fixing and a rinsing station, wherein
- said fixing station comprises at least two distinct tanks, the fixing of the photographic material occurring for at least 80 % in the first tank, 5 10
  - the silver content of fixer in the first tank is kept below a certain maximum level by electrolytic silver recovery, 15
  - said material is squeezed at its crossover from the first to the next tank to limit carry-over of fixer to the next tank,
  - the silver content of fixer in the last tank is kept below a level of 0.05 g/l, and 20
  - concentrated fixer chemicals are added to the first tank to keep the concentration of the fixer at an operative level.
10. A method according to claim 9, wherein said concentrated fixer chemicals are added in solid form. 25
11. A method according to claim 9 or 10, wherein silver is continuously removed from the fixer in the last tank of said fixing station. 30

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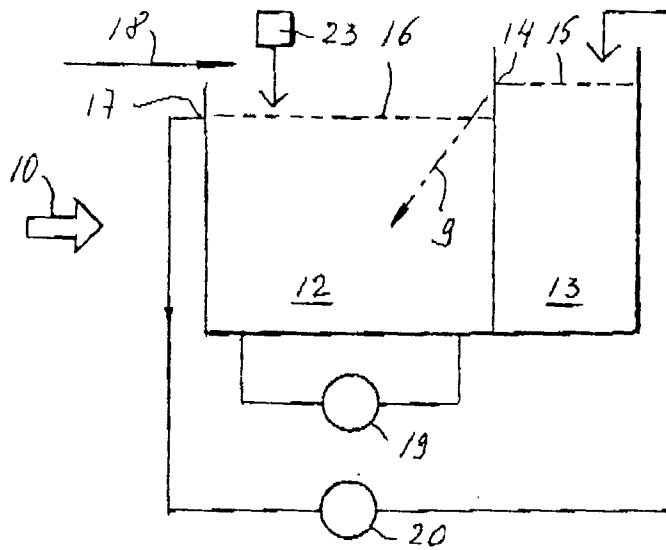


Fig. 1

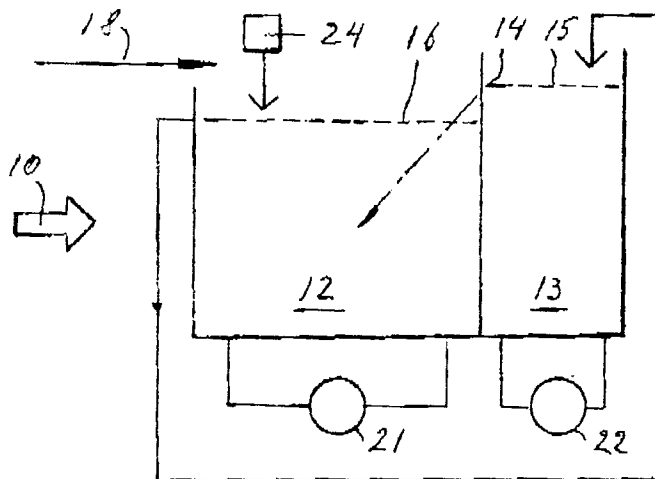


Fig. 2

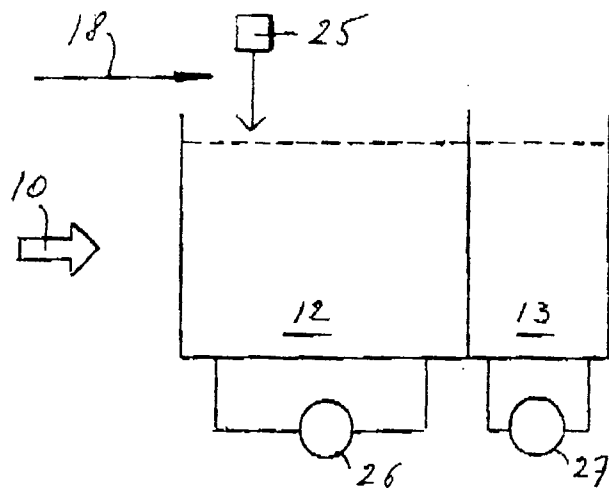


Fig. 3



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## EUROPEAN SEARCH REPORT

Application Number

EP 92 20 3450

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)
Y	DATABASE WPIL Section Ch, Week 9208, February 1992 Derwent Publications Ltd., London, GB; Class G06, AN 92-061114 & JP-A-4 006 291 (KONICA CORP) 10 January 1992 * abstract *	1,3,4, 9-11	G03C5/38 G03C5/26
Y	WO-A-9 115 806 (KODAK LIMITED ET AL.) * claims; figure *	1,3,4, 9-11	
Y	CHEMICAL ABSTRACTS, vol. 47, no. 7, 10 April 1953, Columbus, Ohio, US; CRABTREE ET AL. 'Two-bath fixation of prints' column 3158 ; * abstract * & PSA JOURNAL vol. 19B, 1953, pages 10 - 16 CRABTREE ET AL. 'Two-bath fixation of prints'	1,3,4, 9-11	
A	EP-A-0 219 841 (FUJI PHOTO FILM CO.,LTD.) * claims; example 1; table 1 *	1-11	
A	PATENT ABSTRACTS OF JAPAN vol. 011, no. 340 (P-634)7 November 1987 & JP-A-62 123 463 ( KONISHIROKU PHOTO IND CO LTD ) 4 June 1987 * abstract *	1-11	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 13 JULY 1993	Examiner HILLEBRECHT D.A.
<b>CATEGORY OF CITED DOCUMENTS</b>			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		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 & : member of the same patent family, corresponding document	