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(54) Method of processing photographic silver halide material

Verfahren zur Verarbeitung eines photographischen Silberhalogenidmaterials

Procédé de traitement d'un matériau photographique à l'halogénure d'argent

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(56) References cited:
EP-A- 0 325 277
EP-A- 0 368 340
WO-A-91/07698
US-A- 4 529 687
US-A- 5 063 144

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Description

[0001] This invention relates to a method of processing photographic silver halide material such as photographic film and paper. In particular it relates to a method of processing colour negative film.

[0002] Colour negative films are processed in an industry standard process called C-41. Most C-41 systems are run on the basis that a replenisher solution is added to the developer and excess developer is removed by letting it overflow. The developer solution thus achieves a stable condition in which chemicals used up during processing are replenished to maintain a working concentration and seasoning products e.g. bromide and iodide ions and antifoggant fragments from DIR couplers entering the developer solution from the film are kept at an acceptable level. Recent C-41 systems are run on a developer replenishment rate of from 500 to 1800 ml/m^2 of film processed. Colour papers and black-and-white photographic materials can also be processed by replenishment systems.

[0003] Conventional developers contain bromide ions and additional bromide ions are introduced into development solutions by the reduction of silver bromide during the development process. The level of bromide ion in colour negative developers strongly influences the rate of image development. A low level will give a faster rate of development other things being equal.

[0004] It is desirable to reduce the amount of CD4 (4-(N-ethyl-N-2-hydroxyethyl)-2-methylphenylenediamine sulphate) effluent produced during the development of colour negative films. One way to achieve this is to lower the CD4 concentration in the developer and to compensate somewhere else in the overall system to restore the necessary development activity. A lower bromide ion level in the development solution can help in this regard. There is a minimum bromide ion level that can be reached by normal replenishment methods and to go beyond this to lower levels it is necessary to remove the bromide ion by artificial means. However when this is done, it becomes difficult to control exactly the level of bromide ion because of variability in film type and the ageing and variability of the removal procedure.

[0005] A low effluent replenishment system for colour negative developers is described and claimed in our European Patent Specification No. 0 500 592. This discloses a zero-overflow replenishment system for C-41 developer in which excess bromide ion generated by the film is removed by using an ion-exchange resin in-line with the developer tank. This is controlled by careful monitoring of film throughput, replenishment rates and the rate of flow through the ion-exchange column. This system provides a very low replenishment rate. The only loss to drain is the chemistry carried over in the film into the next tank. However a difficulty in this system is maintaining the desired bromide level by balancing the removal rate with the input rate from the film.

[0006] According to the present invention we provide a method of processing photographic silver halide material in a processing tank in which developer solution is treated to remove developer seasoning products and is replenished with a sufficiently small volume of replenisher components that substantially no overflow is produced characterised in that the developer solution and replenisher components added to the tank do not contain bromide ions and that the solution formed during processing is treated with bromide ion removal means to remove continuously essentially all bromide ions formed therein and to maintain a bromide ion-free solution during the processing of the material.

[0007] Thus bromide ion is substantially absent from the developer or developer replenisher used in the method of the invention and bromide ion formed by the reduction of silver bromide during development is removed substantially completely as it is formed so that bromide ion effectively takes no part in the development reaction.

[0008] The method of the invention is applicable to the processing of any form of silver halide photographic material such as colour negative film, colour paper and black and white materials. It is very suitable for processing colour negative film, particularly according to the general procedures of the C-41 process. Colour negative films which may be processed include for example films that are commercially available and films described in Research Disclosure Item 17643, December 1978, pages 22-31, Published by Kenneth Mason Publications of Emsworth, Hampshire, United Kingdom.

[0009] Generally bromide ion produced during development is removed from development solution which is continuously withdrawn from a development tank into a treatment loop with the treated solution being thereafter returned to the tank. Bromide ion removal can be effected by any suitable means including ion-exchange, electrodialysis, dialysis and reverse osmosis, with ion-exchange removal being preferred. Whatever the removal means, it has suitably sufficient capacity to achieve removal of substantially all potential bromide. The method of the present invention is an extension of the low effluent replenishment system for colour negative developers which is described and claimed in our European Patent Specification No. 0 500 592. It comprises the use of a reformulated developer solution which does not contain bromide ions, in addition to removal of bromide. Any bromide generated by the film is removed by means having sufficient capacity to remove bromide completely as it passes into the solution. This is easy to achieve and eliminates any need to balance exactly the removal and generation rates found to be necessary in our earlier system.

[0010] When ion-exchange is used as the removal method, the ion-exchange resin is preferably anionic (for the exchange of anions). A preferred type of anionic resin is based on a polystyrene matrix cross-linked, for example, with 3% to 5% of divinylbenzene.Its strongly basic character is derived from quaternary ammonium groups. Examples of suitable anionic exchange resins are:

IRA 400	Rohm and Haas
Dowex 1-X8	Dow Chemical, and
Duolite A113	Diamond Shamrock.

[0011] The ion-exchange resin is preferably located in a cartridge through which the contents of the developer tank are pumped either continuously or when required. When it has been exhausted it may be discarded or regenerated as will be well understood.

[0012] The small amount of replenisher which is added to the development solution may be in the form of a solution or a solid. It may be added in a variety of ways. In a first way of addition, the replenisher components are added as an activator solution and a solution of colour developing agent. In a second way of addition, the replenisher components may be added as three separate solutions having the following compositions:

PART A	
Potassium carbonate	470 g/l
Potassium hydroxide	11 g/l
Diethylenetriamine-pentaacetic acid pentasodium salt	106 g/l
Sodium metabisulphite	43 g/l
PART B	
Hydroxylamine sulphate	272 g/l
PART C	
Sodium metabisulphite	16.5 g/l
CD4	472 g/l

[0013] In a third way of addition, additions of activator solution and solid CD4 colour developing agent may be made, the activator composition being suitably as follows:

Potassium sulphate	24.0 g/l
Hydroxylamine sulphate	13.4 g/l
Anti-cal	6.5 g/l
Potassium carbonate	37.5 g/l

where Anti-cal is the penta sodium salt of diethylene triamine penta acetic acid and the pH is 11.6.

[0014] Approximate replenishment rates for the above 3 part replenisher are as follows:

Part A	16.8 to 49.5 ml/m^2 of film
Part B	1.87 to 6.5 ml/m^2 of film
Part C	3.5 to 6.5 ml/m^2.of film.

[0015] The method of the invention allows developer solutions to be used which contain lower levels of colour developing agents compared with the solutions used in the standard C-41 process. The levels which can be used suitably are between 10% and 100% of those used in the standard process and preferably in the range 25% to 50% of those used in the standard C-41 process.

[0016] In the method of the invention a zero-sulphite developer can be used with advantage since sulphite ions are removed to some extent during its operation. This adds the advantage that any variability in sulphite level introduced by operation of the method will be eliminated.

[0017] The method of the invention has a number of advantages some of which are as follows:

1. The control of the bromide removal procedure is simple and is essentially reduced to having sufficient capacity to remove all the bromide generated in a given time. These reasons make the zero -overflow replenishment system a very viable option for effluent reduction.

2. The zero-overflow replenishment system gives the lowest effluent possible for a given developer formulation in a single tank configuration. It is approximately 1/10th that of current C-41 LORR chemistry.

3. The method of the invention can be used in conjunction with other methods of effluent reduction such as reformulated developer with lower CD4 level. If the CD4 level in the developer is halved the total system has about 1/20th of the CD4 effluent of C-41 LORR.

4. The removal of bromide ion rapidly and efficiently can be carried out more efficiently in a small volume tank so that the entire tank contents can be circulated through the column in one or two minutes.

[0018] The invention is illustrated by the accompanying drawings wherein:

Figure 1 is a diagram of a developer tank with its inlets and outlets; and
Figure 2 is a graph of concentration in g/l against number of bed volumes which shows the removal of bromide ion by ion exchange in the Example.

[0019] Figure 1 shows a developer tank to which additions of activator solution and solid CD4 colour developing agent are made. There is a carry-out of developer solution on the film and, should the volume drop, due to evaporation, the level is made up with water. The ion-exchange cartridge is attached to the tank as shown and developer is circulated through it.

[0020] The ion-exchange resin used is preferably anionic as described above and is preferably located in a cartridge also as described above. The small amount of replenisher necessary may be a solution or a solid and may be added by one of the ways described above.

[0021] The invention is further illustrated by the following Example:

EXAMPLE

[0022] In this example bromide ion was removed from C-41 developer solution as shown in Figure 1. Bromide removal was by ion-exchange and the resin used in the experiment was IRA 400 regenerated with potassium carbonate (5%). The complete removal of bromide ion at the same time as replenishing with the minimum volume might at first sight be thought to need a large column or frequent renewal of a smaller column thereby making the method impractical. A simple consideration shows that this is not the case. In the earlier zero-overflow replenishment system (EP-A-0 500 592) all excess bromide is removed to maintain a tank level of 1.3 g/l sodium bromide. This means that all the extra bromide generated by the film is removed by the ion-exchange column.The amount remaining in solution is the same as in fresh unused developer, i.e. 1.3 g/l.

[0023] Since all the bromide generated by the film is also removed by the ion-exchange column in the zero bromide method; the basic capacity needed is the same in each case. This amounts to about a 500g cartridge for a Model 25 film processor per week. In order to have a certainty of bromide removal it is desirable to introduce a safety margin in the zero bromide case of the order of from 10% to 20%.

[0024] The results are shown in Figure 2 of the drawings. This is a graph of concentration in g/l against number of bed volumes and has Curves 1, 2 and 3 showing concentrations of sodium bromide, sodium sulphite and sodium sulphate respectively. From Figure 2 it can be seen that for 10 bed volumes the bromide ion level is essentially zero.

Claims

1. A method of processing photographic silver halide material in a processing tank in which developer solution is treated to remove developer seasoning products and is replenished with a sufficiently small volume of replenisher components that substantially no overflow is produced characterised in that the developer solution and replenisher components added to the tank do not contain bromide ions and that the solution formed during processing is treated with bromide ion removal means to remove continuously essentially all bromide ions formed therein and to maintain a bromide ion-free solution during the processing of the material.

2. A method according to claim 1 characterised in that the photographic silver halide material is colour negative film.

3. A method according to either of the preceding claims characterised in that the bromide ion removal means is ion-exchange, electrodialysis, dialysis and/or reverse osmosis.

4. A method according to claim 3 characterised in that the bromide ion removal means is ion-exchange.

5. A method according to claim 4 characterised in that an anion exchange resin (for the exchange of anions) is used.

6. A method according to claim 5 characterised in that the anion exchange resin is based on a polystyrene matrix cross-linked with 3% to 5% of divinylbenzene.

7. A method according to any one of the preceding claims characterised in that the developing solution contains a reduced level of colour developing agent compared with that present in the standard C-41 process.

8. A method according to claim 7 characterised in that the reduced level of colour developing agent is in the range 25% to 50% of that present in the standard C-41 process.

Patentansprüche

1. Verfahren zum Verarbeiten von photographischem Silberhalogenidmaterial in einem Verarbeitungsbehälter, in dem Entwicklerlösung behandelt wird, um Entwickleralterungsprodukte zu entfernen, und mit einem ausreichend kleinen Volumen an Ergänzungskomponenten ergänzt wird, daß im wesentlichen kein Überlaufen bewirkt wird, dadurch gekennzeichnet, daß die Entwicklerlösung und Ergänzungskomponenten, die dem Behälter zugesetzt werden, keine Bromidionen enthalten und daß die während der Verarbeitung gebildete Lösung mit einer Maßnahme zur Entfernung von Bromidionen behandelt wird, um kontinuierlich im wesentlichen alle Bromidionen, die darin gebildet werden, zu entfernen und eine Bromidionen-freie Lösung während der Verarbeitung des Materials aufrechtzuerhalten.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das photographische Silberhalogenidmaterial ein Farbnegativfilm ist.

3. Verfahren nach einem der vorangegangenen Ansprüche, dadurch gekennzeichnet, daß die Maßnahme zur Entfernung von Bromidionen Ionenaustausch, Elektrodialyse, Dialyse und/oder Umkehrosmose ist.

4. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß die Maßnahme zur Entfernung von Bromidionen Ionenaustausch ist.

5. Verfahren nach Anspruch 4, dadurch gekennzeichnet, daß ein Anionenaustauscherharz (für den Austausch von Anionen) verwendet wird.

6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß das Anionenaustauscherharz auf einer mit 3% bis 5% Divinylbenzol vernetzten Polystyrolmatrix basiert.

7. Verfahren nach einem der vorangegangenen Ansprüche, dadurch gekennzeichnet, daß die Entwicklungslösung eine verringerte Konzentration an Farbentwicklungsmittel im Vergleich zu jener, die bei dem C-41-Standardprozeß vorliegt, enthält.

8. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß die verringerte Konzentration an Farbentwicklungsmittel im Bereich von 25% bis 50% von jener, die bei dem C41-Standardprozeß vorliegt, liegt.

Revendications

1. Procédé de traitement d'un produit photographique aux halogénures d'argent dans une cuve de traitement où l'on traite la solution de développement afin d'éliminer les produits de saisonnement du révélateur, ladite solution de développement étant renouvelée en utilisant un volume de composants de renouvellement suffisamment faible pour que l'on n'observe pratiquement aucun trop-plein, ledit procédé étant caractérisé en ce que la solution de développement et les composants de renouvellement ajoutés à la cuve ne contiennent pas d'ions bromure et que la solution formée au cours du traitement est traitée par des moyens permettant d'éliminer les ions bromure, afin d'éliminer continuellement pratiquement tous les ions bromure formés dans la solution et de maintenir une solution exempte d'ions bromure au cours du traitement du produit.

2. Procédé selon la revendication 1, caractérisé en ce que le produit photographique aux halogénures d'argent est un film négatif en couleurs.

3. Procédé selon l'une ou l'autre des revendications précédentes, caractérisé en ce que les moyens d'élimination des ions bromure englobent l'échange d'ions, l'électrodialyse, la dialyse et/ou l'osmose inversé.

4. Procédé selon la revendication 3, caractérisé en ce que les moyens d'élimination des ions bromure consistent en un procédé d'échange d'ions.

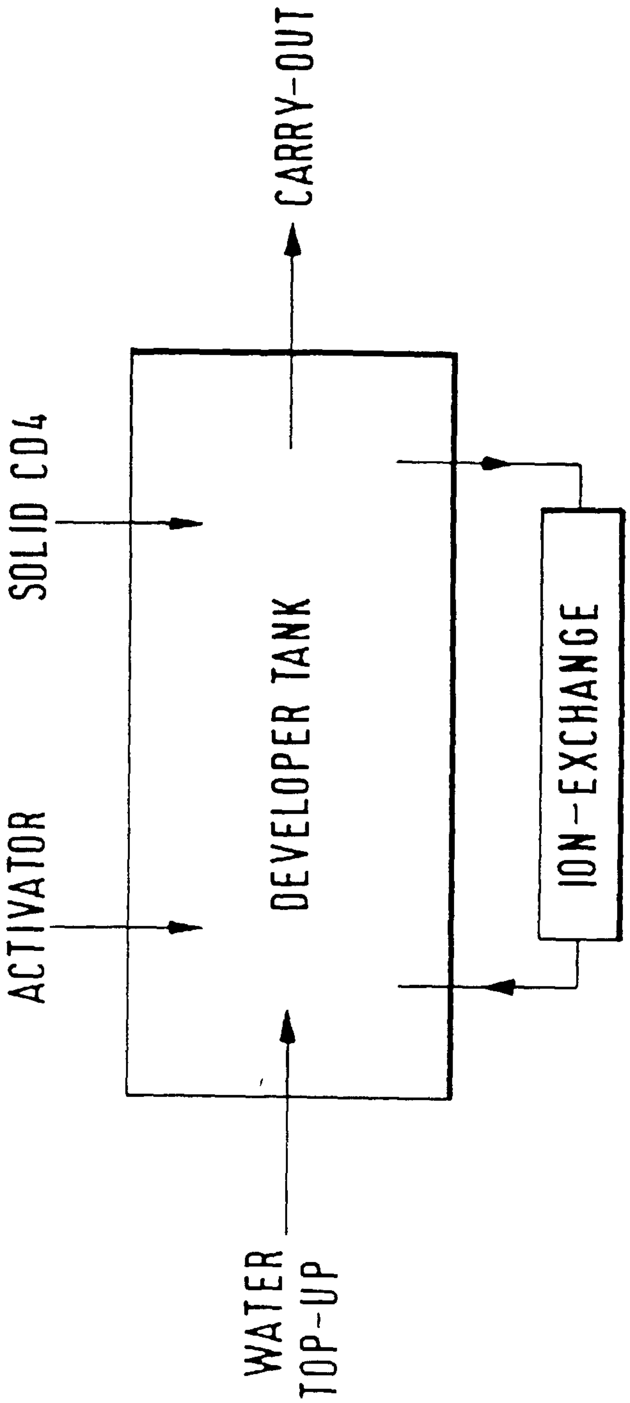
5. Procédé selon la revendication 4, caractérisé en ce que l'on utilise une résine échangeuse d'anions (pour l'échange des anions).

6. Procédé selon la revendication 5, caractérisé en ce que la résine échangeuse d'anions comprend une matrice de polystyrène réticulée au moyen de 3 à 5% de divinylbenzène.

7. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que la solution de dévelcppement contient une concentration réduite en développateur chromogène par rapport à la concentration présente dans le procédé standard C-41.

8. Procédé selon la revendication 7, caractérisé en ce que la concentration réduite en développateur chromogène est comprise entre 25 et 50% de celle présente dans le procédé standard C-41.

Fig.1.


CARRY-OUT
SOLID CD4
ACTIVATOR
DEVELOPER TANK
ION-EXCHANGE
WATER
TOP-UP

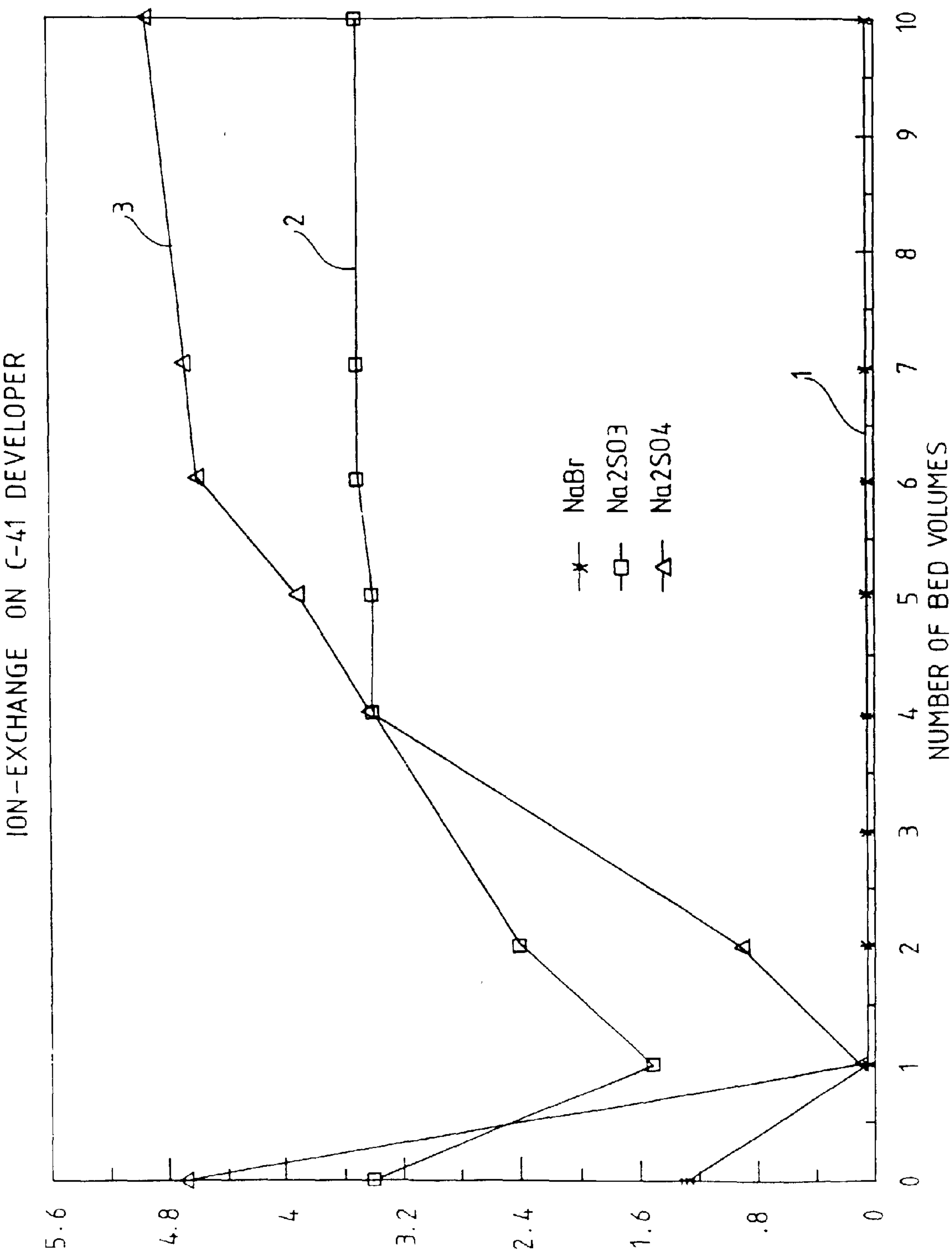

ION-EXCHANGE ON C-41 DEVELOPER
NaBr
Na2SO3
Na2SO4
1
2
3
5.6
4.8
4
3.2
2.4
1.6
.8
0
CONCENTRATION(g/l)
0
1
2
3
4
5
6
7
8
9
10
NUMBER OF BED VOLUMES

Fig.2.