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(54) **Method of processing photographic material.**

(57) A method of processing a photographic material in which the wash water or stabiliser solution is treated with an absorbing agent in order substantially to reduce the amount of retained developing agent in the solution. The method is preferably a redox amplification process, especially one with no 'tailend'. The absorbing agent may be an ion exchange resin but is advantageously activated carbon.

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This invention relates to a method of processing a photographic material and is particularly, though not exclusively, concerned with processing developed colour print material carried on a paper support. It is, however, also applicable to material, either colour or black and white, carried on a film support, and also black and white material on a paper support.

In conventional photographic development processes photographic material is successively passed through a number of steps which includes serially developing, other processing steps and washing. The final washing step removes chemical from the material to ensure it is stable and no subsequent chemical action takes place. The post development processing step may comprise a plurality of individual steps where the material is successively treated to solutions in baths each of which has a different effect on the material. Thus the processing steps may include treating the material in baths containing respectively stop, bleach, fix or bleach-fix solutions.

In redox (RX) amplification processes colour materials are developed to produce a silver image (which may contain only small amounts of silver) which then catalyses redox amplification to form a dye image. The redox amplifying solution contains a reducing agent, for example a colour developing agent, and an oxidising agent which is more powerful than silver halide and which will oxidise the colour developing agent in the presence of the silver image which acts as the catalyst. The oxidised colour developer reacts with a colour coupler (usually contained in the photographic material) to form image dye. The amount of dye formed depends on the time of treatment or the availability of colour coupler rather than the amount of silver in the image as is the case in conventional colour development processes.

A particular application of this RX technology is in the processing of silver chloride colour paper, especially such paper with low silver levels. There are some RX processes being developed which require no 'tailend' i.e. no bleach, bleach-fixing or even fixing step.

In a photographic process, if the developing agent is not efficiently removed from the processed material, staining can occur which is immediate with black and white developing agents. In the production of colour prints the stain does not often appear straight away but the density of the stain increases on keeping, causing marking of the print, since the developer will continue to act, particularly under conditions of light and heat exposure.

In order to avoid staining it is the practice for the prints to be subject to a very intense washing process to ensure that all the retained developer is removed.

The need to remove the retained developer normally requires a substantial amount of washing either under a constantly moving flow of water or by taking the print through a series of wash tanks where chemicals including the retained developer are washed from the print.

If the amount of washing necessary is able to be reduced then the apparatus for processing the print becomes cheaper in price as a lower number of tanks are needed and, furthermore, there is conservation of water, since less water is necessary for washing. As a result of this the effluent from the process is reduced. For maximum stability of the image the final wash must be very efficient so that all traces of silver complexes and all but the last traces of fixing agent are removed.

This final wash stage may be eliminated, however, in rapid processing systems, e.g. in 'plumbless' minilabs, by the use of a stabilising bath whereby the fairly stable soluble silver complexes are left in the final image. When stabilisation processing is used there must be no subsequent washing as any dilution will greatly reduce the subsequent image stability.

Related PCT application International Publication No. WO91/17478 discloses the use of an absorbing agent to reduce the amount of retained developing agent in one or more processing steps after development but specifically before washing.

It is an object of the present invention to provide an improved method of processing a photographic material in which the retained developing agent is substantially reduced from the wash itself or stabilising solution to below the acceptable level.

In most processes it is the removal of this retained developing agent that governs the amount of washing required; once free of developing agent, the washing rate is governed by the removal of other active species. The developing agent is diluted during washing in successive tanks, the amount in each tank being governed by the amount carried over in the gelatin layers from the previous tank and the flow rate of the water through the tank and the number of tanks. Reducing the amount of washing necessary by reducing the developing agent to almost zero in the wash or stabiliser tanks allows this water to be recycled a number of times and in some processes, where the developing agent is the only processing agent that degrades the image, indefinitely.

According to the present invention, there is provided a method of processing a photographic material characterised in that the wash water or stabiliser solution is treated with an absorbing agent in order substantially to reduce the amount of retained developing agent in the solution. Preferably the method of

processing is a redox amplification process, especially one with no 'tailend' and minimal discharge.

The absorbing agent may be an ion exchange resin which may be anionic, such as AMBERLITE IRA-400™ or ZEROLIT NIP™, cationic, such as DUOLITE C225™ or ZEROLIT 236™, mixed bed such as DUOLITE MB5113™ or DUOLITE MB6113™ or 'neutral', such as AMBERLITE XAD-2™ or XAD-7™. Advantageously, however, activated carbon, especially activated charcoal is used.

The absorbing agent may be brought into contact with the wash water or stabiliser solution in any suitable manner, for instance by addition of the absorbent to the liquid, shaking to provide maximum contact followed by a means of separation such as filtration, centrifugation and/or flotation. Preferably however the absorbent is retained in a suitable container through which liquid can be brought into efficient contact with the absorbent by means of a suitable pump. The circulation rate should be sufficiently low, for example, less than 20 bed volumes per minute, preferably less than 10, to allow sufficient contact time for absorption to take place and this is dependent upon the shape and size of the container and the nature of the absorbent. The process may be carried out at any temperature from about 2 to about 90 °C but is conveniently carried out at the temperature of the previous processes, and at any pressure appropriate to the apparatus but conveniently at atmospheric pressure.

The colour developing agent used may be any primary aromatic amine, such as a p-aminophenol or p-phenylenediamine but conveniently N-ethyl -N-β-methanesulphonamidoethyl-3-methyl-4-amino-aniline (CD3) is used, preferably in the form of its sesquisulphate.

This method of treating wash water is especially useful in a small self-contained processor, into which processing solutions must be supplied in ready-mixed form, perhaps in a cartridge. For those RX processes which require no 'tailend', there is so little silver or silver halide in the image that the image is not degraded, and only a developer followed by a stabiliser is necessary to produce a high quality, stable print.

The invention will now be described with reference to the following example which in no way limits the scope of the invention.

Example 1

A model wash bath was set up: a small 150 x 200 mm processing tray was filled with 400ml of water. A system was set up to circulate this water by means of a peristaltic pump through a chromatography column filled with 10g of a test absorbent. The water was circulated at about 50ml/min. A 125 x 200 mm sheet of low silver paper (silver coating weight 156mg/m^2) with emulsions and dispersions similar to EKTACOLOR™ 2001 paper was processed for 45 seconds at 35 °C in a developer-amplifier with the following formula:

Component	Concentration
CD3	3.5g/l
Potassium carbonate	10.0g/l
Potassium chloride	0.35g/l
Diethylhydroxylamine(85% in water) (anti-oxidant)	5.0g/l
H_2O_2 (30%)	5.0g/l
1-hydroxy-ethylidene, -1,1-diphosphonic acid (60% in water)	0.6g/l
diethylenetriaminepentaacetic acid (40% in water of pentasodium salt)	0.6g/l
water to	1 litre
pH adjusted to 10.3	

The paper was squeegeed and then put in the model wash tank and washed for 1 minute at 20 °C with the recycling pump going. This sheet of paper was removed and discarded. The water was continually recycled and after 10 minutes a sample of the wash water coming off the bottom of the absorbing column was taken and analysed for CD3 by HPLC. The processing of paper sheets was repeated until the CD3 level in the wash water after treatment was found to exceed 5ppm. This was the maximum level of CD3 that could be tolerated by this paper in the water, before staining caused by CD3 was observed. The number of sheets of paper processed was recorded and from this the amount of CD3 absorbed could be estimated by using the following formula:-

$$\frac{\text{No. sheets processed} \times \text{conc}^{n}\ \text{CD3 (g/l)} \times \text{vol (l) carried over by a sheet in developer-amplifier}}{\text{wt of absorbent (g)}}$$

The volume of carryover for the 125 x 200 mm sheet was determined by calculating the difference between the weights of the dry and wet sheet and found to be 0.712×10^{-3} ml/sheet.

The absorbent in the column was changed and the whole experiment was repeated. The results for the different absorbents are shown in the table below :

Addition	Sheets Processed before wash contains 5ppm CD3	Resin Type	Estimated amount CD3 removed by absorbent in g/g absorbent
None	1		---
AMBERLITE XAD-2™	40	Neutral	0.010
AMBERLITE XAD-7™	60	Neutral	0.015
AMBERLITE IRA-400™	11	Anionic	0.003
DUOLITE C225™	12	Cationic	0.003
DUOLITE MB5113™	23	Mixed bed	0.005
DUOLITE MB6113™	23	Mixed bed	0.005
ZEROLIT NIP™	31	Anionic	0.007
ZEROLIT 236™	35	Cationic	0.008
Activated charcoal	110		0.027

It will be noted that the absorbing agents used are all standard commercially available agents. The AMBERLITE agents are obtained from Rohm & Haas Co, DUOLITE from the Diamond Shamrock Corporation, ZEROLIT from Permutit and the activated charcoal from BDH.

From the table it can be seen that all the absorbing agents increase the life of the wash water, with the activated charcoal being the most efficient in absorbing the CD3.

Claims

1. A method of processing a photographic material characterised in that the wash water or stabiliser solution is treated with an absorbing agent in order substantially to reduce the amount of retained developing agent in the solution.

2. A method as claimed in claim 1, wherein the method of processing is a redox amplification process.

3. A method as claimed in claim 2, wherein in the redox amplification process there is no bleach, bleach-fixing or fixing step.

4. A method as claimed in any one of the preceding claims, wherein the processing solutions are used in a ready mixed form.

5. A method as claimed in any one of the preceding claims, wherein the absorbing agent is an activated carbon.

6. A method as claimed in claim 5, wherein the activated carbon is activated charcoal.

7. A method as claimed in any one of claims 1 to 4, wherein the absorbing agent is an ion exchange resin.

8. A method as claimed in claim 7, wherein the resin is cationic.

9. A method as claimed in claim 7, wherein the resin is anionic.

10. A method as claimed in claim 7, wherein the resin is neutral.

11. A method as claimed in claim 7, wherein the resin is a mixture of cationic and anionic resins.

12. A method as claimed in any one of the preceding claims, wherein the developing agent is CD3.

13. A method as claimed in any one of the preceding claims wherein the circulation rate of wash water or stabiliser solution is less than 20 bed volumes per minute.

14. A method as claimed in claim 13, wherein the circulation rate is less than 10 bed volumes per minute.

15. A method as claimed in any one of the preceding claims wherein the method is carried out at the temperature of the previous processes and at atmospheric pressure.

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EUROPEAN SEARCH REPORT

Application Number

EP 93 20 0979

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)
A	GB-A-2 158 258 (KONISHIROKU PHOTO INDUSTRY CO., LTD.) * claims 1-14 *	1-15	G03C5/395 G03C5/31 G03C7/44
A	WO-A-9 117 479 (KODAK LIMITED) * claims 1-8 *	1-15	
A	DE-A-3 424 064 (AGFA-GEVAERT AG) * claims 1-4; example 1 *	1-15	
A	PATENT ABSTRACTS OF JAPAN vol. 10, no. 354 (P-521)28 November 1986 & JP-A-61 151 650 (KONISHIROKU PHOTO IND., CO., LTD.) 10 July 1986 * abstract *	1-15	
A	DATABASE WPI Week 8006, Derwent Publications Ltd., London, GB; AN 80-10523C (06) & JP-A-50 126 420 (FUJI PHOTO FILM K.K.) 4 October 1975 * abstract *	1-15	TECHNICAL FIELDS SEARCHED (Int. Cl.5) G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	04 AUGUST 1993	HINDIAS E.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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