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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 DE FR

(72) Inventor: **Tsoi, Siu Chung, c/o Kodak Ltd.**
Headstone Drive
Harrow,
Middlesex, HA1 4TY (GB)

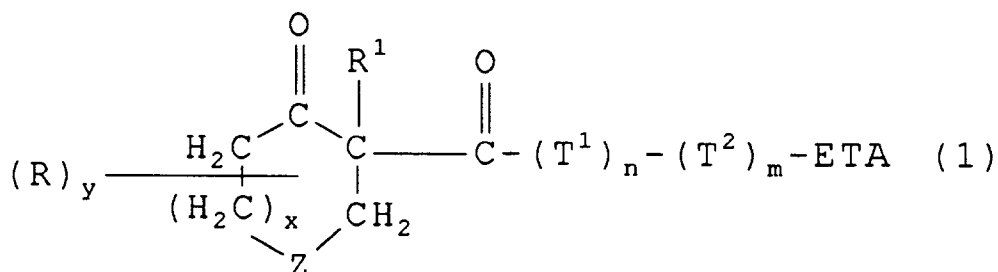
**Inventor: Twist, Peter Jeffery, c/o Kodak Ltd.
Headstone Drive
Harrow,
Middlesex, HA1 4TY (GB)**

Inventor: **Proehl, Gary S., Eastman Kodak Co.**
343 State Street
Rochester, NY-14650 (US)

74 Representative: **Baron, Paul Alexander
Clifford et al
Kodak Limited
Patent Department
Headstone Drive
Harrow
Middlesex HA1 4TY (GB)**

54 Photographic silver halide colour materials.

(57) A process of processing an imagewise exposed colour photographic material comprising at least one silver halide emulsion layer having associated therewith a dye image-forming coupler and which contains in a layer thereof one or more compounds of the general formula:



which release an electron transfer agent (ETA) under alkaline conditions, which process includes the step of treating the material in an alkaline colour developer solution. The preferred ETA's are pyrazolidinones of a type which reduce sensitometric variability in the developed colour image in both high and low activity conditions.

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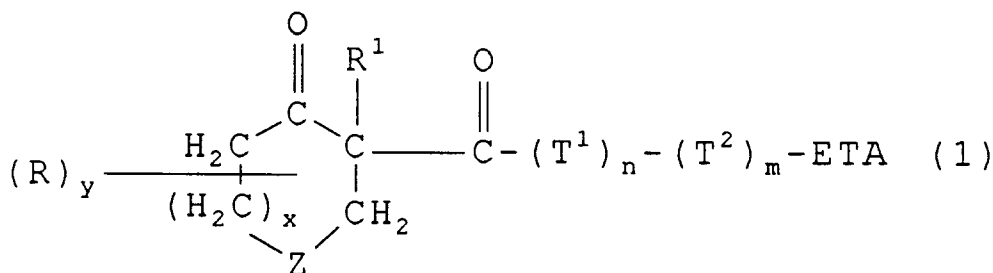
Problem to be Solved by the Invention

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Summary of the Invention

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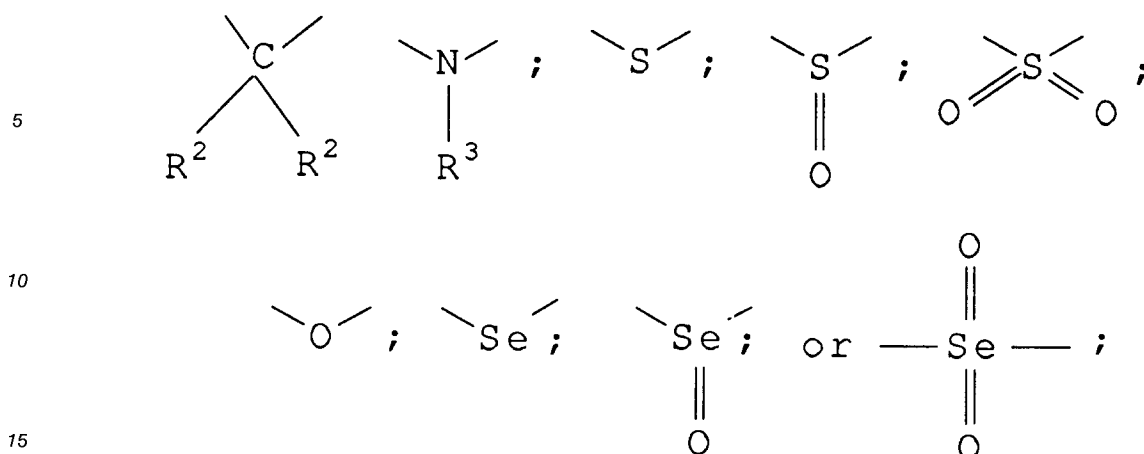


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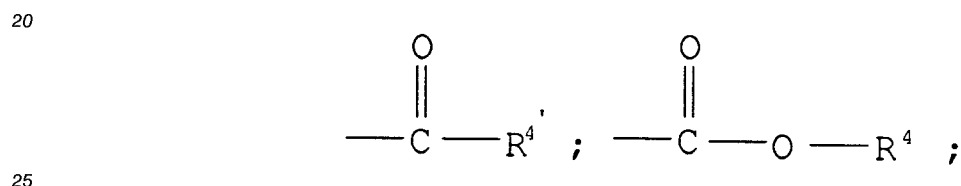
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R³ is H;



—SO₂—R⁴;

substituted or unsubstituted alkyl or aryl or a photographic ballast group;

R⁴ is unsubstituted or substituted alkyl, or aryl;

30 R⁴ is unsubstituted or substituted alkyl, or aryl, or



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R⁵ and R⁶ individually are hydrogen, or unsubstituted or substituted alkyl or aryl; and

Y is 0, 1, 2 or 3;

45 which process includes the step of treating the material with a photographic colour developer composition containing a binucleophile wherein the compound(s) of formula (1) are chosen such that the low activity development is accelerated and the high activity development decelerated thus leading to less variation in sensitometric results under both high and low activity conditions.

Advantageous Effect of the Invention

50 The present colour photographic materials show the advantages of improved performance in the colour developer where variations in process conditions have less effect than previously on sensitometric performance, particularly in the case of multilayer colour materials.

In the present invention not only are the low activity conditions accelerated by the presently used ETA releasers but also high activity conditions are decelerated thus leading to less variation in sensitometric results under both high and low activity conditions. This means that the spread of the characteristic curves as in Figs 3-13 of the accompanying drawings is compressed.

55 It has been found, in particular, that the presence of the ETA releaser reduces variability caused by variations in time and temperature of development, pH, bromide ion concentration and colour developing

agent concentration in the colour developer solution. The reduced risk of sensitometric variations further means that replenishment rates can be reduced thus resulting in less overflow and effluent. The often needed bromide ion removal from the developer solution may also be avoidable.

5 Brief Description of the Drawings

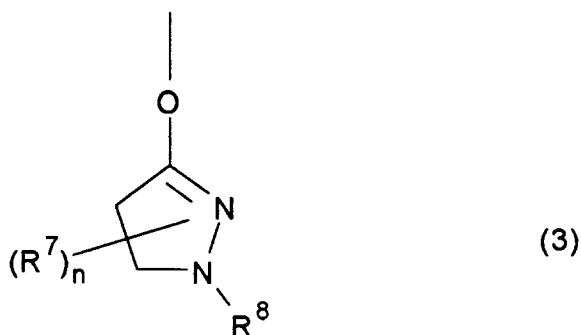
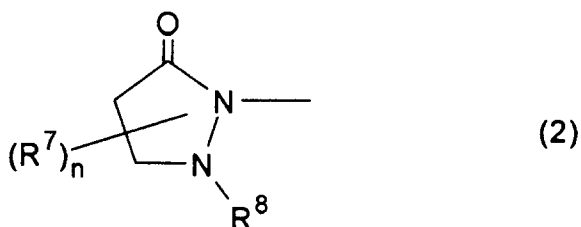
Figures 1-13 in the accompanying drawings illustrate the results of the working Examples below.

Detailed Description of the Invention

The alkyl groups represented by any of R to R⁶ may be alkyl groups having 1 to 25 carbon atoms, preferably 1 to 6 carbon atoms. Of the substituted groups, the substituents may be halogen, alkyl, alkoxy, acyloxy, aryloxy, keto, ether, ester, sulphonamide, sulphamoyl, carbonamide, or carbamoyl groups.

The binucleophile to be contained in the colour developer solution can, for example, be hydroxylamine, hydrogen peroxide, hydrazine all of which may be substituted or a salt thereof.

Preferred ETA groups have the general formula:



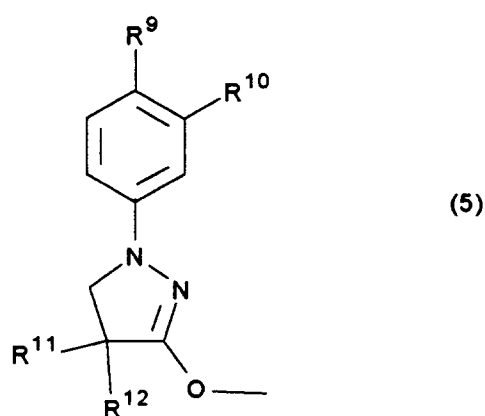
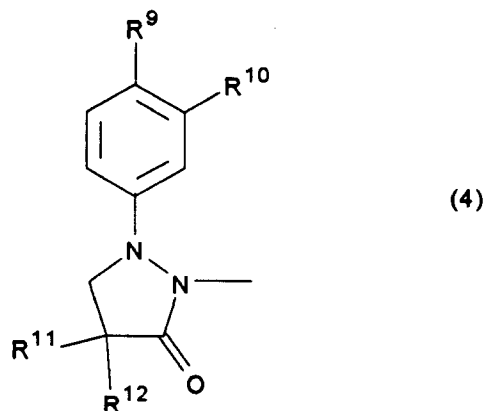
wherein

each R⁷ is an alkyl or substituted alkyl group having 1-10 carbon atoms,

R⁸ is an aryl or substituted aryl group,

n is 0, 1, 2, 3 or 4.

A particularly preferred group of ETA groups have the general formula:



wherein

R⁹ and R¹⁰ are each hydrogen or an alkyl or alkoxy group having 1-3 carbon atoms, or a substituted alkyl or alkoxy group having 1-7 carbon atoms, eg substituted with an aryl or ester group,

R¹¹ and R¹² are each hydrogen or an alkyl or hydroxyalkyl group having 1-3 carbon atoms, and wherein at least one of R⁹ and R¹⁰ is not hydrogen except in the cases where R¹¹ is an acyloxyalkyl or aroyloxyalkyl group when R⁹ and R¹⁰ can both be hydrogen. These ETA groups belong to type (1) described below.

As is known from European application 92900247.5, there are three types of behaviour observed with different types of pyrazolidinone. The reduction of sensitivity to development time is used as an example. Three broad types of behaviour for different ETA's can be observed and these are as follows:

Type (1): A reduction of sensitometric spread with a retardation of overdevelopment and an acceleration of the underdevelopment.

Type (2): A modest reduction of sensitometric spread with a general acceleration of dye formation.

Type (3): A reduction in sensitometric spread with a general retardation of dye formation.

The use of Type (2) ETA's alone is therefore not part of the present invention.

Type (1) is the preferred behaviour exhibited by the preferred compounds especially when used singly. Type (2) is another useful and beneficial behaviour and could, in certain cases, be preferred over Type (1) if an increase in contrast or corresponding trade-off was desired.

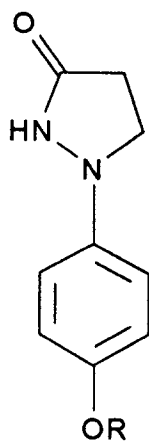
The present invention also includes the use of combinations of ETA's. Combinations of Type (2) and (3), for example, can give an overall behaviour similar to or better than Type (1). Combinations of Type (1) and (3) also give good results in that the spread of the sensitometric curves is particularly well controlled.

Type (2) ETA groups may be of formula (4) or (5) in which R⁹, R¹⁰ are hydrogen or alkyl of 1-3 carbon atoms and R¹¹ and R¹² are an alkyl or hydroxyalkyl group of 1-3 carbon atoms, eg -CH₂OH or -C₃H₇.

Type (3) ETA groups may be of formula (4) or (5) in which R⁹ to R¹² are each hydrogen or alkyl of 1-12 carbon atoms, alkoxy 1-12 carbon atoms both of which may be substituted and wherein the total number of carbon atoms in R⁹ to R¹² is at least 4.

It is recognised that the definitions of the above types of ETA are not mutually exclusive. This is because it is difficult to find an appropriate definition which is mutually exclusive. Examples of the three types are given below. Beyond that the skilled worker will be able to determine to which type a particular ETA belongs by carrying out the procedures described herein.

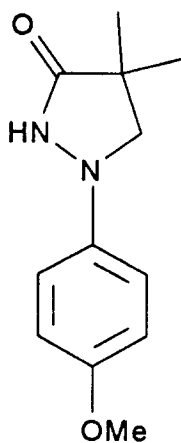
Specific examples of the three types of ETA are as follows:

Type 1

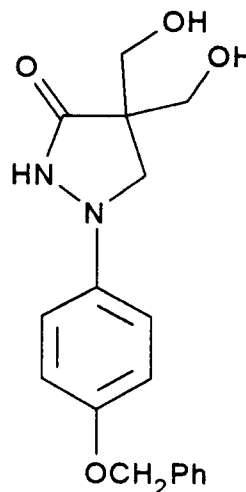
1A R=Me

1B R=Et

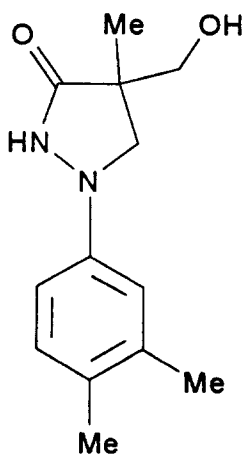
1C R=Propyl-n



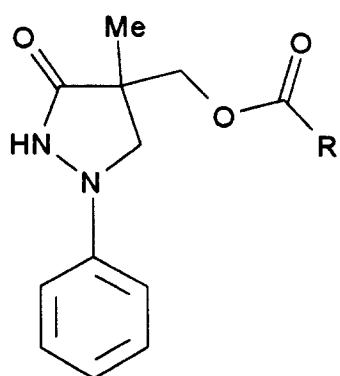
1D



1E



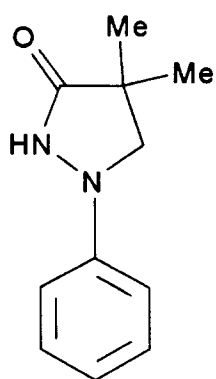
1F



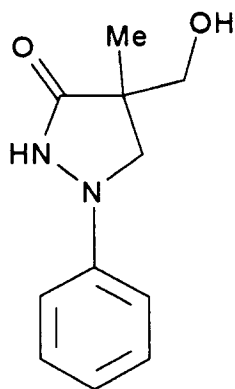
1G R=propyl-n

1H R=butyl-t

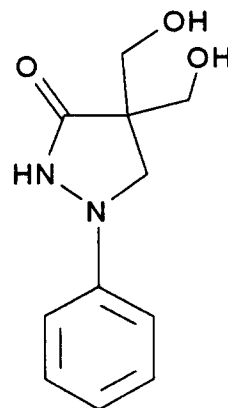
Type 2



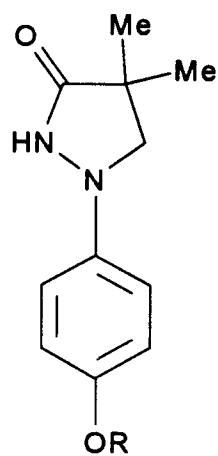
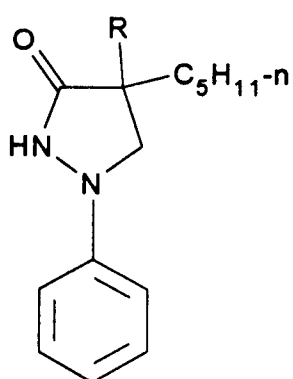
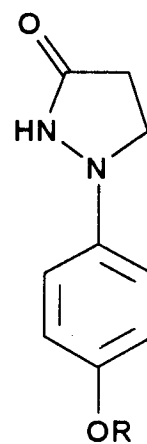
2A



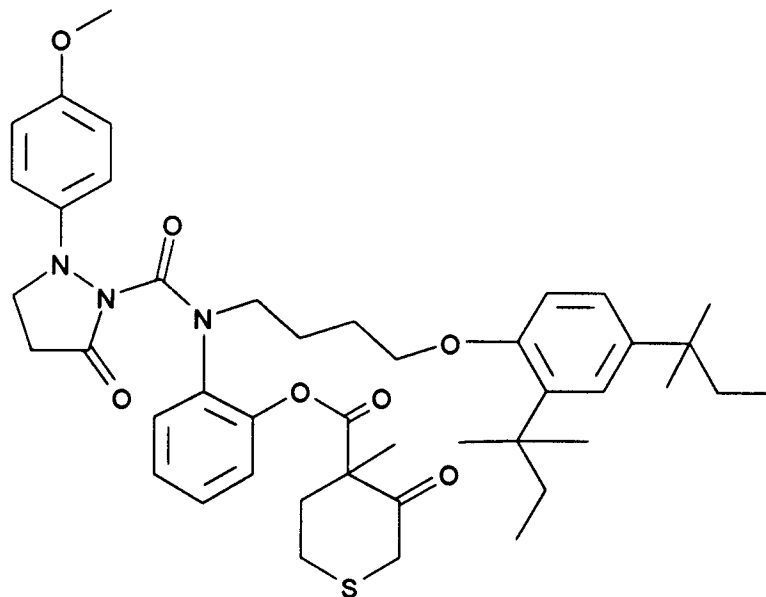
2B

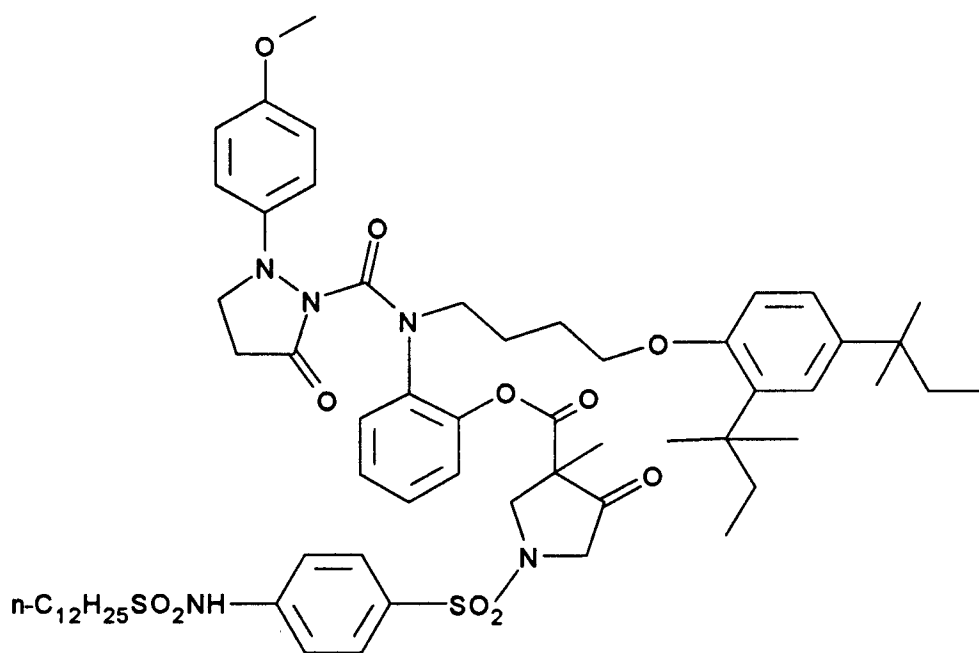


2C

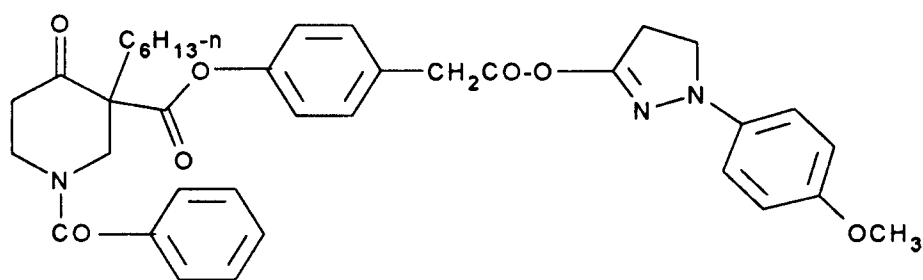
Type 33A $R = C_6H_{13}-n$ 3B $R = CH_2Ph$ 3C $R = H$ 3D $R = Me$ 3E $R = C_4H_9-n$ 3D $R = C_6H_{13}-n$ 3F $R = CH_2Ph$

Specific examples of BETA compounds to be used in the present invention have the formulae below. They are all type (1) except where specified.

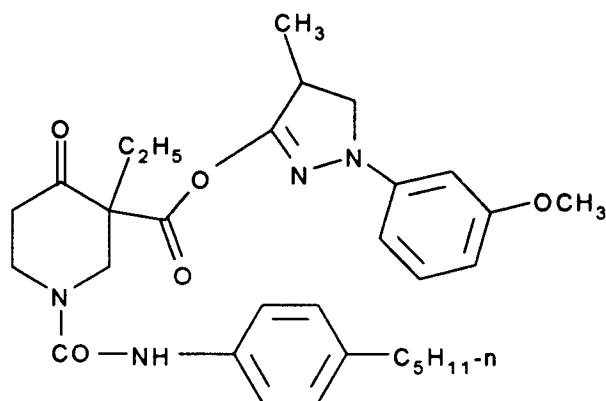
**Compound 1**



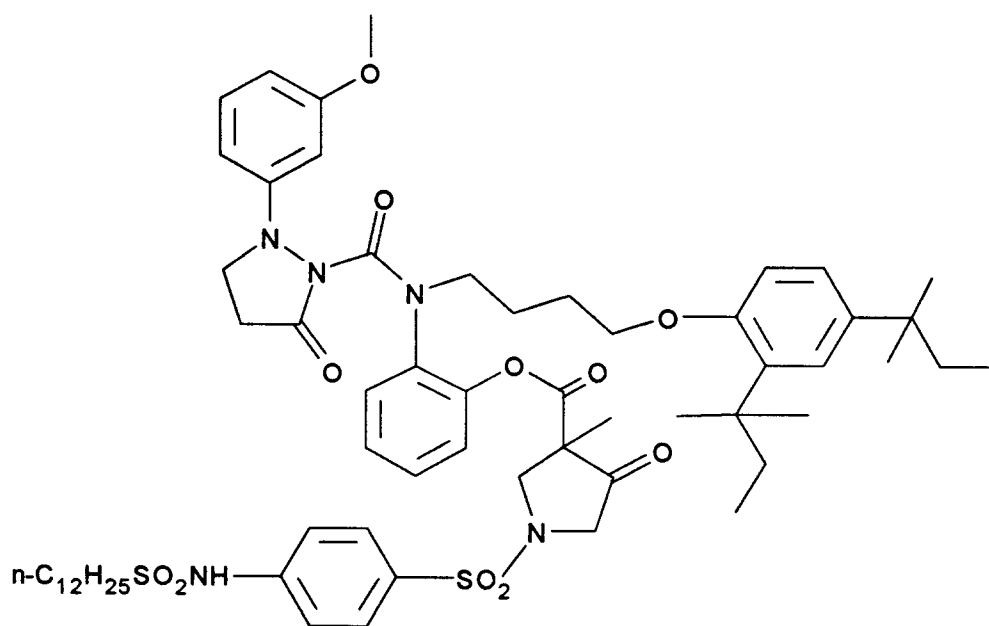
Compound 2



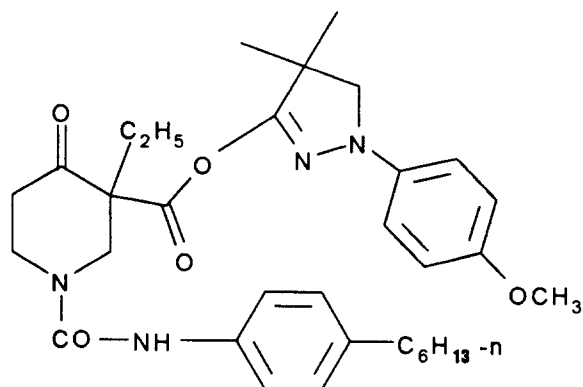
Compound 3



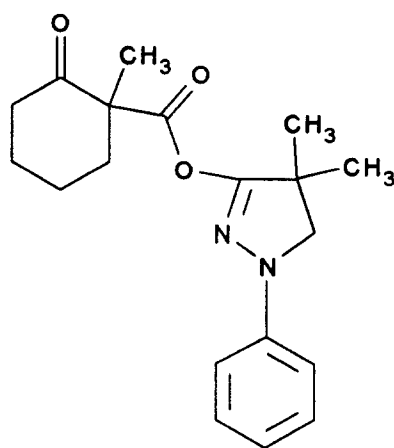
Compound 4



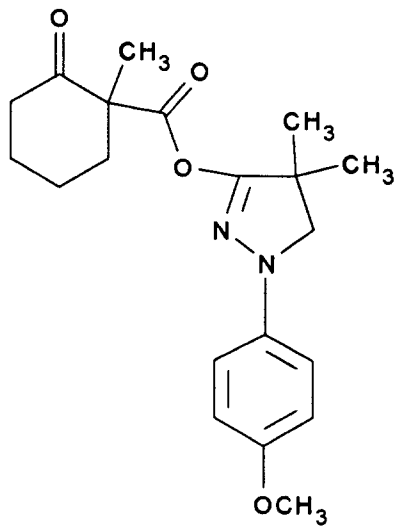
Compound 5



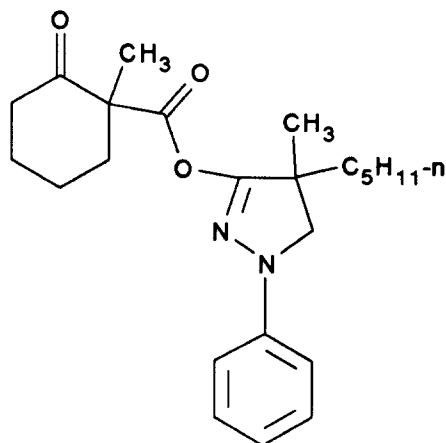
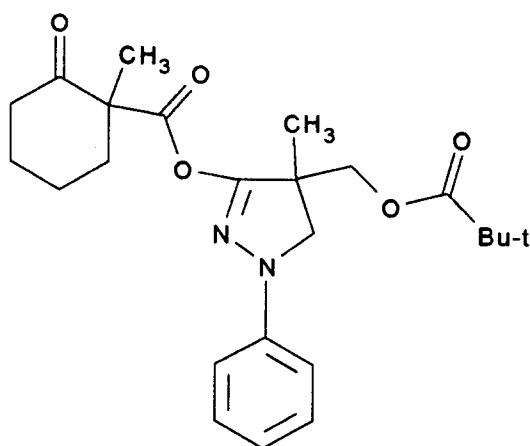
Compound 6



Compound 7 (type 2)



Compound 8

**Compound 9 (type 3)****Compound 10**

The compounds of formula (1) may be incorporated into the photographic materials by methods, in themselves, known. For example they may be dispersed therein in a high-boiling organic solvent, often known as a "coupler solvent". Examples of such solvents are triphenylphosphate, and dibutylphthalate. Normally the coupler is dissolved in the coupler solvent or mixture of solvents and this liquid is dispersed in an aqueous gelatin solution. Sometimes a low boiling solvent is used in the coupler solvent mixture but this is removed after the dispersion has been formed.

The present invention is particularly applicable to the processing of colour negative film but is also applicable to other processes, eg colour paper. The material to be processed comprises a support bearing at least one silver halide emulsion layer having a colour coupler associated therewith. The term "associated therewith" here takes its normal meaning in art. The coupler may be incorporated in the emulsion layer or in a layer adjacent thereto. The preferred colour materials comprise three dye image forming units each containing one or more emulsion layers having couplers associated therewith and each sensitised to a different region of the spectrum. A typical colour material would contain such units sensitised to blue, green and red light and capable of forming yellow, magenta and cyan image dyes respectively.

Examples of colour photographic materials and methods of processing them are described in Research Disclosure Item 308119, December 1989 published by Kenneth Mason Publications, Emsworth, Hants, United Kingdom.

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

EXAMPLE 1

Compound 1 was made into a dispersion in coupler solvent (1) (diethyl lauramide) and solvent (2) (ethyl acetate) in the ratio, (Compound (1):Solvent (1): Solvent (2)) by weight of 1:2:3. The oil phase was then dispersed in gelatin to give 1.0 % Compound 1, 4.0 % gelatin.

Coatings were then made in which compound 1 was coated in a layer underneath a layer containing the silver halide and coupler. This is shown in the table 1 below.

Table 1 Coating Format for Incorporated BETA

	Gelatin (1.0g/sq.m)

	Coupler 1 (0.6g/sq.m)
	Tabular grain silver bromiodide
	emulsion (speed=400 ASA) (1.0g/sq.m)
	Gelatin(2.7g/sq.m)
	Tetraazaindene (antifoggant) 30 ml/mole Ag

	Compound 1 (0.0, 0.05, 0.1, 0.2, 0.4g/sq.m)
	Gelatin(2.7g/sq.m)

	Transparent Support

The BETA compound was coated in a range of levels 0.0, 0.05, 0.1, 0.2 and 0.4 g/sq.m. The ETA released from the BETA is 4'-methoxyphenyl-pyrazolidinone.

EXAMPLE 2

The coatings of Example 1 were processed in standard C-41 developer, which contains 2g/l of hydroxylamine sulphate(HAS), for the following development times: 1, 2.5, 5 and 8 minutes. In Figure 2 the sensitometric response of the control coating for these four development times is shown. In Figure 3 the effect of the highest coated level of BETA for the same set of development times is shown with the curves from the control plot superimposed. It can be seen that with BETA present the sensitometric spread is reduced. This effect is similar to that shown by adding the ETA to the developer but to a smaller extent. In Figure 4 the extent of sensitometric spread is plotted against the coated level of BETA and it can be seen that sensitometric spread is reduced as the level of BETA is increased.

EXAMPLE 3

Compound 1 is designed to release the ETA 4'-methoxy-1-phenylpyrazolidone by the action of the binucleophile, hydroxylamine sulphate (HAS), which is in C-41 developer at 2g/l. Hydroxylamine is present in C-41 developer as an anti-oxidant. In order to demonstrate the action of hydroxylamine in releasing the ETA some C-41 developers were made-up with a range of HAS levels of 0, 1, 2, 6, 24 and 60g/l. The control coating and the one with the highest level of BETA (0.4g/sq.m) were processed in these developers and the comparisons for HAS levels of 0, 6 and 60g/l are shown in Figures 5, 6 and 7 respectively. It can be seen that without HAS there is almost no effect from the coated BETA, but there is when HAS is present. In Figure 1 the reduction in sensitometric sensitivity is plotted against HAS level in the developer

for a BETA (0.4g/sq.m) containing coating and one without BETA. Here it can be seen that there is a small reduction in sensitometric sensitivity with HAS increase for the coating without BETA but a much greater reduction in the coating with BETA.

5 EXAMPLE 4

The following multilayer structures were prepared. The figures in parentheses are coverages in g/m²:

- super coat gelatin (1.0)
- UV protection layer
- 10 High speed Blue sensitive silver halide (0.6) + yellow coupler (0.18)
- Slow speed Blue sensitive silver halide (0.55) + yellow coupler (1.0)
- Scavenger interlayer
- High speed Green sensitive silver halide (0.79) + magenta coupler (0.11)
- Medium speed Green sensitive silver halide (0.45) + magenta coupler (0.2)
- 15 Low speed Green sensitive silver halide (0.5) + magenta coupler (0.39)
- Scavenger interlayer
- High speed Red sensitive silver halide (1.0) + cyan coupler (0.16)
- Medium speed Red sensitive silver halide (0.5) + cyan coupler (0.31)
- Low speed Red sensitive silver halide (0.5) + cyan coupler (0.65)
- 20 Anti-halation layer
- Film base / / / / /

where the silver halide is a bromoiodide emulsion with an average 3% iodide. The following variations in the nature, amount and position of the BETA compound(s) and their effect on the sensitometric results illustrated in the Figures specified were as follows:

25 1. Single BETA in multilayer; Figs 8 and 9

- a. Fig 8 compares a control with a BETA (Compound 8) incorporated in the anti-halation layer of a multilayer at 1.0g/sq.metre. Solid lines are for the red record of the control, dashed lines for the red record with the incorporated BETA. There is a small amount of compression of the spread in sensitometry by the incorporation of the BETA.
- 30 b. Fig 9 compares a control with a BETA (Compound 10) incorporated at 0.33g/sq.metre in both the fast and slow layers of the red sensitive pack of a multilayer. Solid lines are for the red record of the control and the dashed lines for the red record of the incorporated BETA. There is a moderate compression of the sensitometric spread by incorporation of the BETA.

35 2. Combinations of BETAs in multilayer;

Figs 10, 11, 12, 13.

- a. Fig 10 compares the red records of a control with a BETA (Compound 7) incorporated in the anti-halation layer of a multilayer at 0.5g/sq.metre. This is an example of a BETA which releases an accelerating ETA and consequently the dashed curves (BETA) are in the main accelerated relative to solid curves of the control.
- 40 b. Fig 11 compares the red records of a control with a BETA (Compound 9) incorporated in the anti-halation layer of a multilayer at 0.5g/sq.metre. This is an example of a BETA which releases a retarding ETA and the dashed curves for the BETA are retarded relative to the solid curves for the control.
- c. Fig 12 compares the red records of a control with a combination of two BETAs, Compound 7 and Compound 9 incorporated in the anti-halation layer of a multilayer at 0.5g/sq.metre each. This is an example of a combination of an accelerating and a retarding BETA. The dashed curves of the BETA coating show that longer development times are retarded and the shorter development times accelerated relative to the solid lines of the control.
- 45 d. Fig 13 compares the red records of the example of Fig 12 with an additional 0.4g/l of 4'-methoxy-1-phenyl-3-pyrazolidinone in the developer used for the BETA incorporated coating. In this case the longer development times are retarded and the short development times accelerated to a greater extent than without the ETA in the developer.
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Claims

- 55 1. A process of processing an imagewise exposed colour photographic material comprising at least one silver halide emulsion layer having associated therewith a dye image-forming coupler and which contains in a layer thereof one or more compounds of the general formula:



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x is 0, 1 or 2;

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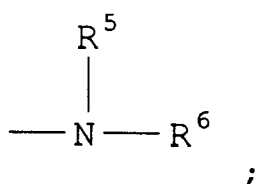
Z is located at any ring position not adjacent to the ketocarbonyl group and is a group having one of the formulae:



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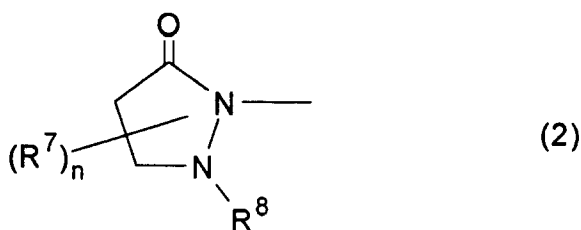


R^{4'} is unsubstituted or substituted alkyl, or aryl, or

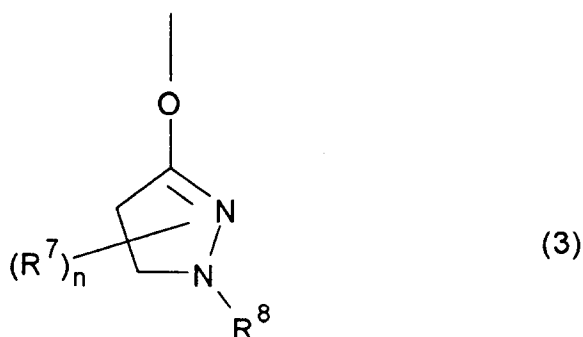


R^5 and R^6 individually are hydrogen, or unsubstituted or substituted alkyl or aryl; and
 Y is 0, 1, 2 or 3;
 which process includes the step of treating the material with a photographic colour developer composition containing a binucleophile wherein the compound(s) of formula (1) are chosen such that the low activity development is accelerated and the high activity development decelerated thus leading to less variation in sensitometric results under both high and low activity conditions.

2. A process as claimed in claim 1 in which the the ETA group has the general formula:

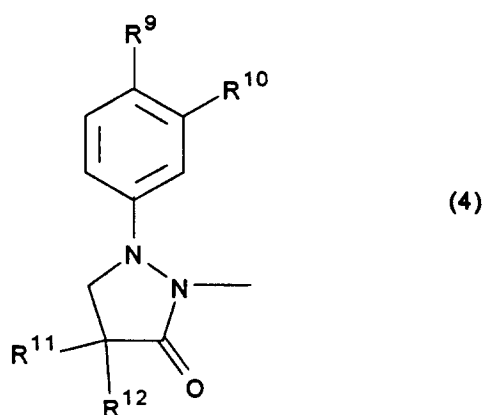


or

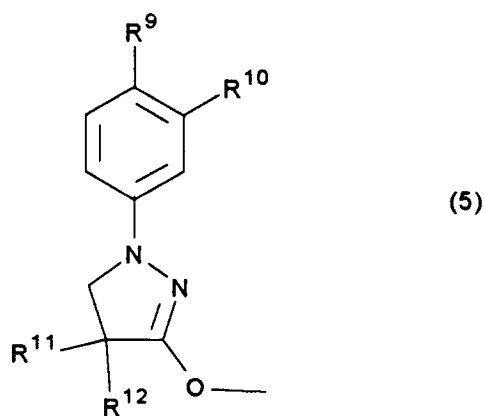


wherein
 each R^7 is an alkyl or substituted alkyl group having 1-10 carbon atoms,
 R^8 is an aryl or substituted aryl group,
 n is 0, 1, 2, 3 or 4.

3. A process as claimed in claim 2 in which the ETA group has the general formula:



or



wherein

R^9 and R^{10} are each hydrogen or an alkyl or alkoxy group having 1-3 carbon atoms, or a substituted alkyl or alkoxy group having 1-7 carbon atoms, eg substituted with an aryl or ester group,

R^{11} and R^{12} are each hydrogen or an alkyl or hydroxyalkyl group having 1-3 carbon atoms, and wherein at least one of R^9 and R^{10} is not hydrogen except in the cases where R^{11} is an acyloxyalkyl or aryloxyalkyl group when R^9 and R^{10} can both be hydrogen.

4. A process as claimed in claim 2 in which the ETA group has the general formula (4) or (5) in which R^9 , R^{10} are hydrogen or alkyl of 1-3 carbon atoms and R^{11} and R^{12} are an alkyl or hydroxyalkyl group of 1-3 carbon atoms, eg $-\text{CH}_2\text{OH}$ or $-\text{C}_3\text{H}_7$.
5. A process as claimed in claim 2 in which the ETA group has the general formula (4) or (5) in which R^9 to R^{12} are each hydrogen or alkyl of 1-12 carbon atoms, alkoxy 1-12 carbon atoms both of which may be substituted and wherein the total number of carbon atoms in R^9 to R^{12} is at least 4.
6. A process as claimed in any of claims 1-5 in which the colour developing solution contains a water-soluble electron transfer agent (ETA).
7. A process as claimed in any of claims 1-6 in which the ETA is a pyrazolidinone.

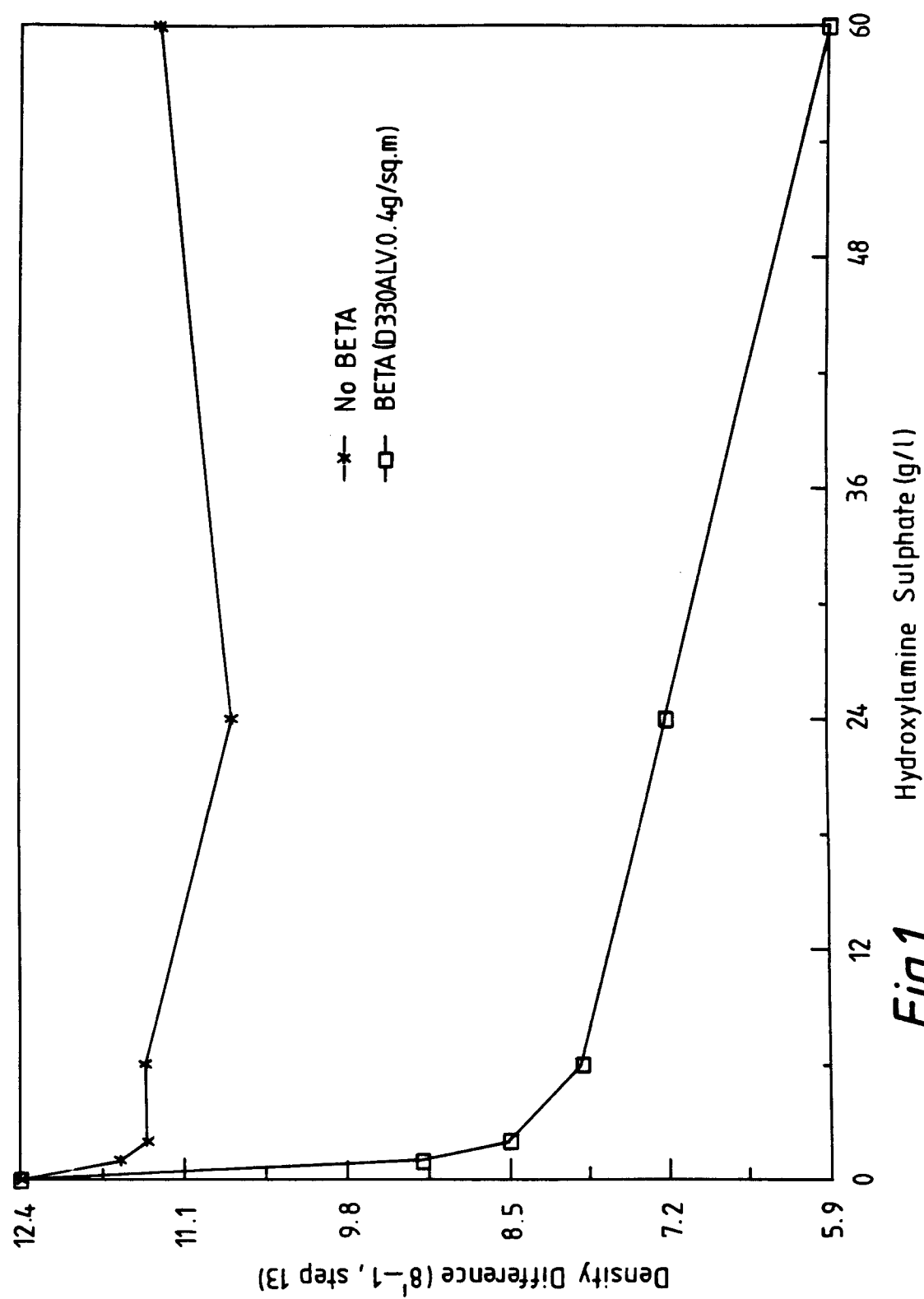
*Fig.1.*

Fig.2.

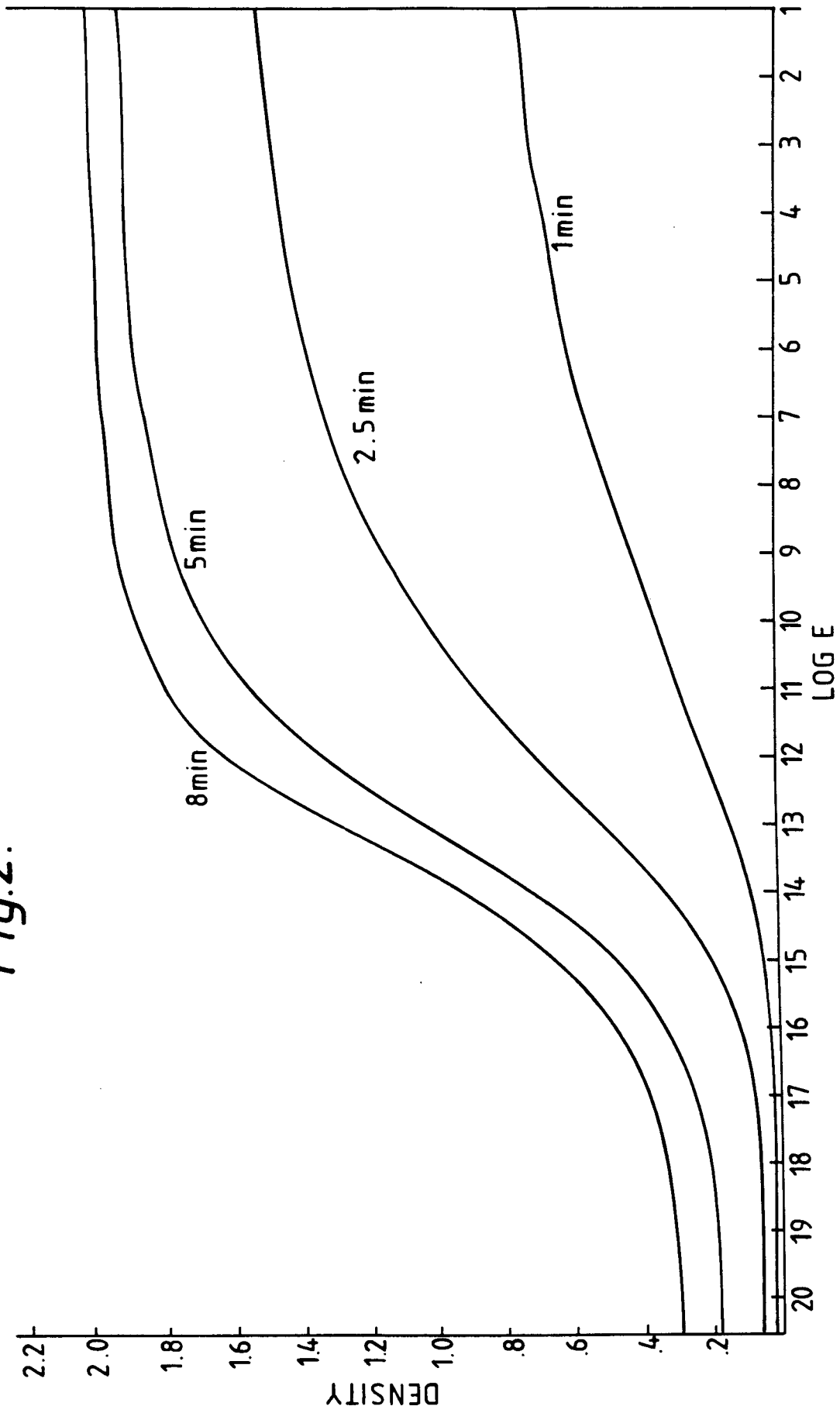
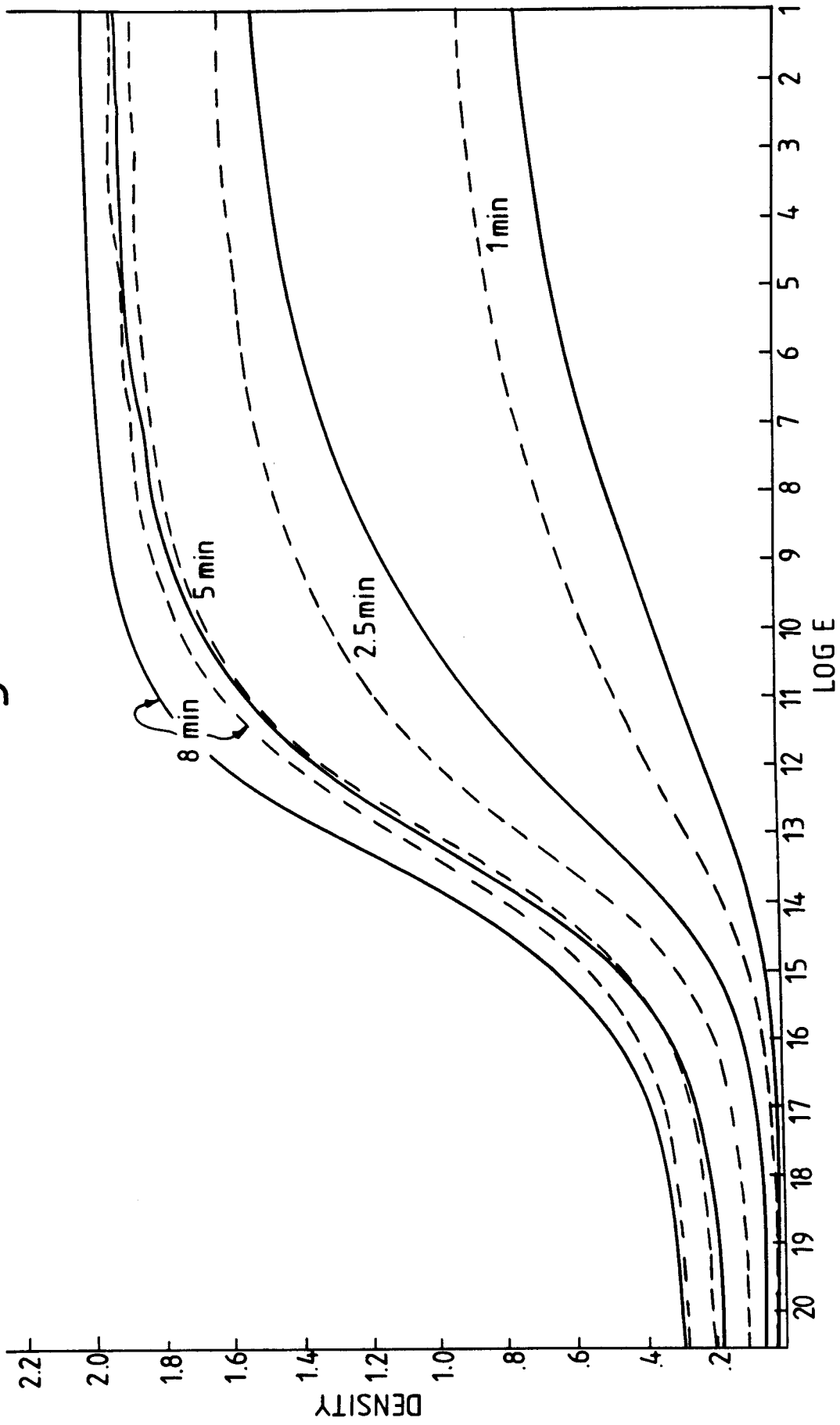


Fig.3.

— Control
 --- Invention



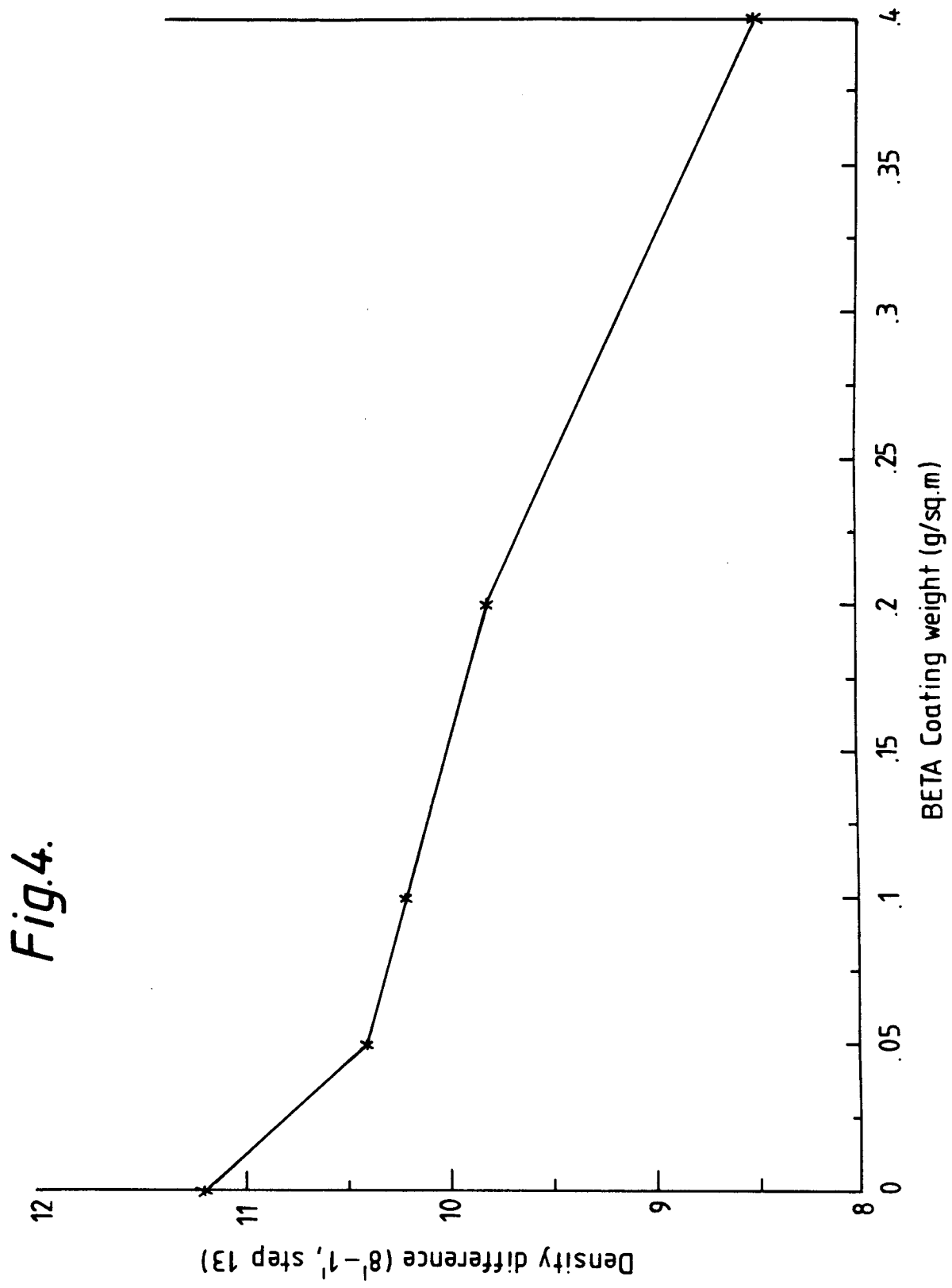


Fig. 5.

— Control
--- Invention

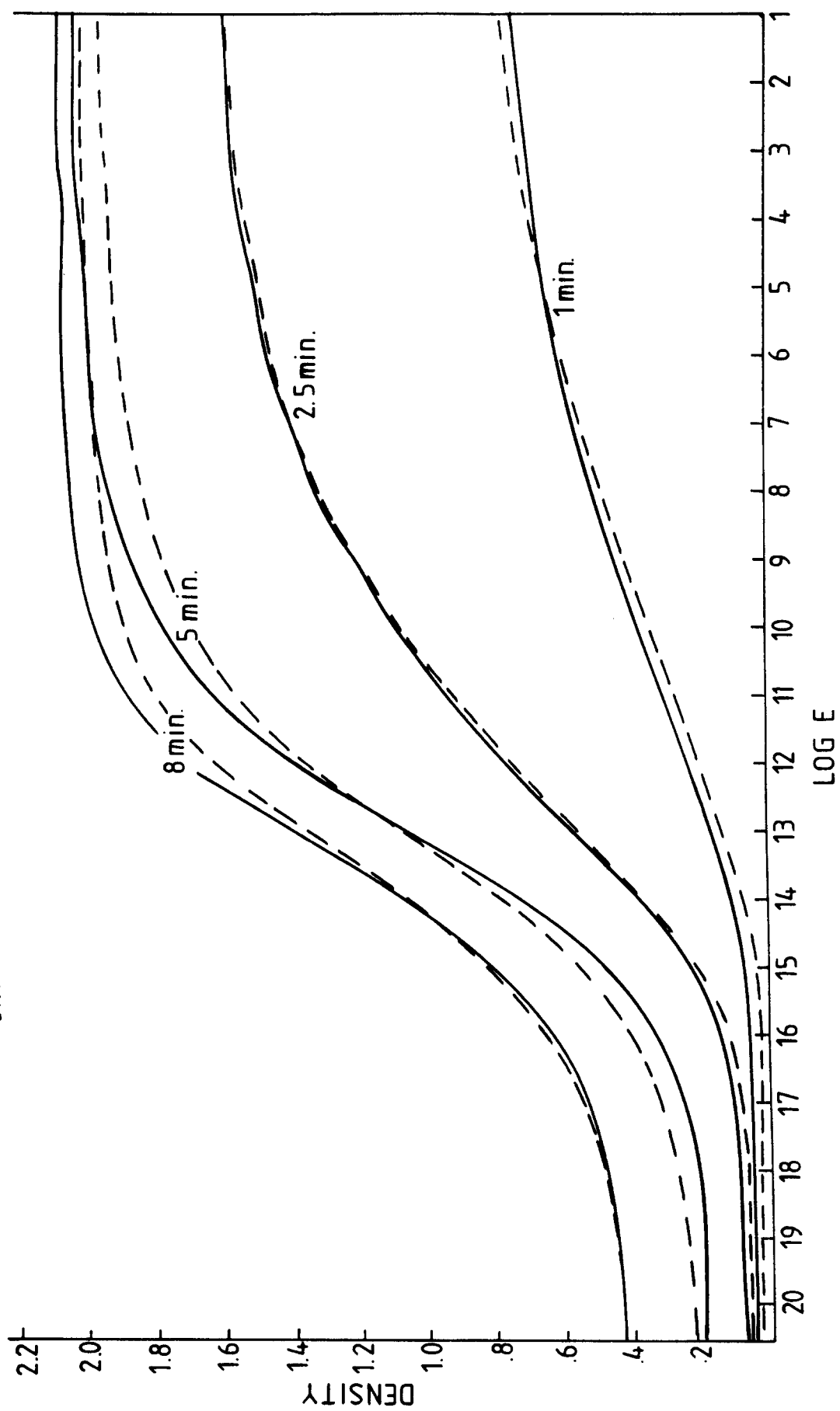


Fig. 6.

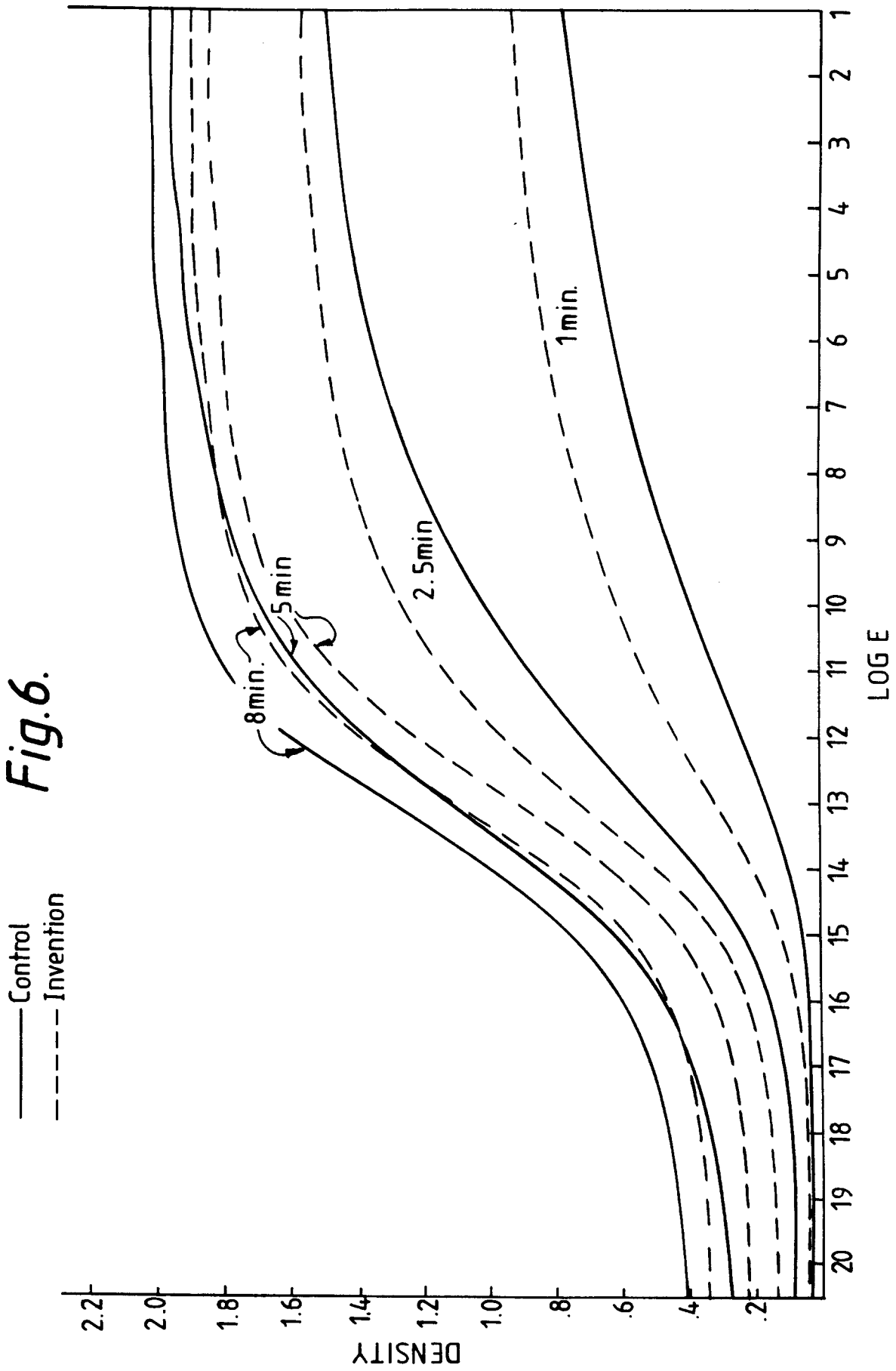
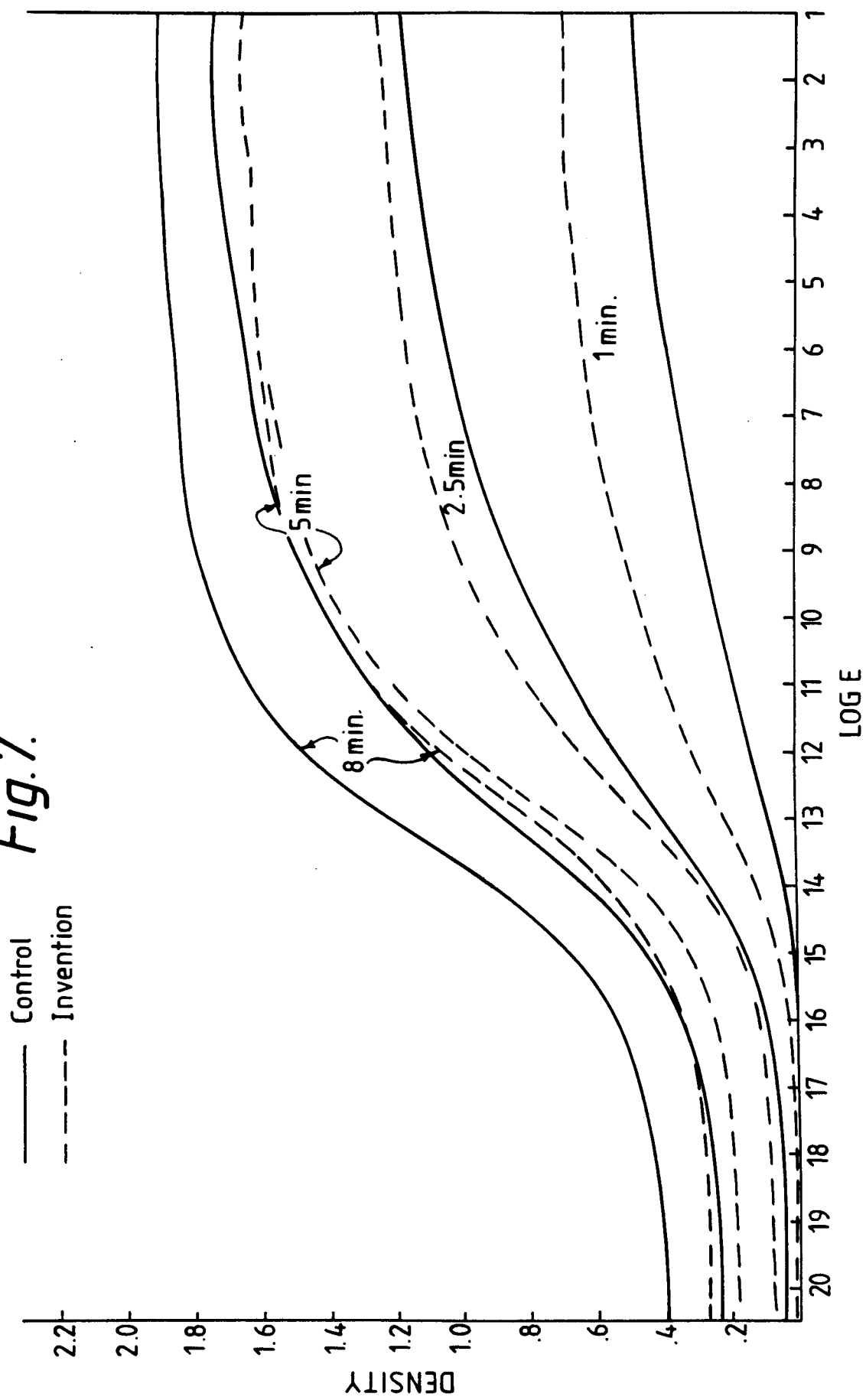
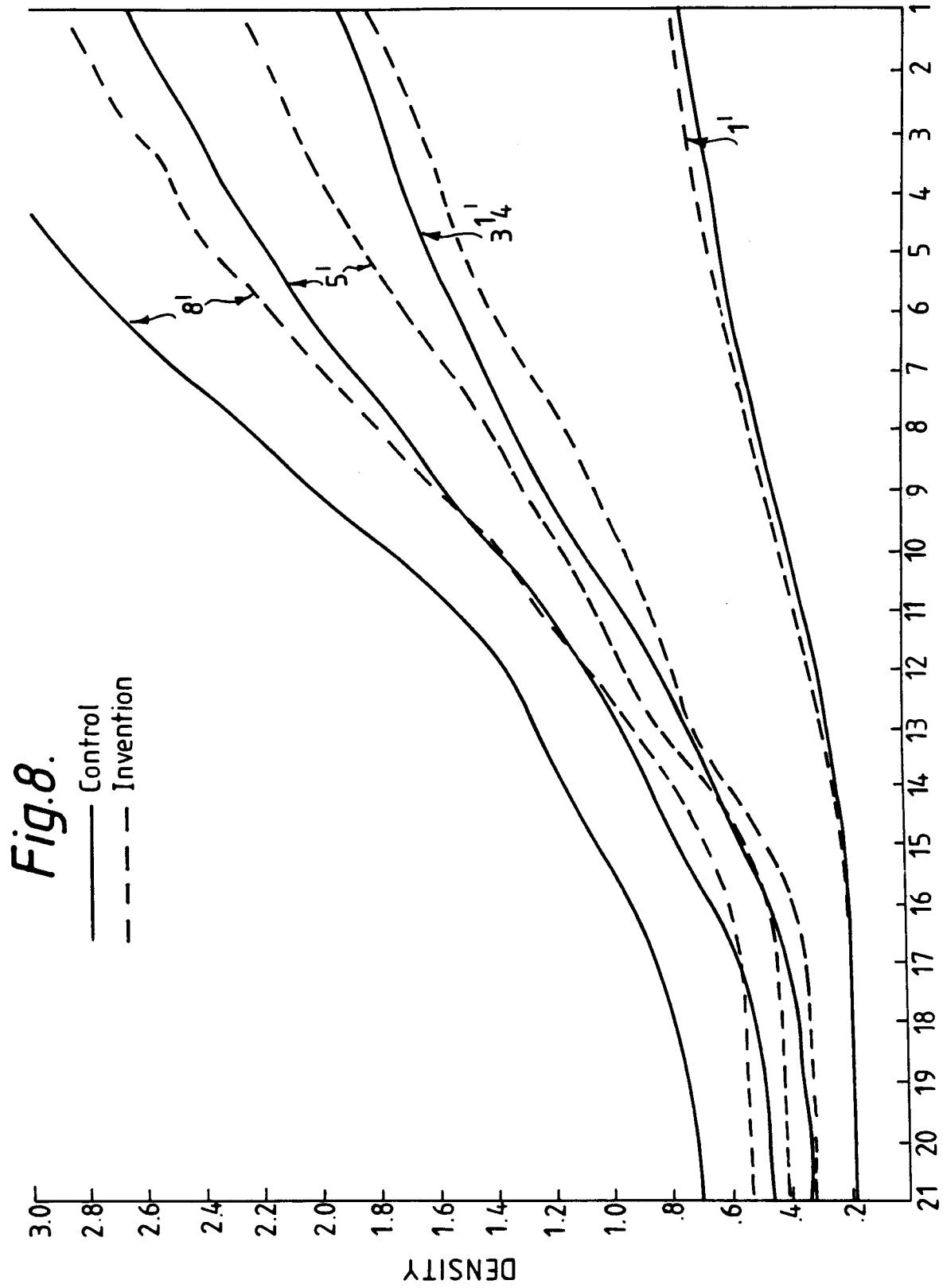
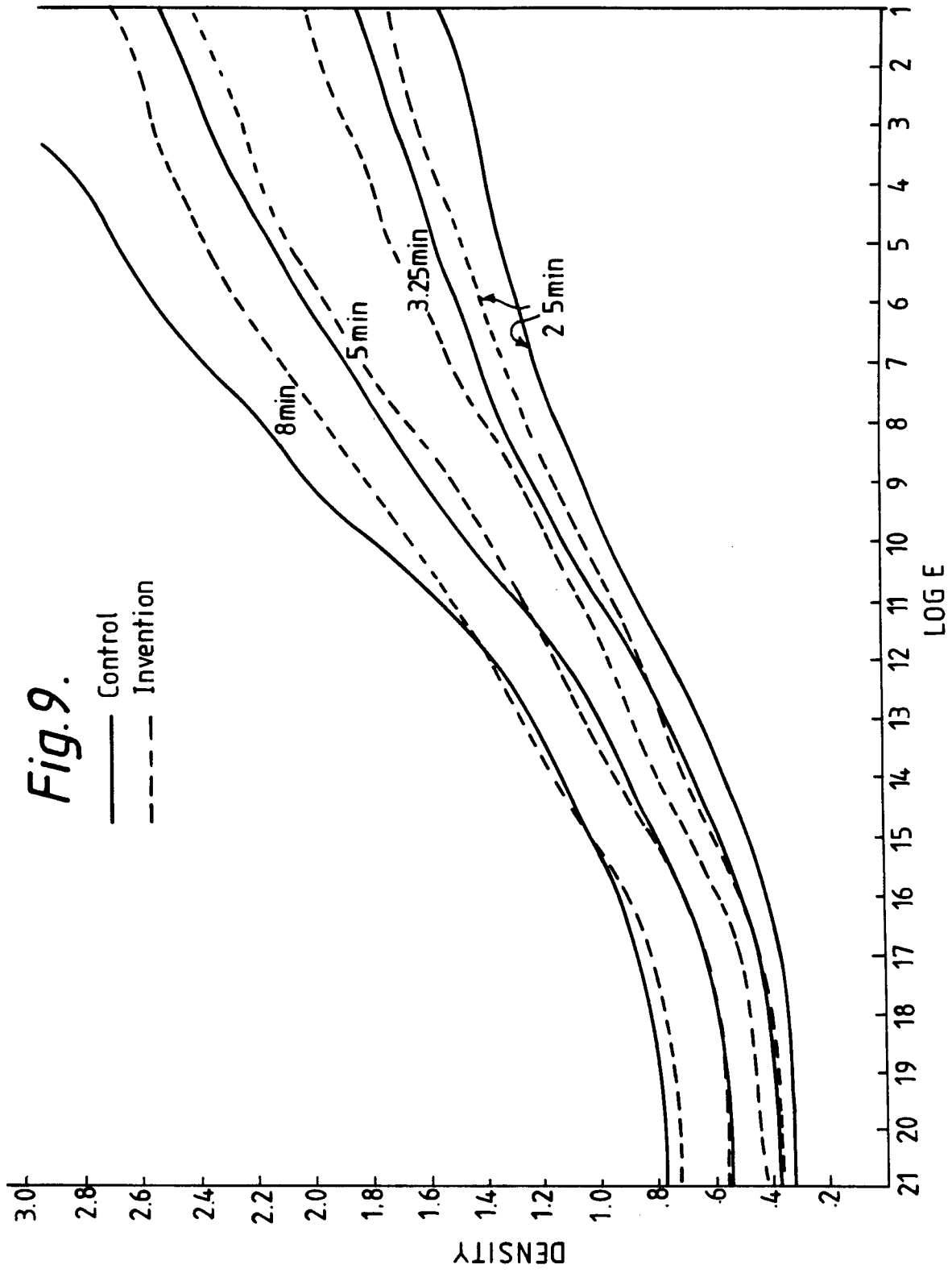
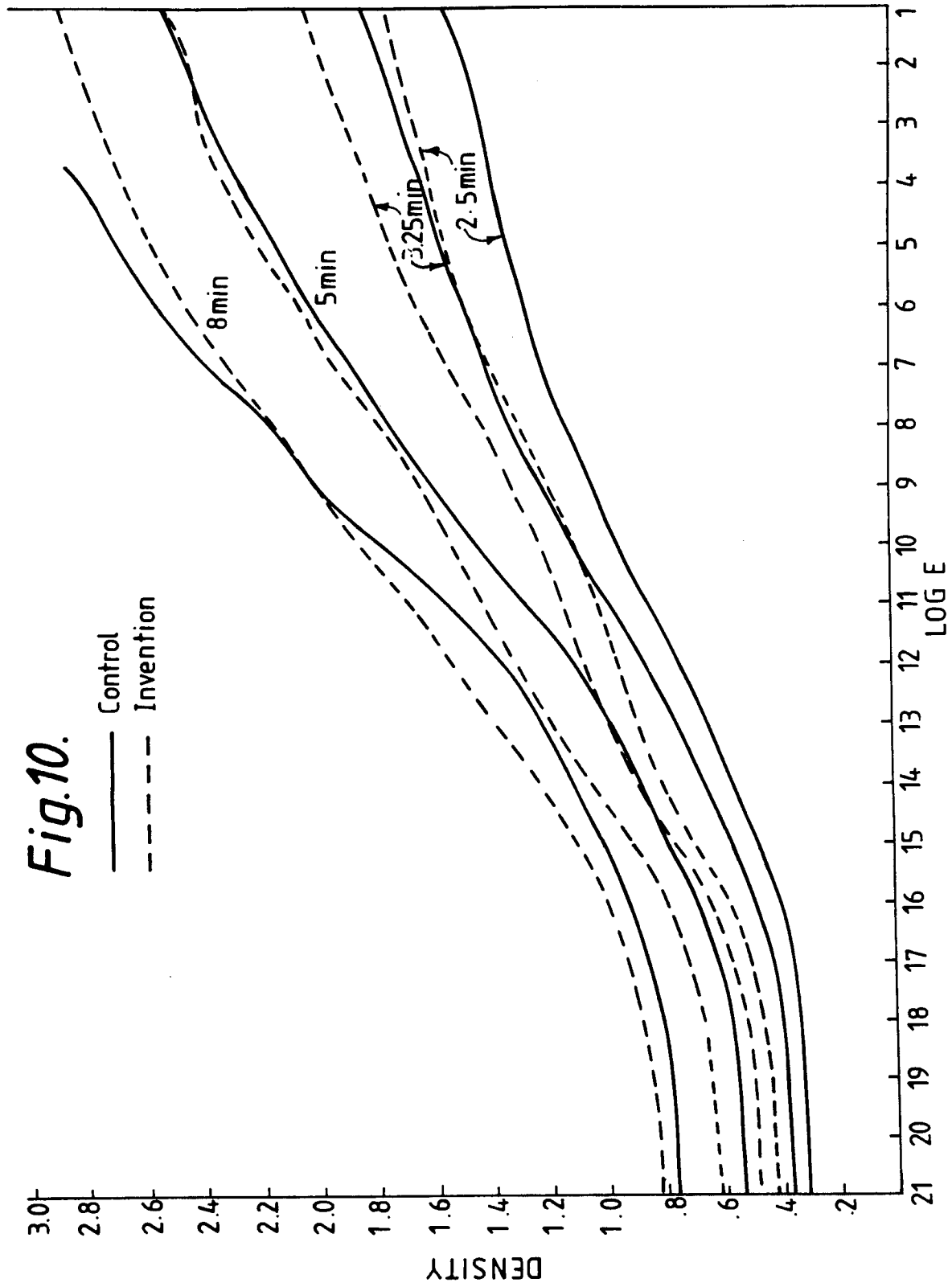


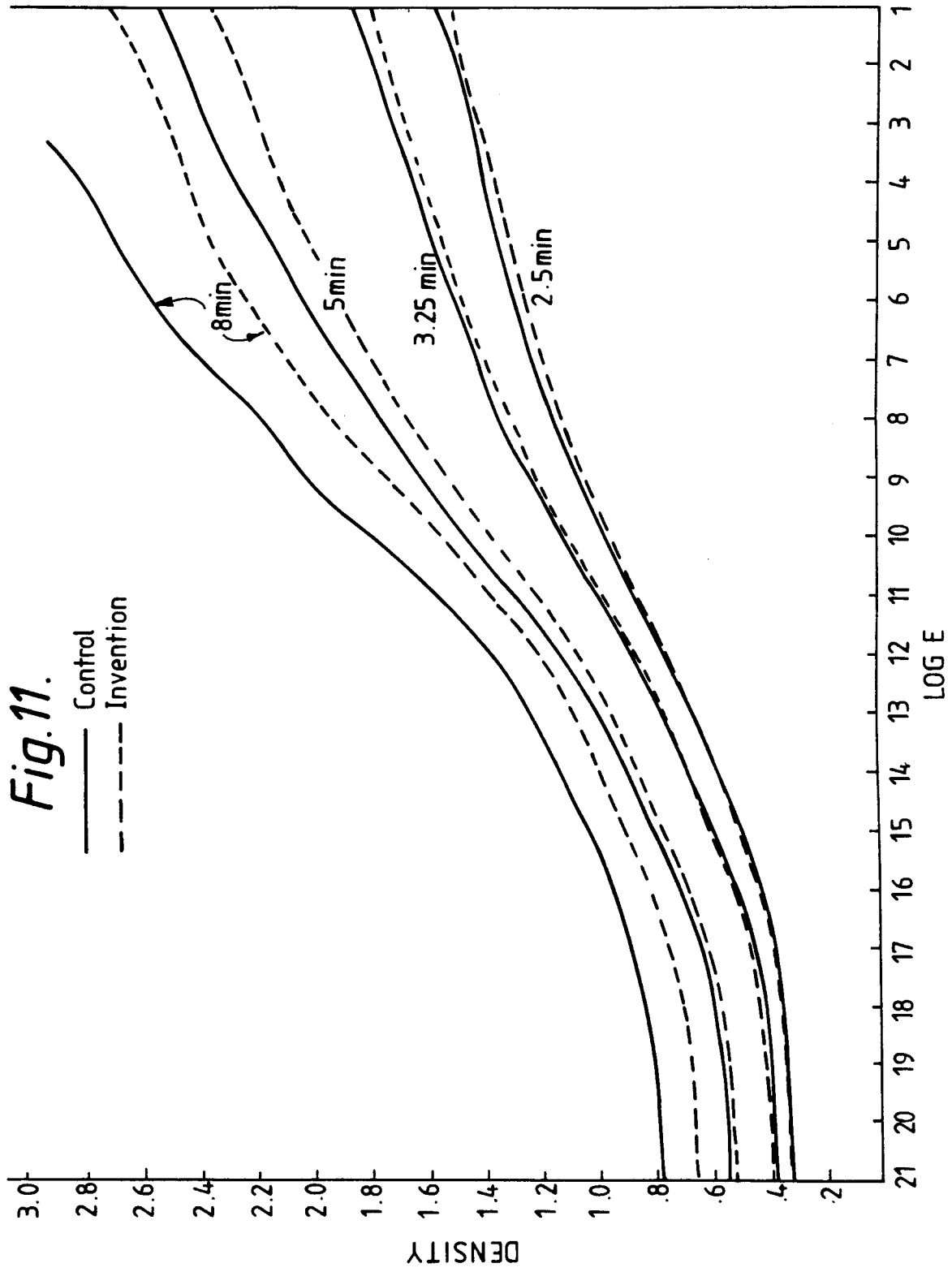
Fig. 7.

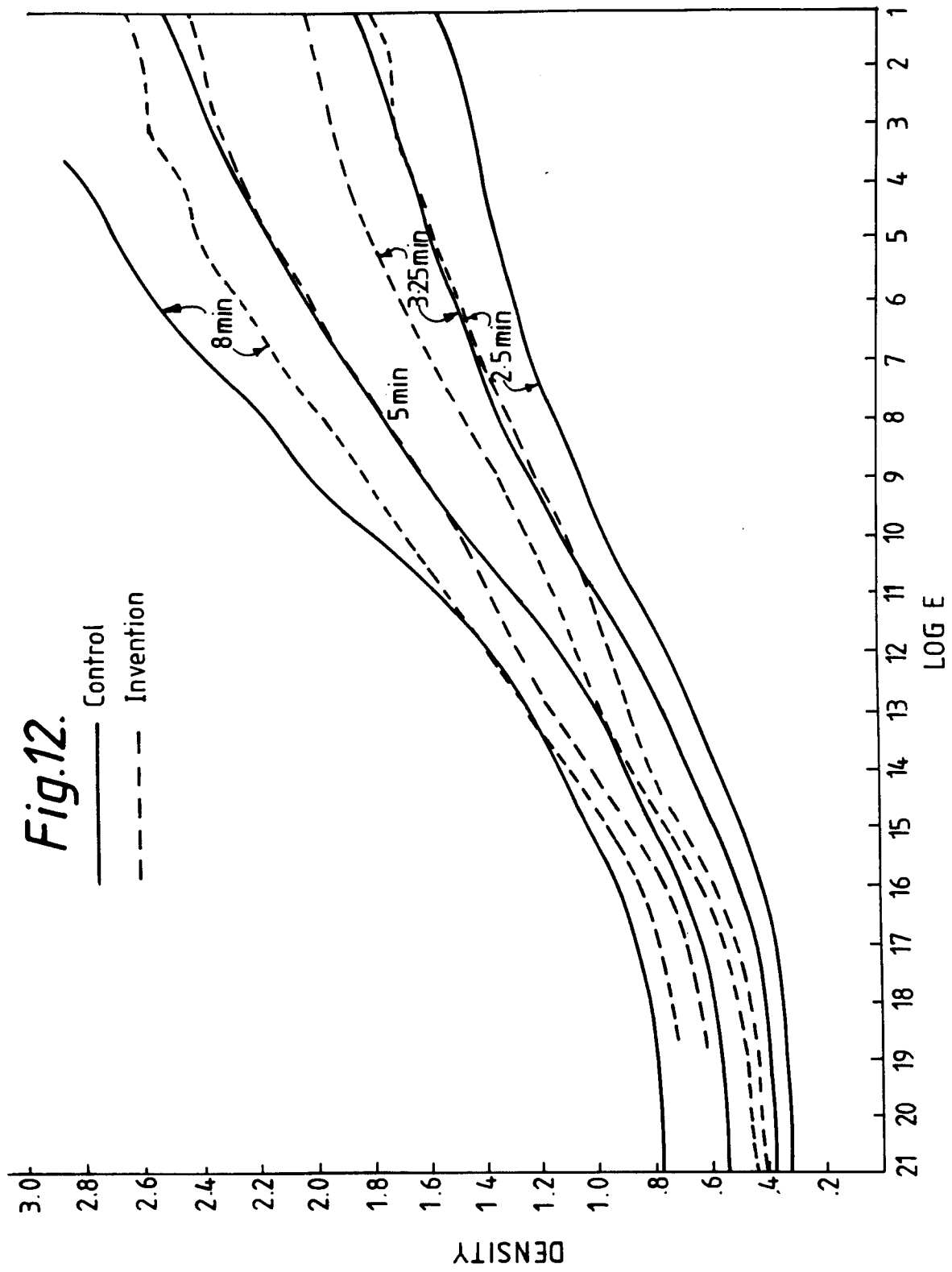


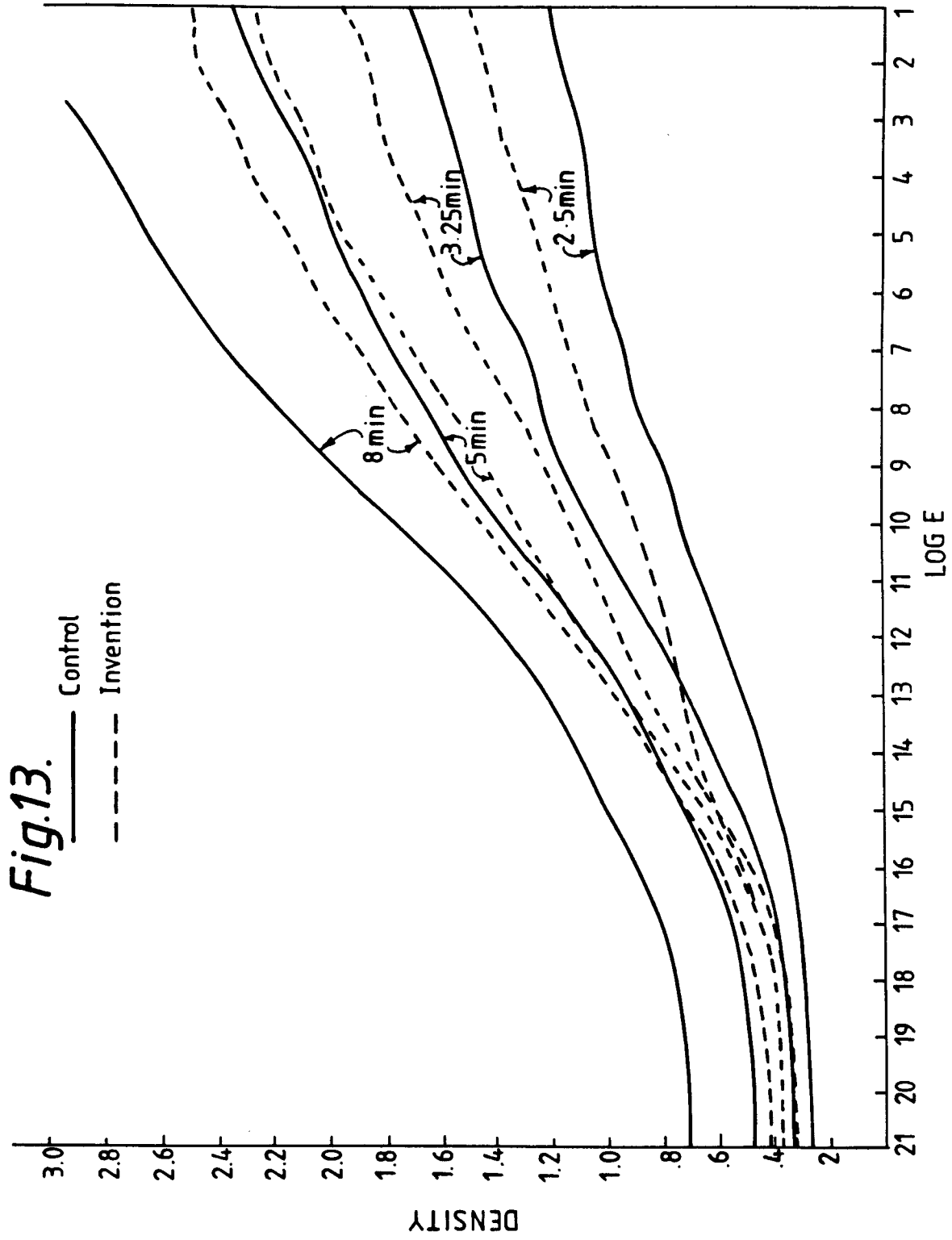














European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 95 20 1087

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.6)
X Y	WO-A-93 03419 (KODAK) * page 2, line 15 - page 3, line 14 * * page 16, line 1 - page 18, line 5; claims 1-4,6-12 * ---	1-5 6,7	G03C7/305
X Y	EP-A-0 394 974 (KODAK) * page 3, line 6 - line 54 * * page 8, line 25 - page 9, line 43; claims 1-3,6-8 * ---	1-5 6,7	
D,Y	WO-A-92 10789 (KODAK) * claims * -----	6,7	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			G03C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 24 July 1995	Examiner Magrizos, S
CATEGORY OF CITED DOCUMENTS 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			