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(71) Applicant: **Kodak Limited**  
**Headstone Drive**  
**Harrow, Middlesex HA1 4TY(GB)**  
(84) **GB**

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

(72) Inventor: **Twist, Peter Jeffrey, c/o Kodak Limited**  
**Patent Department,**  
**Headstone Drive**  
**Harrow, Middlesex, HA1 4TY(GB)**  
Inventor: **Magee, Paul Mary, c/o Kodak Limited**  
**Patent Department,**  
**Headstone Drive**  
**Harrow, Middlesex, HA1 4TY(GB)**  
Inventor: **Wildman, Nigel Richard, c/o Kodak Limited**  
**Patent Department,**  
**Headstone Drive**  
**Harrow, Middlesex, HA1 4TY(GB)**

(74) Representative: **Aufflick, James Neil et al**  
**Kodak Limited**  
**Patent Department**  
**Headstone Drive**  
**Harrow Middlesex HA1 4TY (GB)**

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

(57) A method of processing photographic silver halide material characterised in that it includes a step in which a developing solution is treated with means to remove continuously substantially all bromide ion from the solution and to maintain the solution substantially free from bromide ion during operation of the method.

**EP 0 609 939 A1**

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.

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<sup>2</sup> of film processed. Colour papers and black and white photographic materials can also be processed by replenishment systems.

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.

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.

According to the present invention we provide a method of processing photographic silver halide material characterised in that it includes a step in which a developing solution is treated with means to remove continuously substantially all bromide ion from the solution and to maintain the solution substantially free from bromide ion during operation of the method..

Suitably bromide ion is substantially absent from the developer or replenisher developer 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.

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 by 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.

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 can be used in the low effluent replenishment system for colour negative developers which is described and claimed in our PCT/EP 90/01854.

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.

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.

The replenisher which is added to the development solution may be in the form of a solution, having a pH of 10.09, of the following composition:

Potassium carbonate	37.5 g/l
Sodium bromide	0.45 g/l
Anti-cal	6.5 ml/l
Sodium sulphite	4.85 g/l
Hydroxylamine sulphate	3.4 g/l
CD4	5.9 g/l

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

The method of the invention allows developer solutions to be used which contain lower levels of colour developers 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.

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

1. The method allows a low level of CD4 to be used in a developer solution with a proportionate reduction in the level of CD4 in the effluent.
2. It is easy to ensure complete removal of bromide ion by any of the recognised methods. Iodide ion is removed at the same time.
3. Since the bromide ion level is effectively zero it does not need to be controlled. This also applies to the level of iodide ion.
4. It may be possible to obtain image structure benefits in zero bromide developers.
5. Shorter development times could result from the use of zero bromide developers.
6. The enhanced development could allow the use of lower silver levels, lower coupler levels and/or smaller grain sized emulsions.

The invention is illustrated by the accompanying drawings wherein:

Figure 1 is a diagram of a developer tank with its inlets and outlets;

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 Example 1; and

Figure 3 is a graph of dye-density against log relative exposure showing the results of Example 2.

Figure 4 is a graph of dye density against log relative exposure showing the results of Example 3.

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, e.g. with a pump, preferably only when there is film being processed.

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

The invention is further illustrated by the following Examples:

#### EXAMPLE 1

In this example bromide ion was removed from C-41 developer solution as shown in Figure 1. Analysis of the solution after the ion-exchange treatment gave the results which are summarised in Figure 2, which shows plots for concentrations of (1) sodium bromide, (2) sodium sulphite, (3) sodium sulphate and (4) CD4 against the number of bed volumes. One bed volume is equal to the volume of resin beads in the column and was about 50 ml. The resin used was IRA 400 (Rohm and Haas). This was regenerated with ten bed volumes of potassium carbonate solution, (5%) and then washed with five bed volumes of water. The resin and column were then ready to use and developer from the developer tank was passed through the column and before passing back into the developer tank samples were taken and analysed for colour developing agent (CD4), sodium bromide, sodium sulphite and sodium sulphate. The initial concentrations of these components are shown in Figure 2 at zero bed volumes. These represent untreated C-41 developer. It can be seen in Figure 2 that as more and more volume of C-41 developer is passed through the resin the bromide ion concentration remains very close to zero. Thus it is possible by the use of ion-exchange to remove all the bromide ion from the developer and to maintain the developer substantially free of bromide ion during its operation. This method would thus remove bromide ions generated by the development of silver halide emulsions. If the developer being used was replenished then the developer replenisher would also be substantially free of bromide ion.

**EXAMPLE 2**

A series of single layer coatings with a fast magenta emulsion and a magenta coupler (Iso 400 speed) were processed in standard C-41 developer (a) and in an experimental developer containing zero bromide ion and half the CD4 level of C-41 (b) to (d). The compositions of the developers were as follows:

Standard 4.5 g/L CD4 developer, 1.3 g/L NaBr

Experimental 2.25 g/L CD4 developer, 0.0 g/L NaBr

Using the experimental developer processing took place at 3 different development times i.e. 0.5 minutes (b), 0.75 minutes (c) and 1.0 minutes (d). The development time for the standard was 2.5 minutes.

In all cases the development temperature was 37.8°C.

The results are shown in Figure 3. In this the standard (a) is shown by a broken line and the experimental results (b) to (d) by full lines. Figure 3 shows that with the experimental developer a development time of about 45 seconds is approximately equivalent to the standard C-41 process. Thus it is possible with a zero bromide process to obtain similar sensitometry with a low CD4 level in a much shorter time than the standard 2.5 minutes usually required.

**EXAMPLE 3**

Some single layer coatings were processed in standard C-41 developer and in some experimental developers containing one quarter of the normal colour developing agent level and having zero bromide ion concentration. In the standard developer the concentration of CD-4 was 4.5 g/l while in the experimental developers the concentration of CD-4 was 1.125 g/l. In all cases development took place at 37.8°. The results are shown in Figure 4 which is a graph of dye density against log relative exposure. In Figure 4, Curve a) is for standard C-41 developer containing 1.3 g/l sodium bromide; Curve b) is for experimental developer containing 1.125 g/l CD-4 and zero bromide ion; and Curve c) is for experimental developer containing 1.125 g/l CD-4, zero bromide ion and 0.002 g/l of 5-methyl benzotriazole. Development times were a) 2.5 minutes and b) and c) 2.08 minutes each.

From Figure 4 it can be seen that the developer of Curve c) is a good match for standard C-41 developer (Curve a)).

**Claims**

1. A method of processing photographic silver halide material characterised in that it includes a step in which a developing solution is treated with means to remove continuously substantially all bromide ion from the solution and to maintain the solution substantially free from bromide ion during operation of the method.
2. A method according to claim 1 characterised in that the photographic silver halide material is colour negative film.
3. A method according to claim 2 characterised in that the colour negative film is processed by the C-41 process.
4. A method according to any one of the preceding claims characterised in that the bromide ion removal means is ion-exchange, electrodialysis, dialysis and/or reverse osmosis.
5. A method according to claim 4 characterised in that the bromide ion removal means is ion-exchange.
6. A method according to claim 5 characterised in that an anion exchange resin (for the exchange of anions) is used.
7. A method according to claim 6 characterised in that the anion exchange resin is based on a polystyrene matrix cross-linked with 3% to 5% of divinylbenzene.
8. A method according to claim 3 characterised in that the developing solution contains a reduced level of colour developer compared with that present in the standard C-41 process.

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

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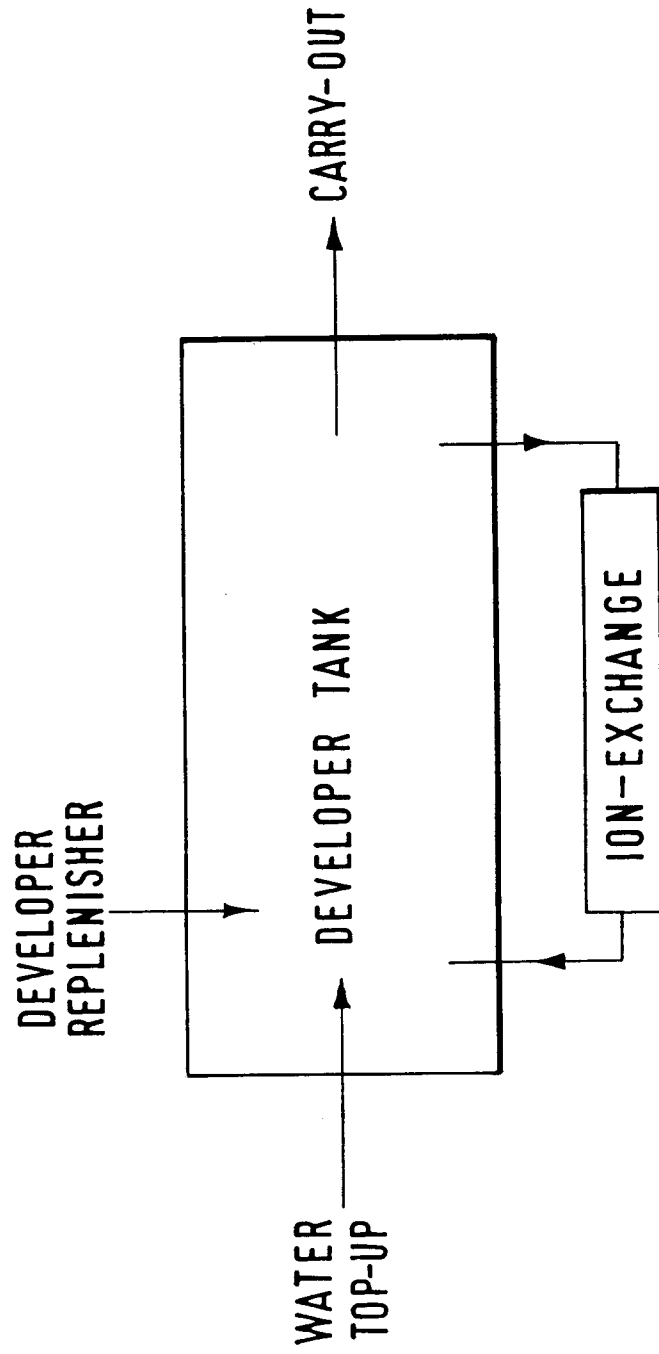
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Fig.1.



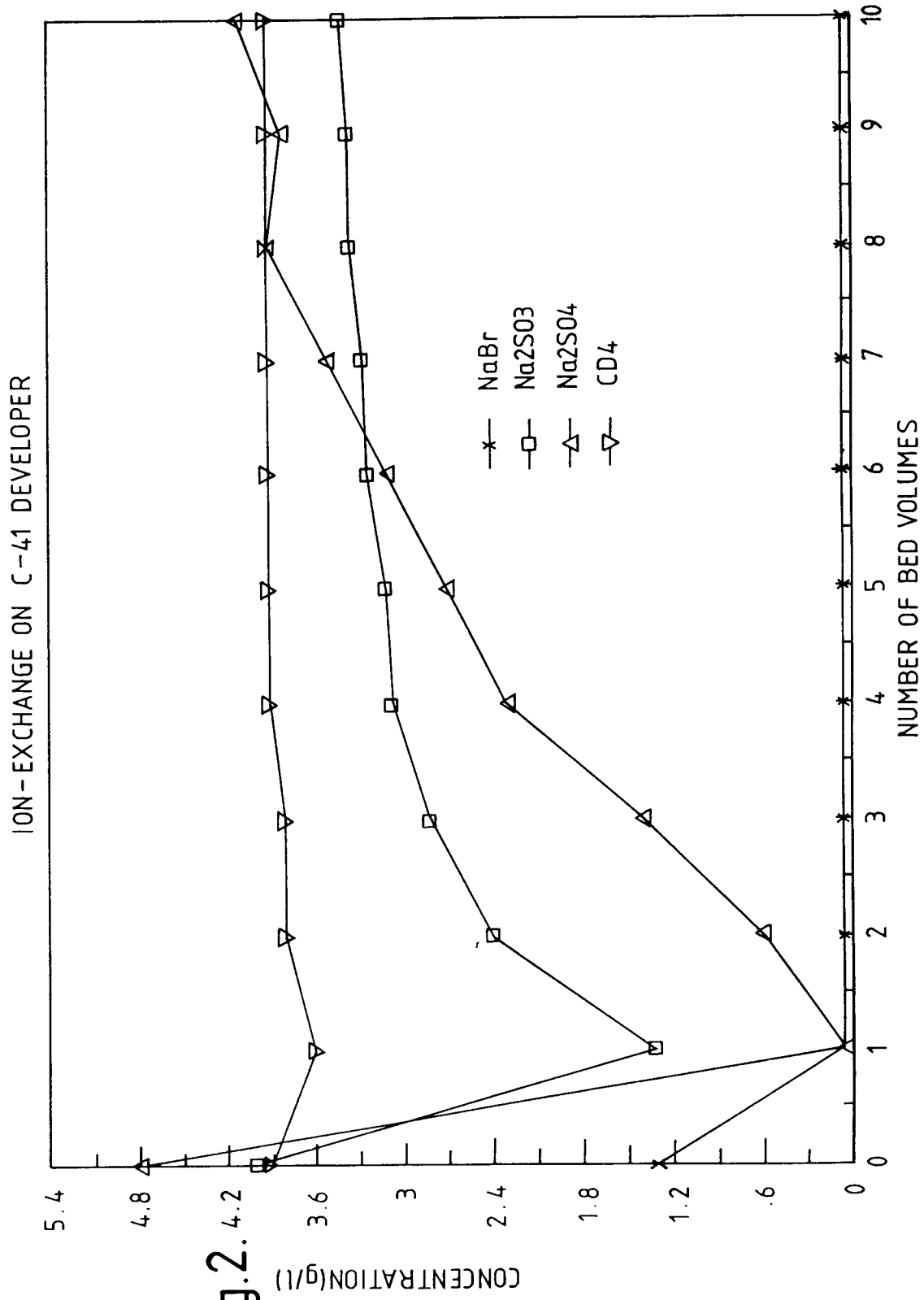


Fig. 3.

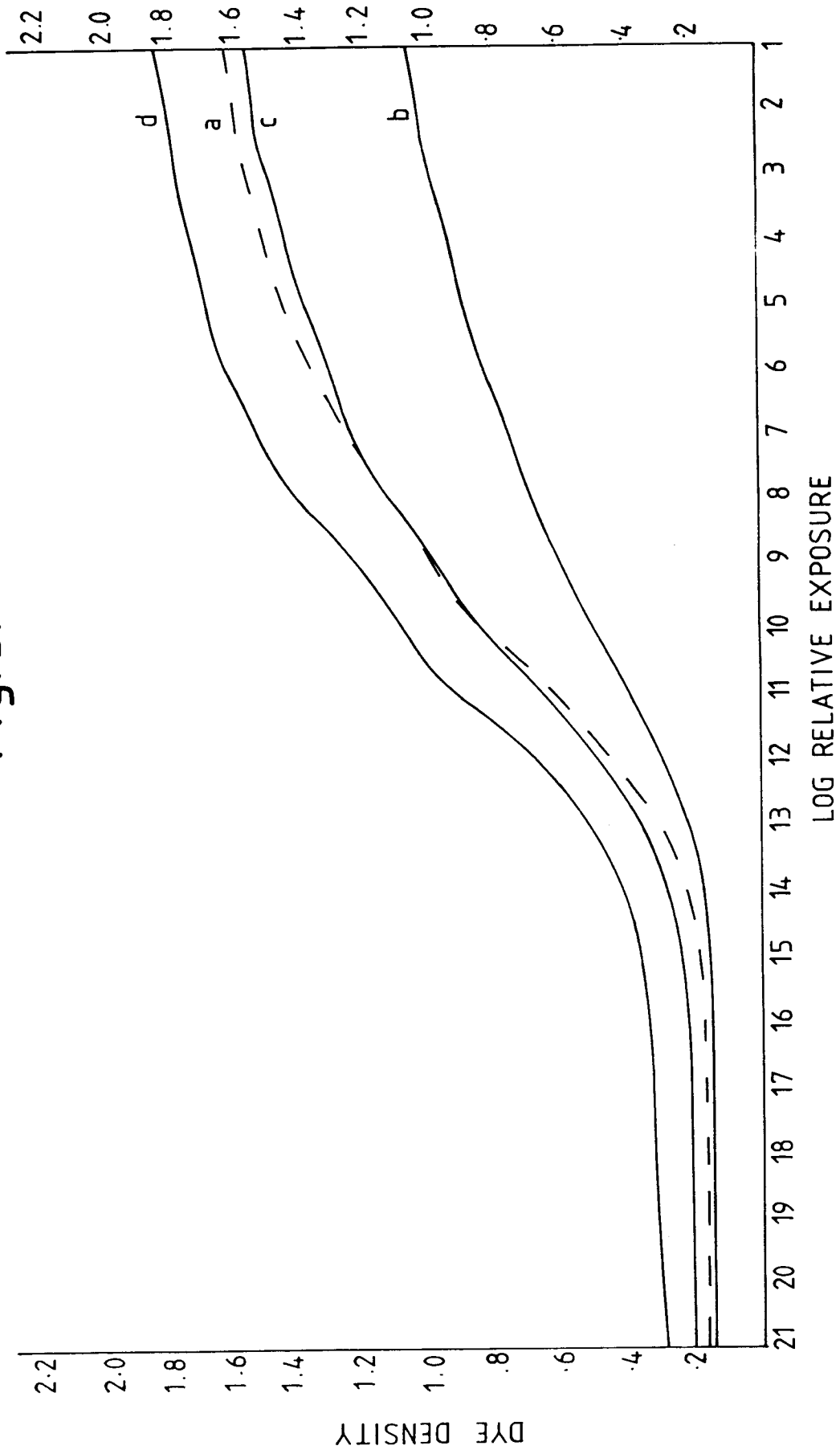
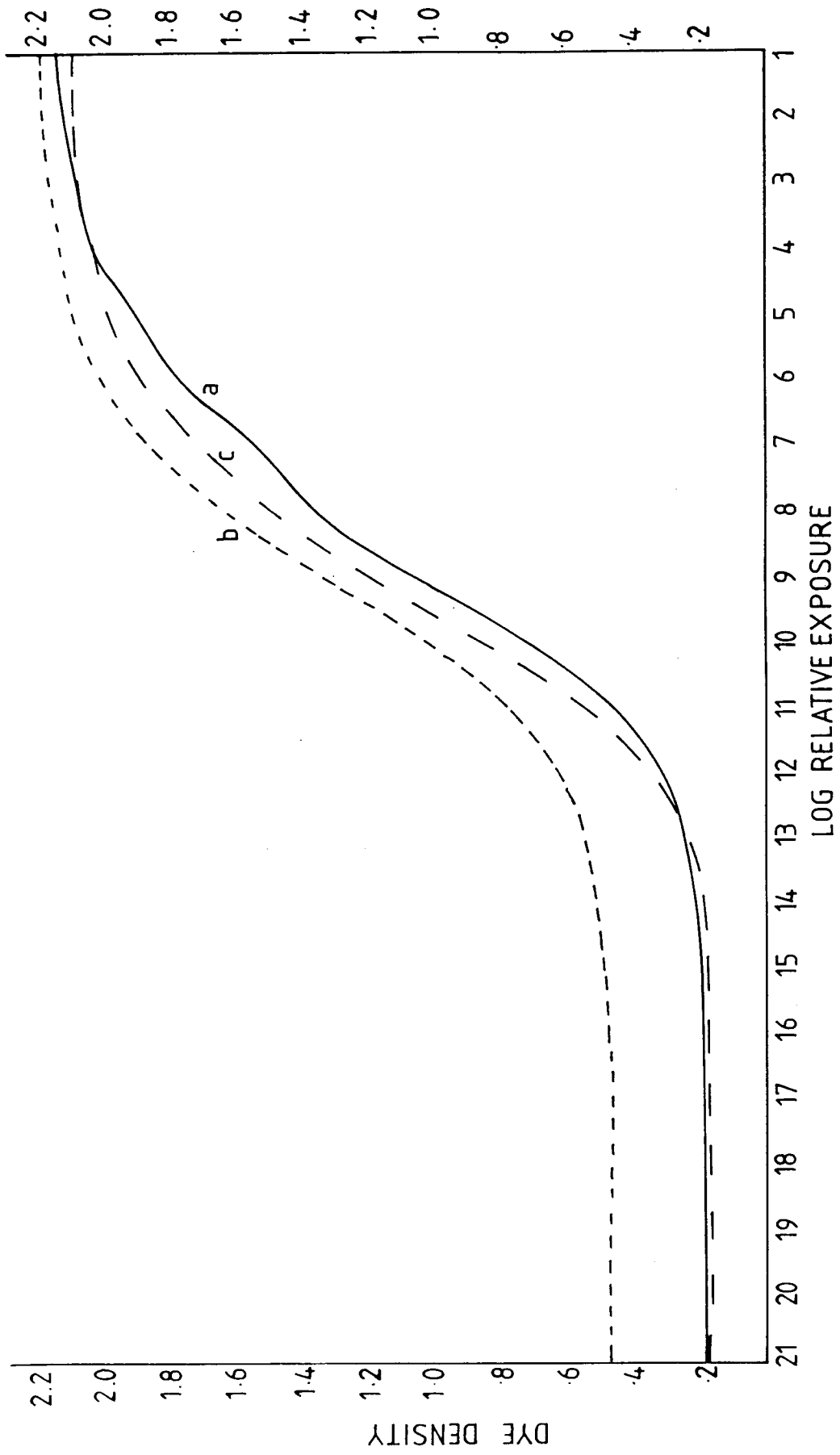




Fig.4.





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## EUROPEAN SEARCH REPORT

Application Number  
EP 94 20 0183

DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
X	US-A-4 529 687 (H HIRAI ET AL) * claim 1 * ---	1,2,4-7
D,A	WO-A-91 07698 (KODAK LIMITED) * page 7, line 24 - line 29 * ---	3,8,9
A	EP-A-0 368 340 (FUJI PHOTO FILM CO. LTD.) * page 28, line 14 - line 18; claim 1 * ---	1
A	US-A-5 051 342 (K SHIBA ET AL) * column 43, line 24 - line 31; claim 1 * -----	1
The present search report has been drawn up for all claims		
Place of search	Date of completion of the search	Examiner
THE HAGUE	17 May 1994	Bolger, W
<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		

TECHNICAL FIELDS  
SEARCHED (Int.Cl.5)  
G03C