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(54) **Photographic processes**

Photographische Verarbeitungsverfahren

Procédés de traitement photographiques

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(56) References cited:

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Description**Field of the Invention**

- 5 [0001] The present invention relates to photographic processes and is more particularly concerned with the processing of colour photographic paper using redox amplification chemistry.

Background of the Invention

- 10 [0002] Redox amplification processes have been described, for example in British Specification Nos. 1,268,126, 1,399,481, 1,403,418 and 1,560,572. In such processes colour materials are developed to produce a silver image (which may contain only small amounts of silver) and then treated with a redox amplifying solution (or a combined developer-amplifier) to form a dye image.

- 15 [0003] The developer-amplifier solution contains a colour developing agent and an oxidising agent which will oxidise the colour developing agent in the presence of the silver image which acts as a catalyst.

[0004] Oxidised colour developer reacts with a colour coupler to form the image dye. The amount of dye formed depends on the time of treatment or the availability of colour coupler and is less dependent on the amount of silver in the image as is the case in conventional colour development processes.

- 20 [0005] Examples of suitable oxidising agents include peroxy compounds including hydrogen peroxide and compounds which provide hydrogen peroxide, eg addition compounds of hydrogen peroxide; cobalt (III) complexes including cobalt hexammine complexes; and periodates. Mixtures of such compounds can also be used.

[0006] A particular application of this technology is in the processing of silver chloride colour paper, especially such paper with low silver levels.

- 25 [0007] Redox amplification processes can be carried out in one a number of ways, for example, in a single developer/amplifier (DEV/AMP), in a developer followed by a peroxide (or other amplification agent) amplifier (DEV, AMP) containing no developing agent, in an amplifier followed by a developer or developer/amplifier (AMP, DEV or AMP, DEV/AMP) or in a developer followed by a developer/amplifier (DEV, DEV/AMP).

Problem to be solved by the Invention

- 30 [0008] When the development and amplification process is to be carried out the ways described above there are chemical stability advantages to holding at least some of the developing agent and oxidant in separate baths. However there is a difficulty in achieving a sufficiently high Dmax.

Object of the Invention

[0009] It is an object of the present invention to provide a method of processing photographic paper using redox development and amplification processes which produce improved results.

Summary of the Invention

- 40 [0010] In accordance with one aspect of the present invention, there is provided a method of forming a photographic colour image by a redox amplification method from an imagewise exposed photographic silver halide material containing at least one dye image-forming colour coupler which comprises treating the material with one of the processing sequences:

- 45
 50 DEV then AMP,
 DEV then DEV/AMP,
 AMP then DEV, or
 AMP then DEV/AMP,

characterised in that the material is treated in a development and amplification sequence more than once.

Advantageous Effect of the Invention

- 55 [0011] The method of the present invention provides an improved Dmax when processing in a developer followed by either a peroxide amplifier containing no developing agent or a developer/amplifier.
 [0012] Colour contamination is reduced compared with the known single application process.

[0013] The high concentration of colour developing agent needed for the single application process can be reduced in the first developer making it easier to replenish, less likely to crystallise-out and more resistant to discolouration from oxidised developing agent.

[0014] The present method while involving more processing steps than the prior art can still be completed in the same total process time.

Brief Description of the Drawings

[0015] For a better understanding of the present invention reference will be made to the accompanying drawings which illustrate the results of the working Examples below in which:-

Figure 1 illustrates a comparison between the sensitometric curves obtained when using split development, that is, developer followed by an amplifier and standard colour paper processing (RA4);

Figure 2 is similar to Figure 1 but where higher colour developing agent levels are used for the same development and amplification times;

Figure 3 is similar to Figure 1 but where lower colour developing agent levels are used and for longer development and amplification times; and

Figure 4 is similar to Figure 1 but illustrating the results obtained using method of the present invention.

Detailed Description of the Invention

[0016] In one embodiment the material is treated in a developer as the first processing step.

[0017] In another embodiment the second processing step comprises treatment in an amplifier or developer/amplifier.

[0018] Optionally a wash step may be introduced between any of the processing steps defined above.

[0019] In one embodiment of the present invention the material is treated in a developer and then an amplification bath and this sequence is repeated one or more times. Alternatively the sequence developer followed by developer/amplifier may be repeated or any combination of these steps may be employed as long as at least one step is repeated.

[0020] It is preferred to remove excess peroxide from the silver halide material after an AMP or DEV/AMP bath before returning it to a colour developing agent-containing bath. This may be achieved by washing or by using a solution that will destroy peroxide, for example a sulphite solution. A similar result can be achieved when returning to developer straight from the amplifier if sulphite is present in the developer. This will react with the hydrogen peroxide of the amplifier to remove it and hence prevent any degradation of the developer.

[0021] While a single repetition of the processing sequence may be employed, more than one repetition can be used enabling colour developing agent levels to be further reduced.

[0022] A particular application of this technology is in the processing of silver chloride colour paper, for example paper comprising at least 85 mole percent silver chloride, especially such paper with low silver levels, for example levels below 300 mg/m², preferably below 200 mg/m² and especially below 150 mg/m².

[0023] The photographic materials can be single colour elements or multicolour elements. Multicolour elements contain dye image-forming units sensitive to each of the three primary regions of the spectrum. Each unit can be comprised of a single emulsion layer or of multiple emulsion layers sensitive to a given region of the spectrum. The layers of the element, including the layers of the image-forming units, can be arranged in various orders as known in the art. In an alternative format, the emulsions sensitive to each of the three primary regions of the spectrum can be disposed as a single segmented layer.

[0024] A typical multicolour photographic element comprises a support bearing a cyan dye image-forming unit comprised of at least one red-sensitive silver halide emulsion layer having associated therewith at least one cyan dye-forming coupler, a magenta dye image-forming unit comprising at least one green-sensitive silver halide emulsion layer having associated therewith at least one magenta dye-forming coupler, and a yellow dye image-forming unit comprising at least one blue-sensitive silver halide emulsion layer having associated therewith at least one yellow dye-forming coupler. The element can contain additional layers, such as filter layers, interlayers, overcoat layers and subbing layers.

[0025] Suitable materials for use in the emulsions and elements used in this invention are described in Research Disclosure, December 1989, Item 308119, published by Kenneth Mason Publications, Ltd., Dudley Annex, 12a North Street, Emsworth, Hampshire P010 7DQ, ENGLAND, which will be identified hereafter by the term "Research Disclosure."

[0026] Preferred colour developing agents are p-phenylenediamines. Especially preferred are:

4-amino N,N-diethylaniline hydrochloride,

4-amino-3-methyl-N,N-diethylaniline hydrochloride,
 4-amino-3-methyl-N-ethyl-N-(b-(methanesulphonamido) ethyl)aniline sesquisulphate hydrate,
 4-amino-3-methyl-N-ethyl-N-(b-hydroxyethyl)aniline sulphate,
 4-amino-3-b-(methanesulphonamido)ethyl-N,N-diethylaniline hydrochloride and
 4-amino-N-ethyl-N-(2-methoxyethyl)-m-toluidine di-p-toluene sulphonic acid.

[0027] With negative working silver halide a negative image can be formed. Optionally positive (or reversal) image can be formed.

[0028] The following Examples are included for a better understanding of the invention.

Example 1

[0029] A developer and amplifier of the composition shown in Table 1 were made up and used to generate sensitometric strips. The photographic colour paper used was currently available silver chloride-based colour paper having a total silver coverage of 670 mg/m² as the control and a similar paper having a total silver coverage of 145 mg/m² as the paper for the redox amplification process of the invention.

TABLE 1

Component	Developer	Amplifier
solution 1*	1.2g/l	1.2g/l
potassium carbonate	20.0g/l	20.0g/l
potassium bromide	1.2mg/l	-
potassium chloride	0.35g/l	-
potassium sulphate	2.3g/l	-
solution 2**	2.0ml/l	-
CD3***	10.8g/l	-
pH	10.3	10.3
hydrogen peroxide (30% solution)	-	5.0ml/l
time	20.0s	10.0s
temperature	35°C	35°C

where

*solution 1 is a 60% solution of 1-hydroxy ethylidene-1,1-diphosphonic acid,

**solution 2 is an 85% solution of diethyl hydroxylamine,

and

***CD3 is N-[2-4-amino-N-ethyl-m-toluidino)ethyl]-methanesulphonamide sesquisulphate hydrate.

[0030] After the strips were placed in developer for 20s followed by amplifier for 10s, they were then placed in the RA4 bleach-fix bath for 45s and then washed for 2min. Sensitometric curves were obtained and plotted from the strips processed in this way. These curves are shown as dotted lines in Figure 1. The results obtained for the control strips processed in the RA4 process were also plotted and these are shown as solid lines in Figure 1.

[0031] From Figure 1, it can be seen that the Dmax for the red and blue in particular are low compared with the RA4/control strips.

Example 2

[0032] An experiment similar to that described in Example 1 was then carried out but with the CD3 level increased to 12.0g/l. The results obtained are shown in Figure 2. As before, the redox amplification process is shown as dotted lines and the RA4/control strips as solid lines.

[0033] Figure 2 illustrates an improvement in the Dmax values but the Dmax value obtainable for the red record is

still below aim even though the CD3 level in the developer is higher than acceptable.

Example 3

5 [0034] The developer and amplifier formula were adjusted as shown in Table 2 for this example.

TABLE 2

Single and Multiple Application Redox Formulations		
Component	Developer	Amplifier
solution 1	0.6g/l	-
solution 3*	2.0ml/l	-
potassium carbonate	10.0g/l	-
potassium bromide	1.2mg/l	-
potassium chloride	0.35g/l	-
solution 2	2.0ml/l	-
5-methyl benzotriazole	1.0mg/l	-
CD3	8.0g/l	-
pH	10.3	-
hydrogen peroxide (30%)	-	5.0ml/l
time	40.0s	20.0s
temperature	35°C	35°C
where solutions 1 and 2 and CD3 were as defined in Example 1		

*solution 3 is a 41% solution of the penta sodium salt of diethylene triamine penta acetic acid.

40 [0035] As before, the developer and amplifier were followed by the bleach-fix of Example 1 for 45s and a wash for 2min. The results obtained are shown in Figure 3 as dotted lines with the results for RA4 shown as solid lines. As can be seen from Figure 3, there are some deficiencies in the redox amplification process curve when compared with the RA4/control strips curve in terms of low contrast, soft toes, high Dmin and lack of Dmax.

Example 4

45 [0036] Using the developer and amplifier formula given in Table 2, a double application of developer and amplifier was applied to the strips in the following sequence at 35°C:-

developer	20s
amplifier	5s
wash	10s
developer	20s
amplifier	5s

[0037] The results obtained are shown in Figure 4. Here contrast and Dmax levels are matching those obtained for RA4/control strips and in the case of the green record now too high. The Dmin level is also too high but now that adequate Dmax is available it is likely that coating or formulation optimisation would eliminate this.

[0038] It is to be noted that sensitometry can be achieved with full Dmax using the multiple application of the developer and amplifier in the same total process time as for a single application of the developer and amplifier.

[0039] The high concentration of colour developing agent needed for the single application process can be reduced in the developer making it easier to replenish, less likely to crystallize out and more resistant to discolouration from oxidised developing agent.

Claims

1. A method of forming a photographic colour image by a redox amplification method from an imagewise exposed photographic silver halide material containing at least one dye image-forming colour coupler which comprises treating the material with one of the processing sequences:

DEV then AMP,
DEV then DEV/AMP,
AMP then DEV, or
AMP then DEV/AMP,

wherein DEV means colour developer, AMP means amplifier (AMP) and DEV/AMP means developer/amplifier, characterised in that the material is treated in a development and amplification sequence more than once.

2. A method as claimed in claim 1 in which the material is treated in a developer as the first step.
3. A method as claimed in claim 1 or 2 in which the second step comprises treatment in an amplifier or developer/amplifier.
4. A method as claimed in any of claims 1 to 3 in which peroxide is removed from the material with a wash in water or a sulphite solution introduced between treatment in a peroxide-containing composition and treatment in a developing agent-containing composition.
5. A method as claimed in any of claims 1 to 4 in which the processing sequence comprises, in this order, the following steps: develop, amplify, wash (in water or sulphite solution), develop and amplify.
6. A method as claimed in any of claims 1 to 5 in which the photographic material comprises emulsions having at least 85% silver chloride.
7. A method as claimed in any of claims 1 to 6 in which the photographic material has a total silver coating weight below 300 mg/m^2 (as silver).
8. A method as claimed in any of claims 1 to 6 in which the photographic material is a multicolour photographic material comprising a support bearing at least one yellow dye image-forming unit comprised of at least one blue-sensitive silver halide emulsion layer having associated therewith at least one yellow dye-forming coupler, at least one magenta dye image-forming unit comprising at least one green-sensitive silver halide emulsion layer having associated therewith at least one magenta dye-forming coupler and at least one cyan dye image-forming unit comprising at least one red-sensitive silver halide emulsion layer having associated therewith at least one cyan dye-forming coupler.

Patentansprüche

1. Verfahren zum Erzeugen eines fotografischen Farbbildes durch ein Redox-Verstärkungsverfahren aus einem bildweise belichteten fotografischen Silberhalogenidmaterial mit mindestens einem farbstoffbilderzeugenden Farbkuppler, welches die Behandlung des Materials mit einer der folgenden Verarbeitungsfolgen umfasst:

DEV dann AMP,
DEV dann DEV/AMP,
AMP dann DEV, oder

AMP dann DEV/AMP,

wobei DEV Farbentwickler, AMP Verstärker und DEV/AMP Entwickler/Verstärker bedeutet, **dadurch gekennzeichnet**, dass das Material in einer Entwicklungs- und Verstärkungsfolge mehr als ein Mal behandelt wird.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass das Material in einem ersten Schritt in einem Entwickler behandelt wird.
3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, dass der zweite Schritt das Behandeln in einem Verstärker oder Entwickler/Verstärker umfasst.
4. Verfahren nach einen der Ansprüche 1 bis 3, dadurch gekennzeichnet, dass Peroxid durch Wässern in Wasser oder in einer Sulfitlösung entfernt wird, welche zwischen der Behandlung in einer peroxidhaltigen Mischung und der Behandlung in einer entwicklungsmittelhaltigen Mischung erfolgt.
5. Verfahren nach einen der Ansprüche 1 bis 4, dadurch gekennzeichnet, dass die Verarbeitungsfolge in der genannten Reihenfolge folgende Schritte umfasst: entwickeln, verstärken, wässern (in Wasser oder Sulfitlösung), entwickeln und verstärken.
6. Verfahren nach einen der Ansprüche 1 bis 5, dadurch gekennzeichnet, dass das fotografische Material Emulsionen mit mindestens 85% Silberchlorid umfasst.
7. Verfahren nach einen der Ansprüche 1 bis 6, dadurch gekennzeichnet, dass das fotografische Material ein gesamtes Silberbeschichtungsgewicht von unter 300 mg/m² aufweist (als Silber).
8. Verfahren nach einen der Ansprüche 1 bis 6, dadurch gekennzeichnet, dass das fotografische Material ein mehrfarbiges fotografisches Material ist, welches einen Träger umfasst, der mindestens eine gelbfarbstoffbildende Einheit trägt, welche mindestens eine blauempfindliche Silberhalogenidemulsionsschicht umfasst, der mindestens ein gelbfarbstoffbildender Kuppler zugeordnet ist, weiterhin mindestens eine magentafarbstoffbildende Einheit, die mindestens eine grünempfindliche Silberhalogenidemulsionsschicht umfasst, der mindestens ein magentafarbstoffbildender Kuppler zugeordnet ist, und weiterhin mindestens eine zyanfarbstoffbildende Einheit, die mindestens eine rot empfindliche Silberhalogenidemulsionsschicht umfasst, der mindestens ein zyanfarbstoffbildender Kuppler zugeordnet ist.

Revendications

1. Procédé de formation d'une image photographique en couleurs utilisant un procédé par amplification redox à partir d'un produit photographique aux halogénures d'argent exposé en conformité avec une image contenant au moins un coupleur chromogène formateur d'image de colorant, ledit procédé comprenant le traitement du produit dans une des séquences de traitement suivantes :

DEV, puis AMP,
DEV, puis DEV/AMP,
AMP, puis DEV, ou
AMP, puis DEV/AMP,

où DEV signifie révélateur chromogène, AMP signifie solution d'amplification (AMP) et DEV/AMP signifie solution de développement/amplification, ledit procédé étant caractérisé en ce que l'on traite plus d'une fois le produit dans une séquence de développement et d'amplification.

2. Procédé selon la revendication 1, dans lequel la première étape comprend le traitement du produit dans un révélateur.
3. Procédé selon la revendication 1 ou 2, dans lequel la seconde étape comprend le traitement du produit dans une solution d'amplification ou dans une solution de développement/amplification.
4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel on élimine le peroxyde du produit par lavage à l'eau ou avec une solution de sulfite introduite entre l'étape de traitement dans une composition contenant du

péroxyde et l'étape de traitement dans une composition contenant un développeur.

- 5
5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel la séquence de traitement comprend, dans cet ordre, les étapes suivantes : développement, amplification, lavage (dans de l'eau ou une solution de sulfite), développement et amplification.
6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel le produit photographique comprend des émulsions contenant au moins 85% de chlorure d'argent.
- 10
7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel le produit photographique a un titre total d'argent inférieur à 300 mg/m^2 (argent).
- 15
8. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel le produit photographique est un produit photographique multicolore comprenant un support portant au moins une unité formatrice d'image de colorant jaune comprenant au moins une couche d'émulsion aux halogénures d'argent sensible au bleu à laquelle est associé au moins un coupleur formateur de colorant jaune, au moins une unité formatrice d'image de colorant magenta comprenant au moins une couche d'émulsion aux halogénures d'argent sensible au vert à laquelle est associé au moins un coupleur formateur de colorant magenta et au moins une unité formatrice d'image de colorant cyan comprenant au moins une couche d'émulsion aux halogénures d'argent sensible au rouge à laquelle est associé au moins un coupleur formateur de colorant cyan.
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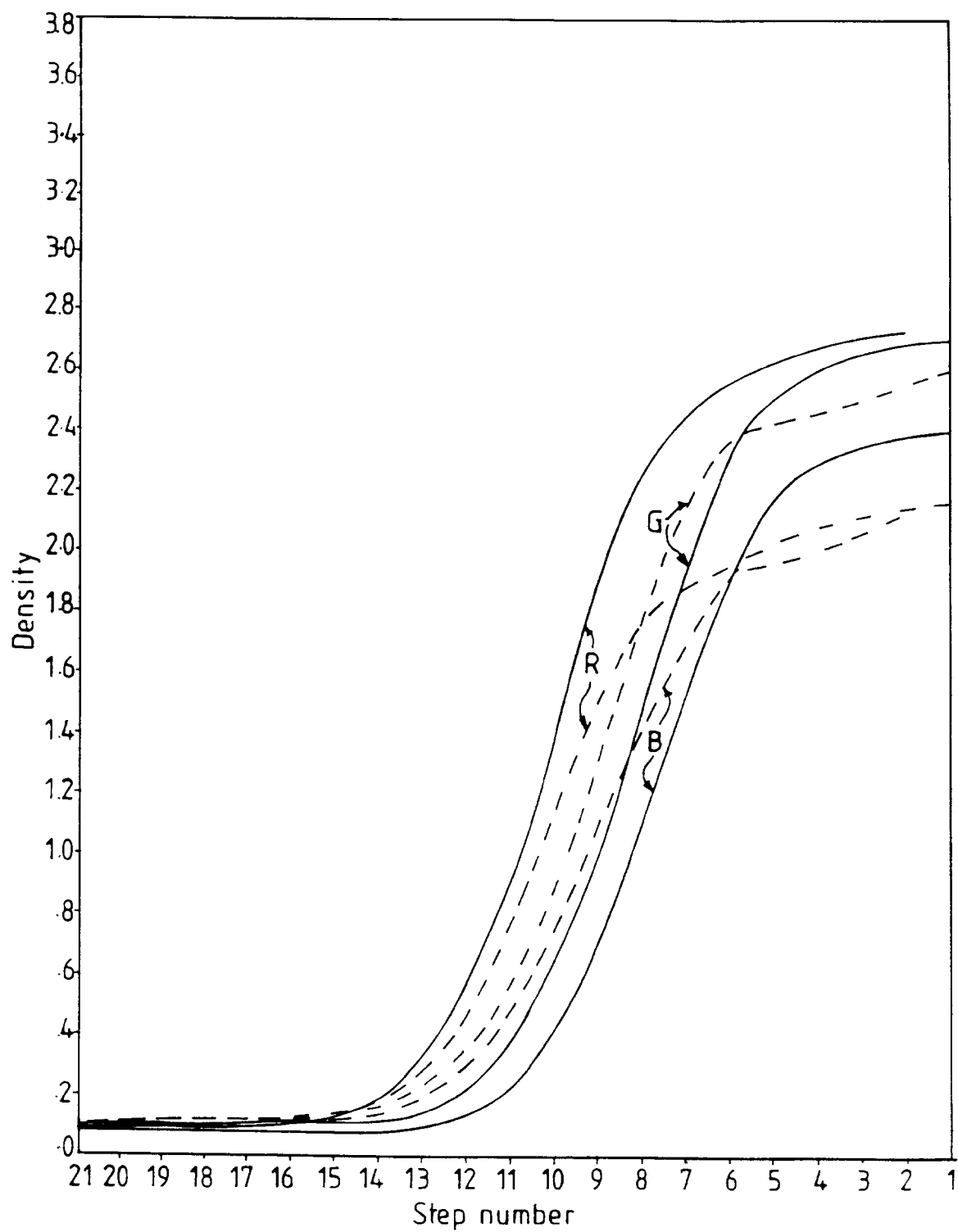


FIG.1.

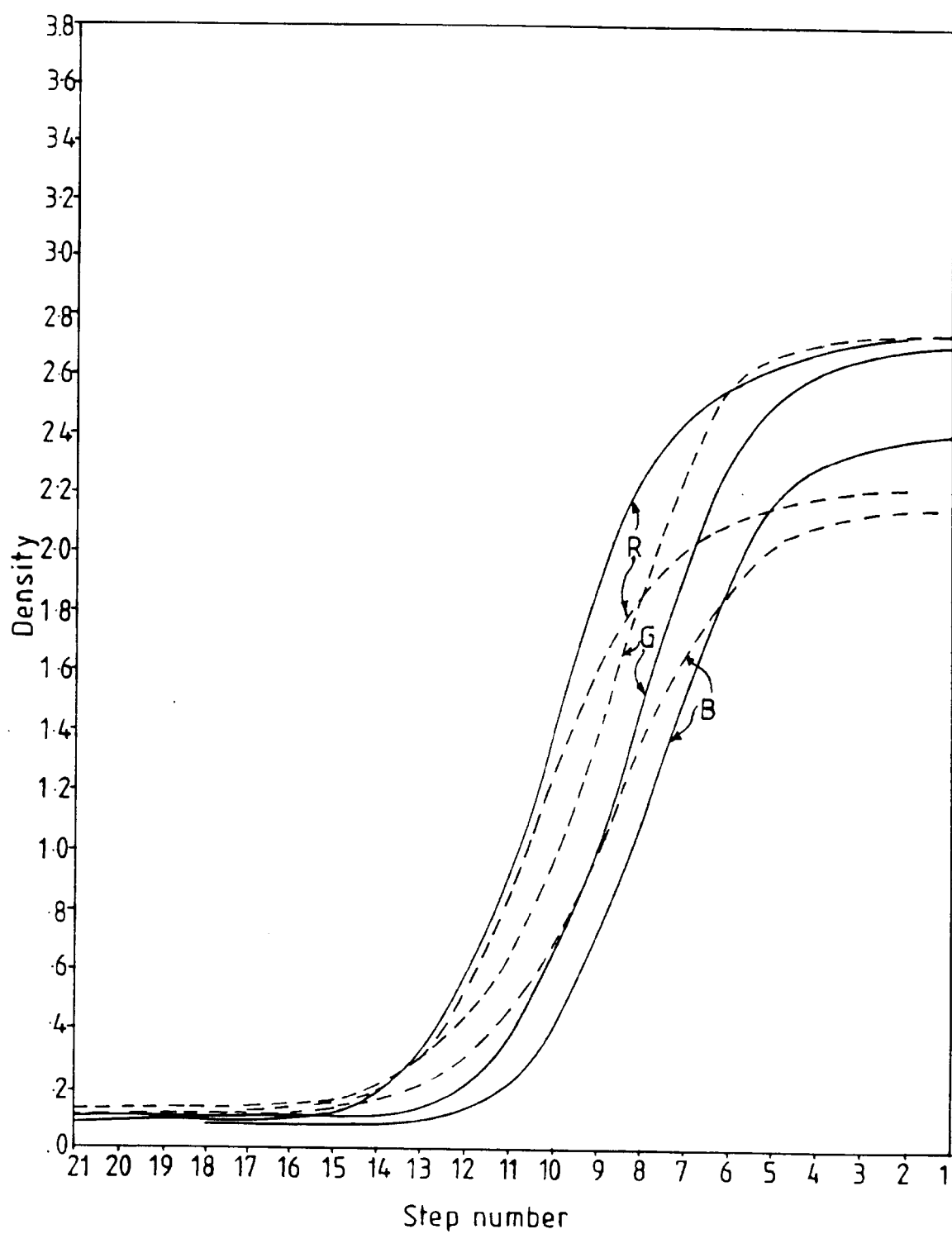


FIG.2.

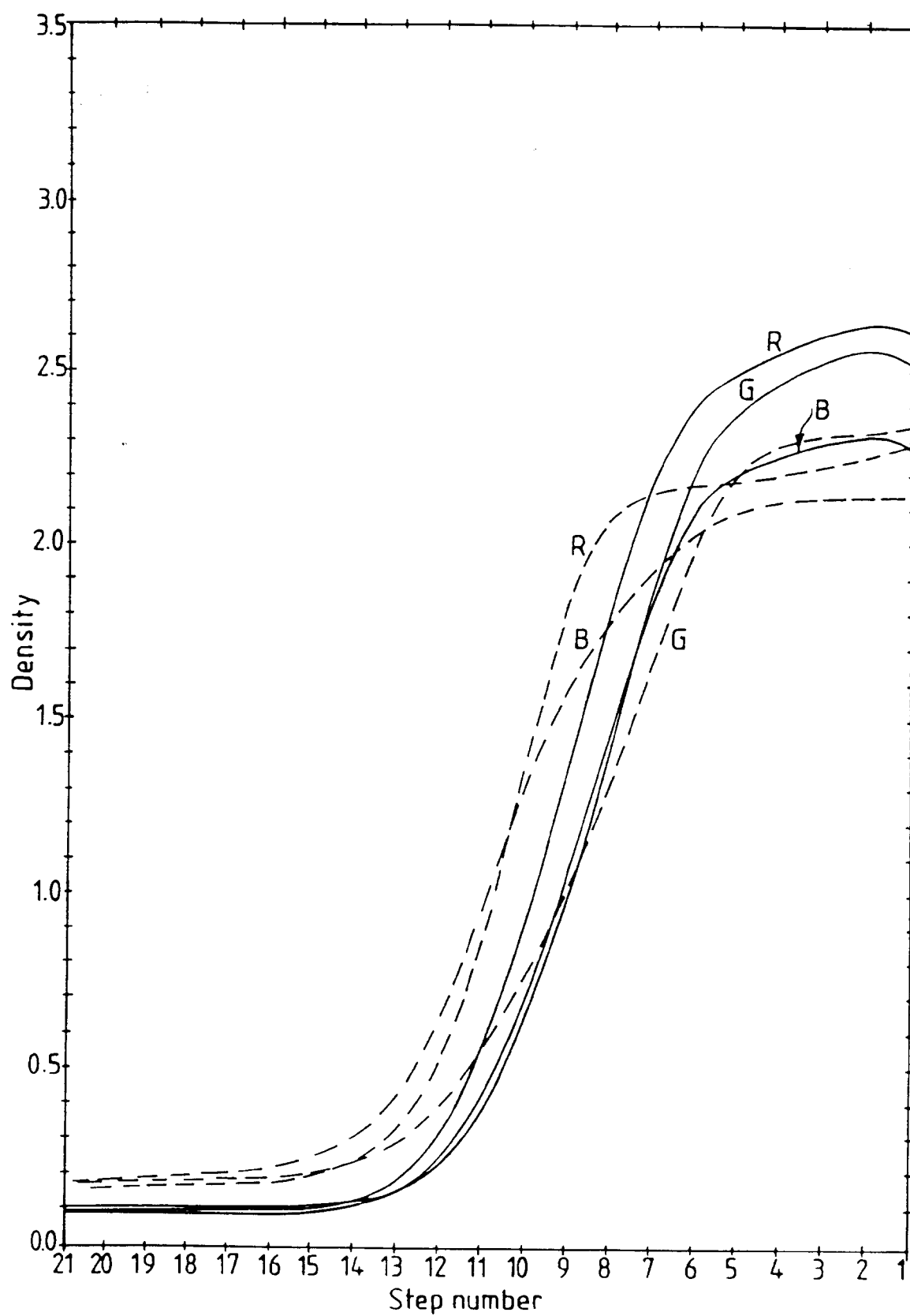


FIG. 3.

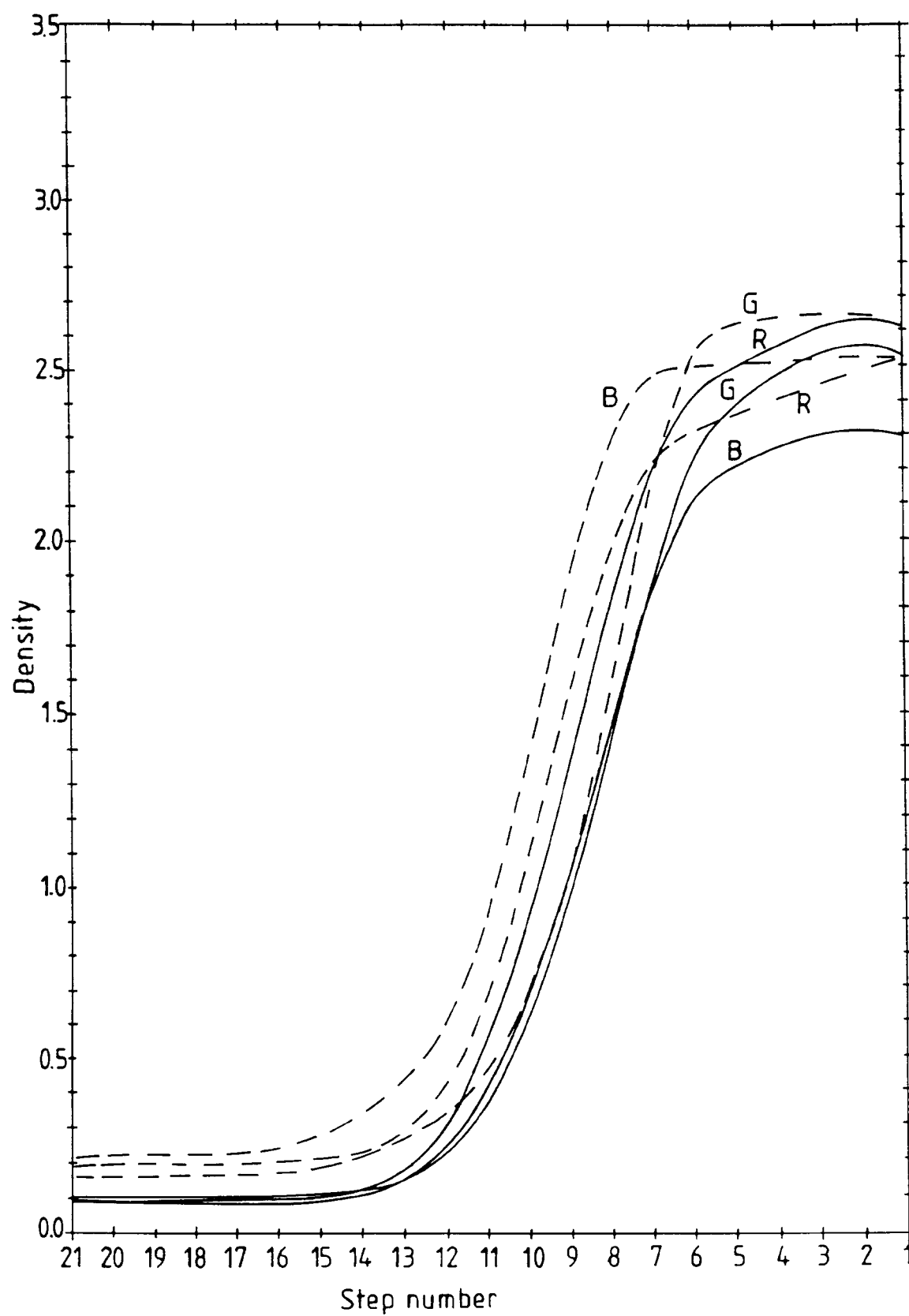


FIG. 4.