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(54) **A method of reducing variability in sensitometry under both high and low activity conditions development of a colour photographic material**

Verfahren zur Verminderung der Variabilität von sensitometrischen Ergebnissen bei der Entwicklung eines farbphotographischen Materials unter den Bedingungen hoher oder geringer Aktivität

Procédé pour donner des résultats sensitométriques de variabilité réduite pour le développement d'un matériau photographique en couleurs dans des conditions d'activité élevée ou faible

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(56) References cited:
EP-A- 0 394 974 WO-A-92/10789
WO-A-93/03419

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Description**Field of the Invention**

[0001] This invention relates to a method of reducing variability in sensitometry under both high and low activity conditions development of photographic silver halide colour materials. Another related patent application is European publication no. 0 679 942.

Background of the Invention

[0002] Our European publication no. 0 561 860 describes a method of developing an imagewise exposed silver halide colour material to provide sensitometric results of reduced variability which comprises carrying out colour development in the presence of one or a combination of black-and-white silver halide developing agents (termed herein electron transfer agents or ETAs) incorporated in said silver halide colour material in an inactive form from which the active form is released during processing,

whereby development in low activity conditions is accelerated while that in high activity conditions is decelerated thus reducing the variability in the density versus LogE curve (the characteristic curve) caused by changes in process variables such as time, temperature, colour developing agent concentration and bromide ion concentration. Model examples having the black-and-white silver halide developing agent present in the developer solution are described.

[0003] The specification also mentions that when the black-and-white silver halide developing agent is incorporated in the photographic material it is preferably in a form which is inactive until processing takes place. For example it could be inactivated by a blocking group which is hydrolysed off when the material is immersed in the developing solution (which is usually alkaline).

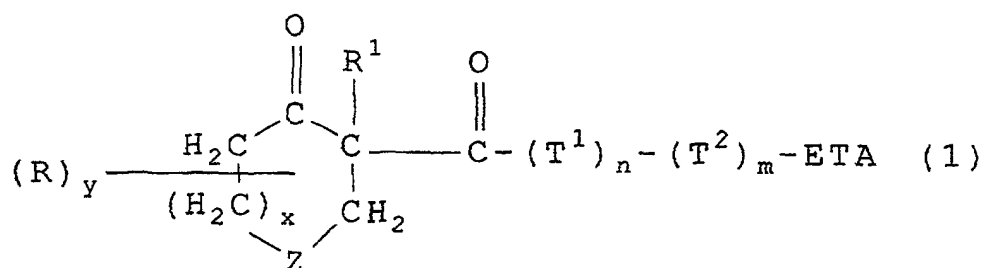
[0004] Our European publication no. 0 551 509 describes a method of processing a colour photographic silver halide material comprising a compound including a photographically useful group (PUG) and a blocking group, enabling more rapid release of the PUG upon processing.

Problem to be Solved by the Invention

[0005] The problem with known hydrolysable blocked pyrazolidinone developing agents (BETAs) is that they only unblock at the required pH if the compound is rather unstable. If the compound is stable enough not to break down in the material they do not unblock fast enough (or at all) to be useful.

Summary of the Invention

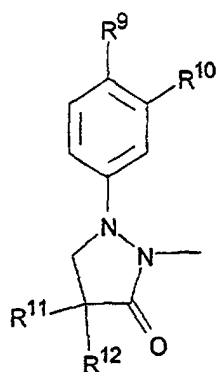
[0006] According to the present invention there is provided a method of reducing variability in sensitometry under both high and low activity conditions, wherein in high activity conditions development of a colour photographic material is decelerated and in low activity conditions development is accelerated, wherein the colour photographic material comprises 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 electron-transfer agent releasing compounds of the general formula:



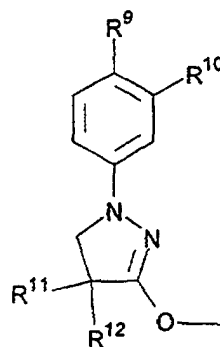
wherein

T¹ and T² individually are releasable timing groups;
n and m individually are 0 or 1, at least one of n and m being 1;

ETA is a group which is released as an electron transfer agent and has one of the formulae



(4)



(5)

or

wherein in type (1)

R^9 and R^{10} are each hydrogen or a C_{1-3} alkyl or alkoxy group or a C_{1-7} substituted alkyl or alkoxy group, R^{11} and R^{12} are each hydrogen or a C_{1-3} alkyl or hydroxyalkyl group, and wherein at least one of R^9 and R^{10} is not hydrogen except where R^{11} is an acyloxyalkyl or aryloxyalkyl group when each of R^9 and R^{10} can be hydrogen;

in type (2)

R^9 and R^{10} are each hydrogen or a C_{1-3} alkyl group and R^{11} and R^{12} are each a C_{1-3} alkyl or hydroxyalkyl group and

in type (3)

R^9 to R^{12} are each hydrogen or an unsubstituted or substituted C_{1-12} alkyl or alkoxy group, wherein the total number of carbon atoms in R^9 to R^{12} is at least 4;

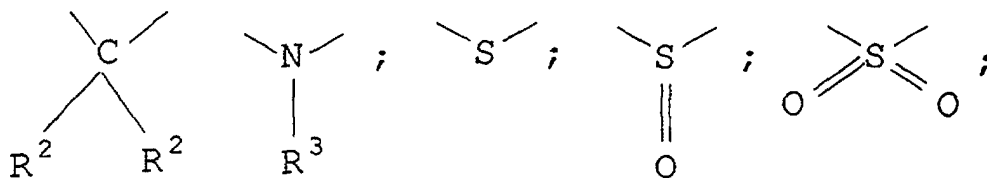
wherein the one or more compounds of formula (I) include an ETA of type (1) alone or a combination of either type (1) and type (3) or type (2) and type (3);

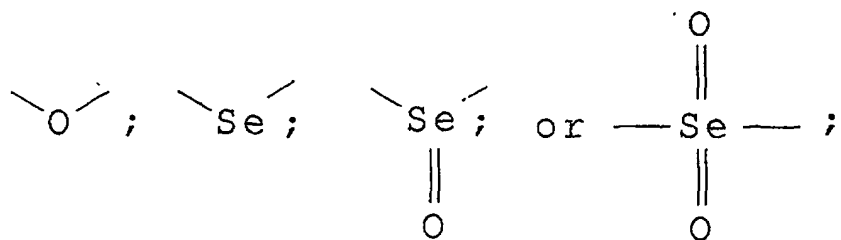
x is 0, 1 or 2;

R is substituted or unsubstituted alkyl
or aryl or a photographic ballast group replacing a ring hydrogen;
 y is 0, 1, 2, or 3;

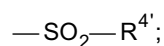
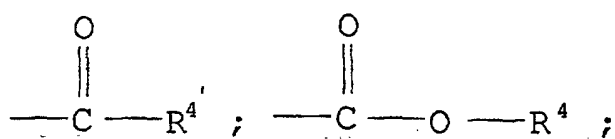
R^1 is unsubstituted or substituted alkyl;

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





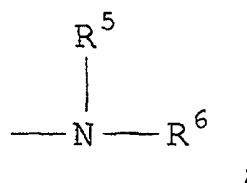
each R^2 is individually a substituted or unsubstituted alkyl, aryl or heterocyclic group, or a carbamoyl, carbonamido, sulfamoyl, sulfonamido, ester or acid group;
 R^3 is H;



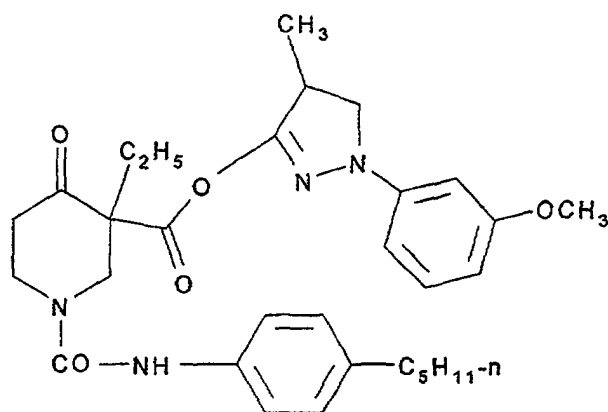
substituted or unsubstituted alkyl or aryl or a photographic ballast group;

R^4 is unsubstituted or substituted alkyl, or aryl;

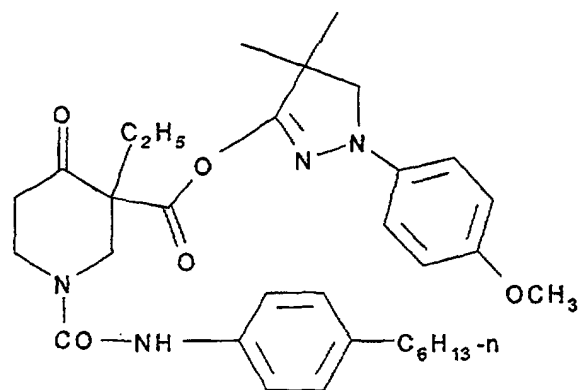
$R^{4'}$ is unsubstituted or substituted alkyl, or aryl, or



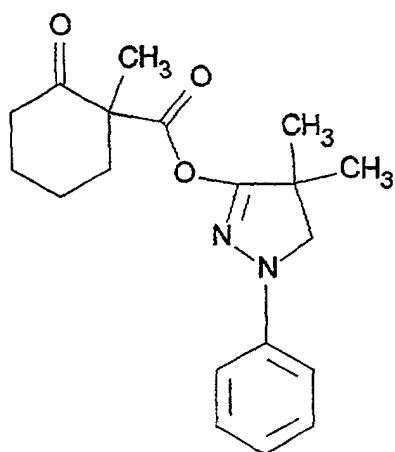
and R^5 and R^6 individually are hydrogen, or unsubstituted or substituted alkyl or aryl; or the compound has one of the structures:



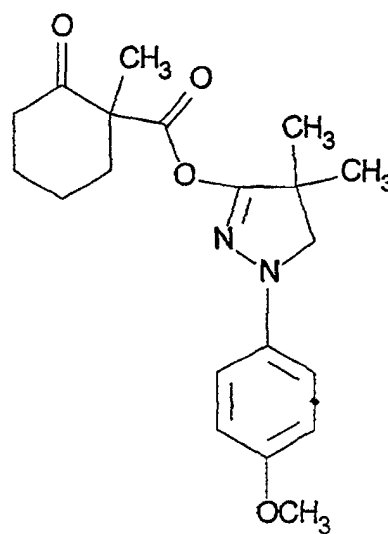
Compound 4



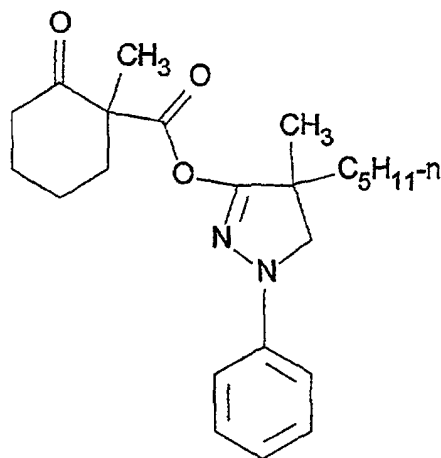
Compound 6



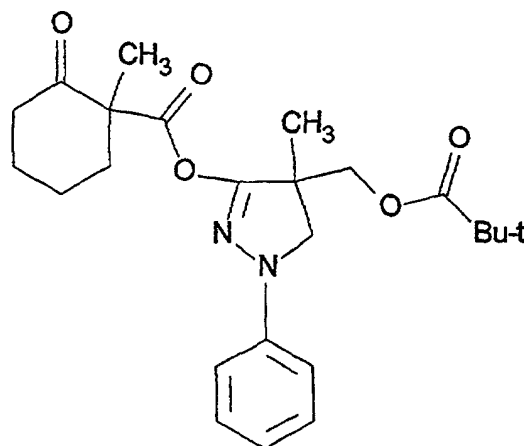
Compound 7



Compound 8



Compound 9

**Compound 10**

which process includes the step of treating the material with a photographic colour developer composition containing a binucleophile.

Advantageous Effect of the Invention

[0007] The colour photographic materials used or useful in the invention 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.

[0008] 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.

[0009] 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.

[0010] 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.

Brief Description of the Drawings

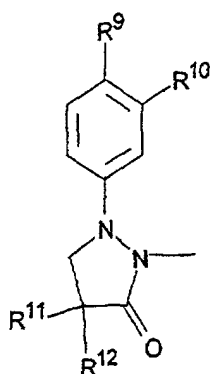
[0011] Figures 1-13 in the accompanying drawings illustrate the results of the working Examples below.

Detailed Description of the Invention

[0012] The alkyl groups represented by any of R to R⁶ may be alkyl groups having 1 to 25 carbon atoms, (C₁₋₂₅) preferably 1 to 6 carbon atoms (C₁₋₆). Of the substituted groups, the substituents may be halogen, alkyl, alkoxy, acyloxy, aroyloxy, keto, ether, ester, sulfonamido, sulfamoyl, carbonamido, or carbamoyl groups.

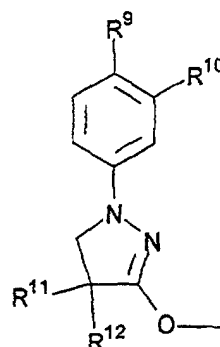
[0013] The binucleophile to be contained in the colour developer composition can, for example, be hydroxylamine, hydrogen peroxide or hydrazine, all of which may be substituted, or a salt thereof. The colour developer composition may contain a water-soluble electron-transfer agent, such as a pyrazolidinone.

[0014] The ETA groups have the general formula:



(4)

or



(5)

wherein R⁹ to R¹² are as hereinbefore defined.

[0015] As is known from European publication no. 0 561 860, there are three types of behaviour observed with different types of pyrazolidinone. The reduction of sensitivity to development time is used as an example.

[0016] Three broad types of behaviour for different ETAs 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) or Type (3) ETAs alone is not part of the present invention.

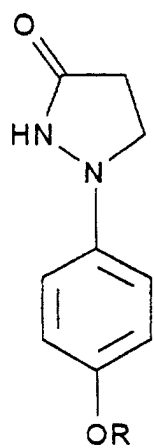
Type (1) is the preferred behaviour exhibited by the preferred compounds especially when used singly.

[0017] The present invention also includes the use of combinations of ETAs. 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.

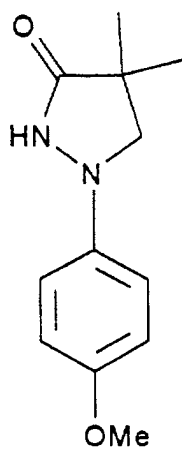
[0018] It is recognised that the definitions of the above types of ETA are not mutually exclusive. This is because it is difficult to find an appropriate definition which is mutually exclusive. Examples of the three types are given below. Beyond that the skilled worker will be able to determine to which type a particular ETA belongs by carrying out the procedures described herein.

[0019] Specific examples of the three types of ETA are as follows:

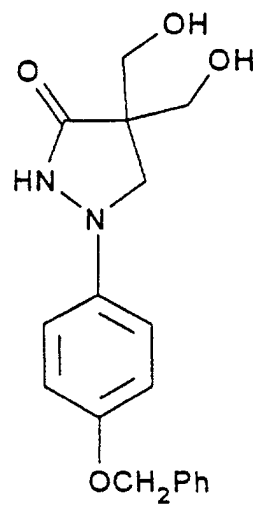
Type 1



1A R=Me



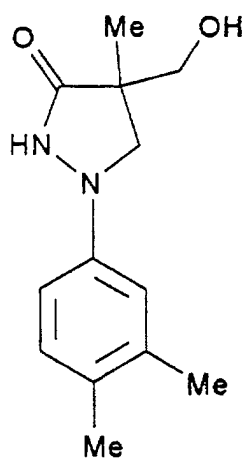
1D



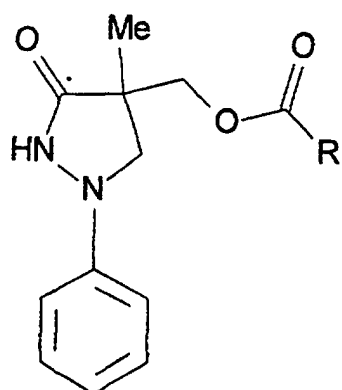
1E

1B R=Et

1C R=Propyl-n



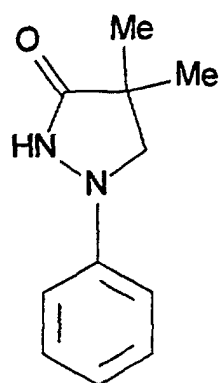
1F



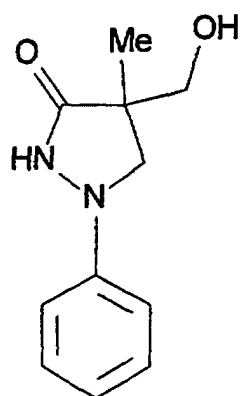
1G R=propyl-n

1H R=butyl-t

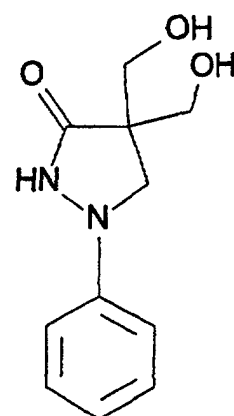
Type 2



2A

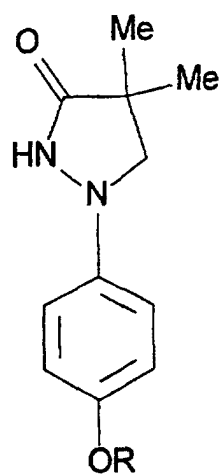
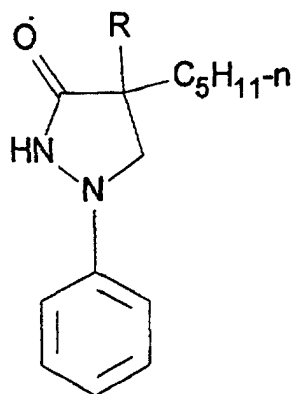
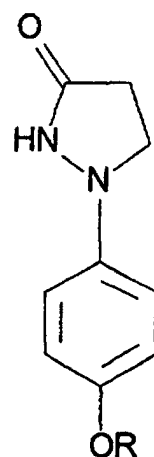


2B

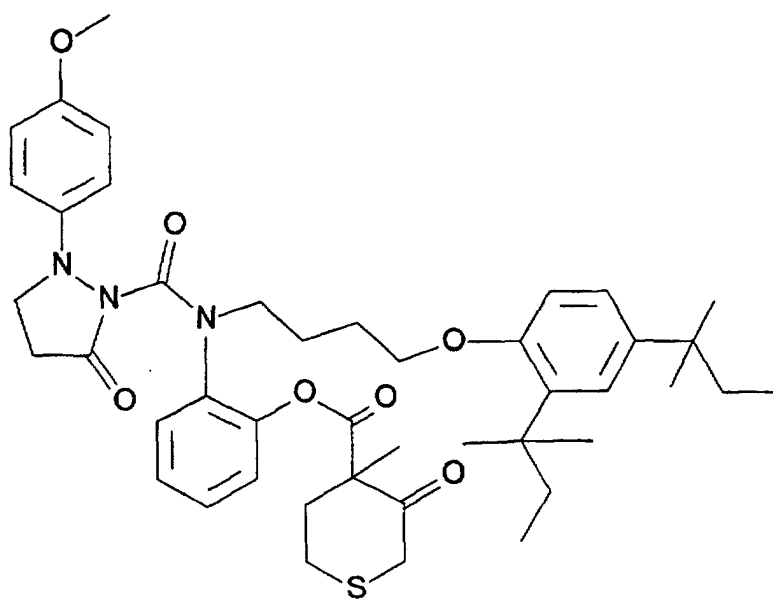


2C

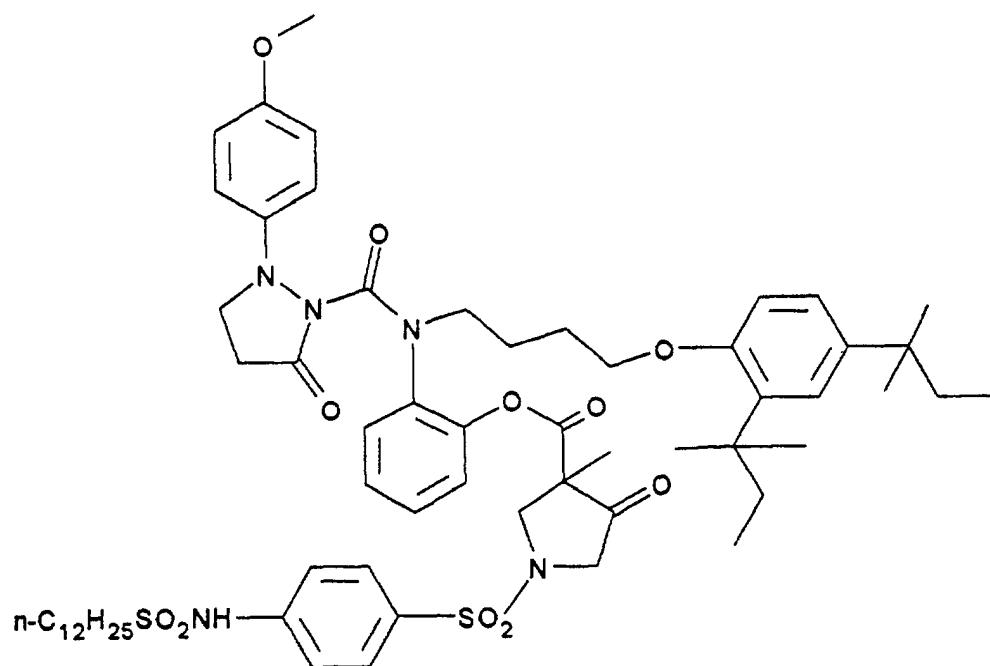
Type 3

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

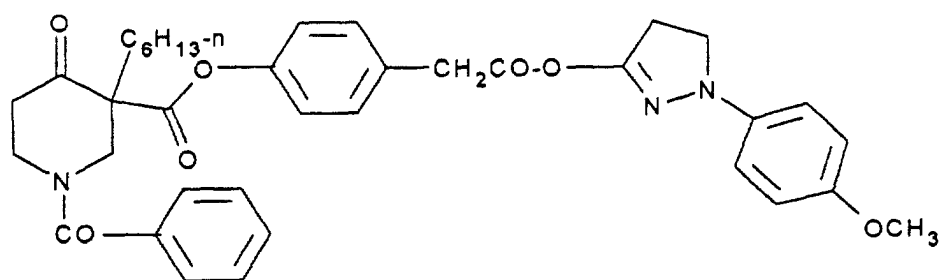
[0020] Specific examples of BETA compounds to be used in the present invention have the formulae below. They are all type (1) except where specified.



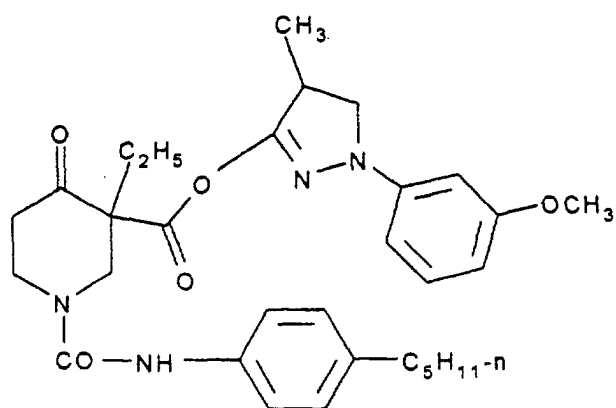
Compound 1



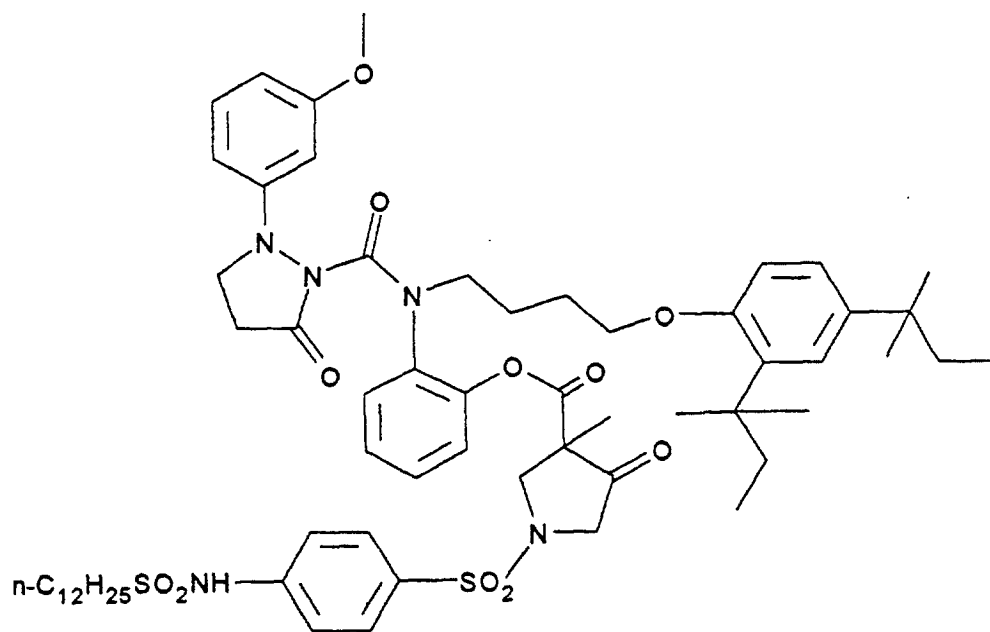
Compound 2



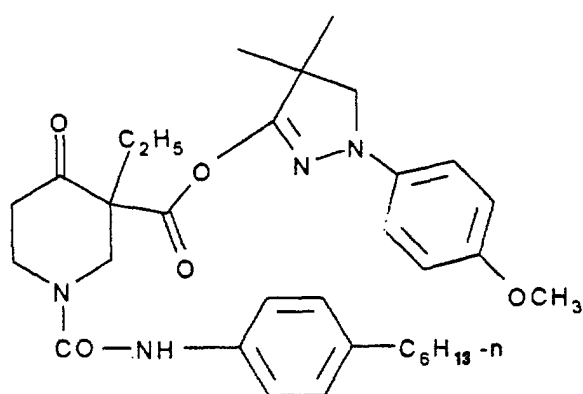
Compound 3



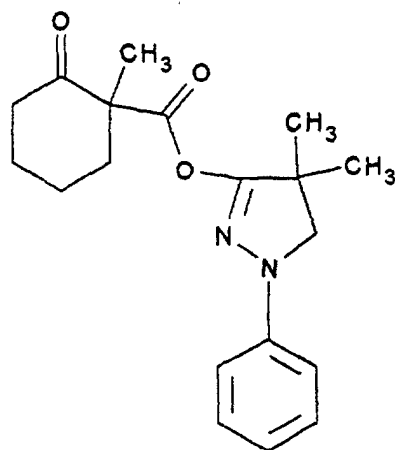
Compound 4



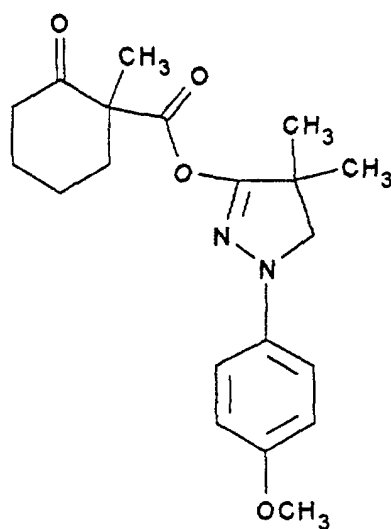
Compound 5



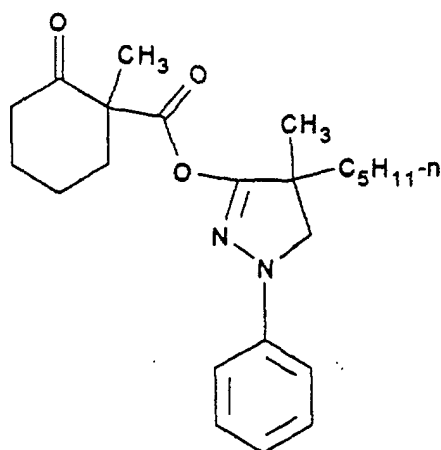
Compound 6



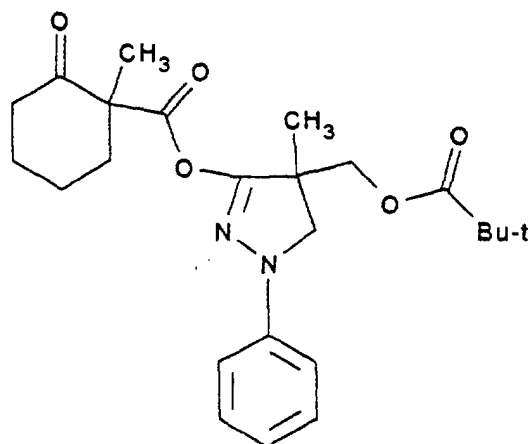
Compound 7 (type 2)



Compound 8



Compound 9 (type 3)



Compound 10

[0021] 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.

[0022] The present invention is particularly applicable to the processing of colour negative film but is also applicable to other processes, e.g. 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.

[0023] 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.

[0024] The following Examples are included for a better understanding of the invention.

EXAMPLE 1

[0025] 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.

[0026] 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/m ²)

	Coupler 1 (0.6g/m ²)
	Tabular grain silver bromiodide
	emulsion (speed=400 ASA) (1.0g/m ²)
	Gelatin(2.7g/m ²)
	Tetraazaindene (antifoggant) 30 ml/mol. Ag

	Compound 1 (0.0,0.05,0.1,0.2,0.4g/m ²)
	Gelatin(2.7g/m ²)

	Transparent Support

[0027] The BETA compound was coated in a range of levels 0.0, 0.05, 0.1, 0.2 and 0.4 g/m². The ETA released from the BETA is 4'-methoxyphenylpyrazolidinone.

EXAMPLE 2

[0028] 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

[0029] Compound 1 is designed to release the ETA 4'-methoxy-1-phenylpyrazolidinone by the action of the bi-nucleophile, 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/m²) 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/m²) 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.

EXAMPLE 4

[0030] The following multilayer structures were prepared. The figures in parentheses are coverages in g/m²:

```

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

```

where the silver halide is a bromiodide 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:

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

[0031]

a. Fig. 8 compares a control with a BETA (Compound 8) incorporated in the anti-halation layer of a multilayer at

10

15

20

25

30

35

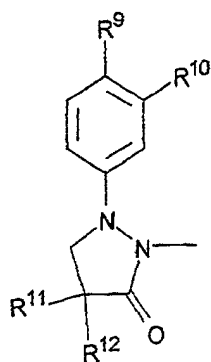
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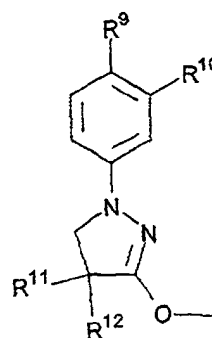
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- 55

ETA is a group which is released as an electron transfer agent and has one of the formulae:



(4)



(5)

or

wherein in type (1)

R^9 and R^{10} are each hydrogen or a C_{1-3} alkyl or alkoxy group or a C_{1-7} substituted alkyl or alkoxy group, R^{11} and R^{12} are each hydrogen or a C_{1-3} alkyl or hydroxyalkyl group, and wherein at least one of R^9 and R^{10} is not hydrogen except where R^{11} is an acyloxyalkyl or aryloxyalkyl group when each of R^9 and R^{10} can be hydrogen;

wherein in type (2)

R^9 and R^{10} are each hydrogen or a C_{1-3} alkyl group and R^{11} and R^{12} are each a C_{1-3} alkyl or hydroxyalkyl group and

in type (3)

R^9 to R^{12} are each hydrogen or an unsubstituted or substituted C_{1-12} alkyl or alkoxy group, wherein the total number of carbon atoms in R^9 to R^{12} is at least 4;

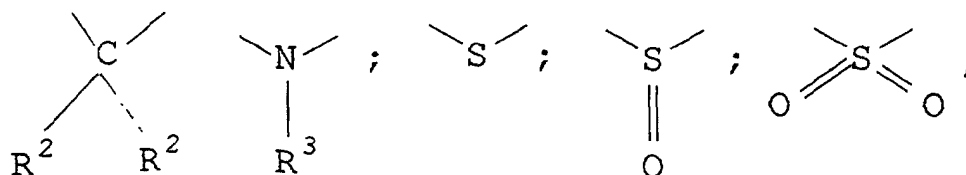
wherein the one or more compounds of formula (I) include an ETA of type (1) alone or a combination of either type (1) and type (3) or type (2) and type (3);

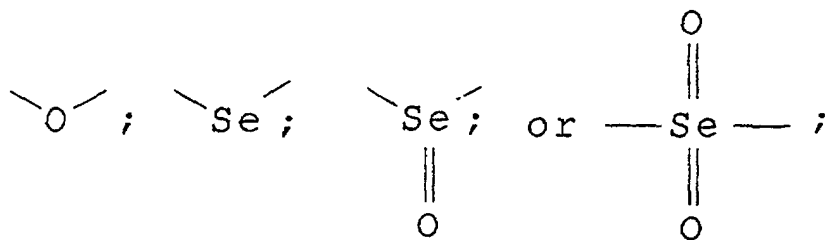
x is 0, 1 or 2;

R is substituted or unsubstituted alkyl
or aryl or a photographic ballast group replacing a ring hydrogen;
 y is 0, 1, 2, or 3;

R^1 is unsubstituted or substituted alkyl;

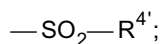
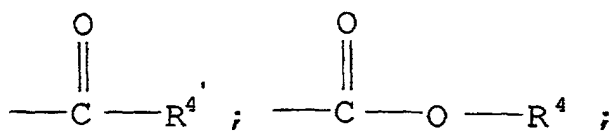
Z is located in the ring not adjacent to the ketocarbonyl group and is a group having one of the formulae:





each R^2 is individually a substituted or unsubstituted alkyl, aryl or heterocyclic group, or a carbamoyl, carbon-amido, sulfamoyl, sulfonamido, ester or acid group;

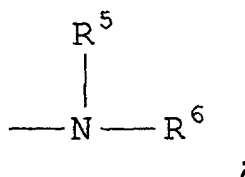
R^3 is H;



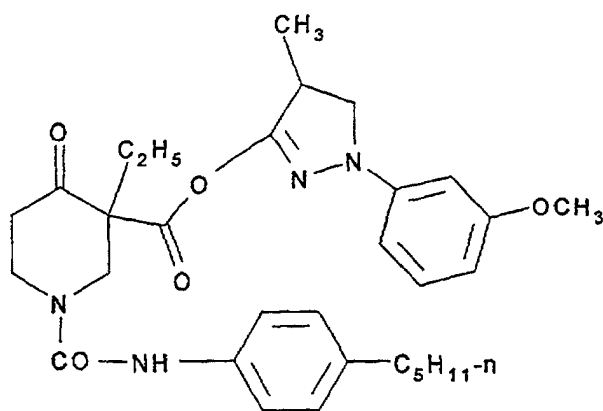
substituted or unsubstituted alkyl or aryl or a photographic ballast group;

R^4 is unsubstituted or substituted alkyl, or aryl;

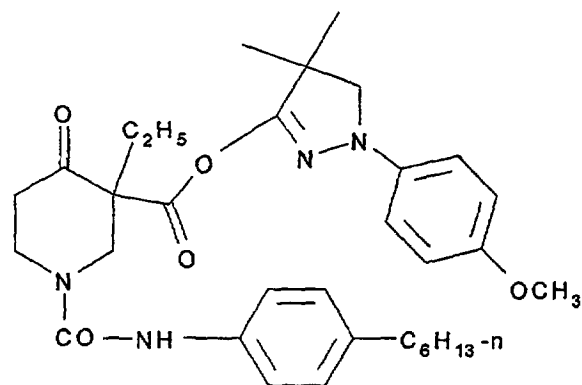
$R^{4'}$ is unsubstituted or substituted alkyl, or aryl, or



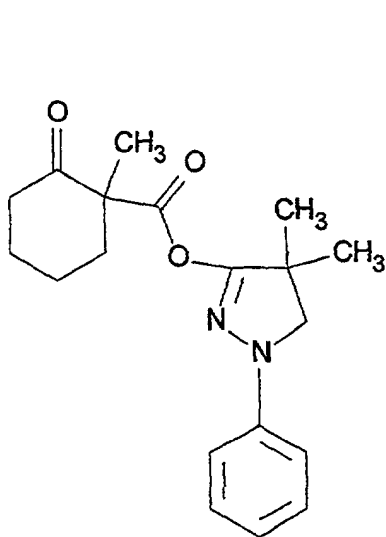
and R^5 and R^6 individually are hydrogen, or unsubstituted or substituted alkyl or aryl; or the compound has one of the structures:



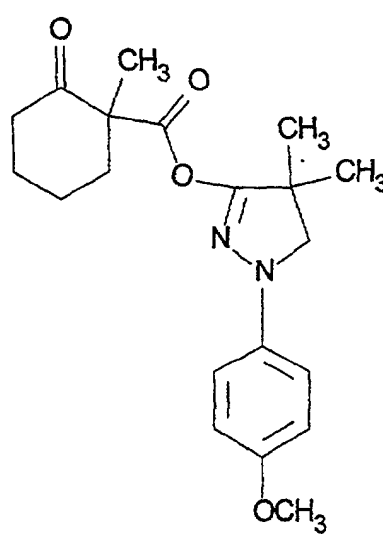
Compound 4



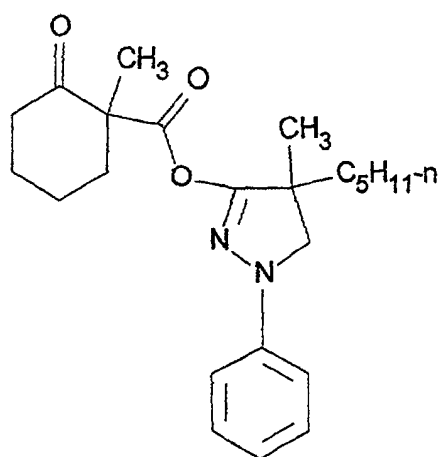
Compound 6



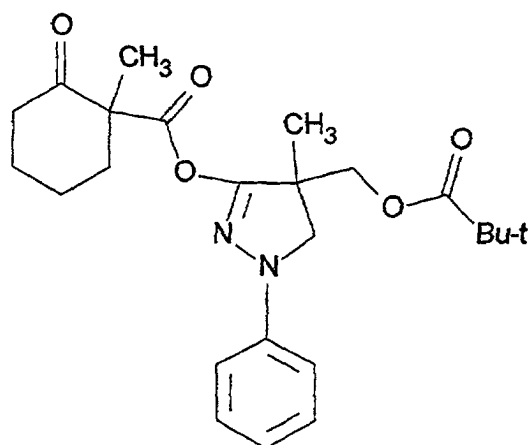
Compound 7



Compound 8



Compound 9

**Compound 10**

which process includes the step of treating the material with a photographic colour developer composition containing a binucleophile.

2. A method as claimed in claim 1 in which the compound of formula (I) has an ETA group of the general formula (4) or (5) wherein R^9 to R^{12} are as defined for type (1).
3. A method as claimed in either of the preceding claims in which the compound of formula (I) has an ETA group of general formula (4) or (5) wherein R^9 to R^{12} are as defined for type (1) and is in combination with a compound of formula (I) having an ETA group of general formula (4) or (5) wherein R^9 to R^{12} are as defined for type (3).
4. A method as claimed in claim 1 in which the compound of formula (I) has an ETA group of general formula (4) or (5) wherein R^9 to R^{12} are as defined for type (2) and is in combination with a compound of formula (I) having an ETA group of general formula (4) or (5) wherein R^9 to R^{12} are as defined for type (3).
5. A method as claimed in any of claims 1-4 in which the colour developing composition contains a water-soluble electron transfer agent.
6. A method as claimed in any of claims 1-5 in which the electron transfer agent is a pyrazolidinone.

Patentansprüche

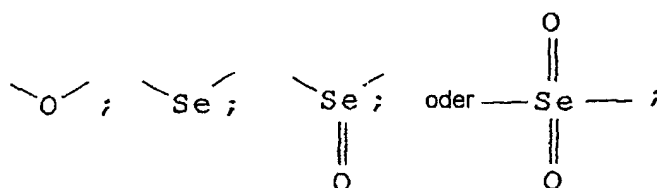
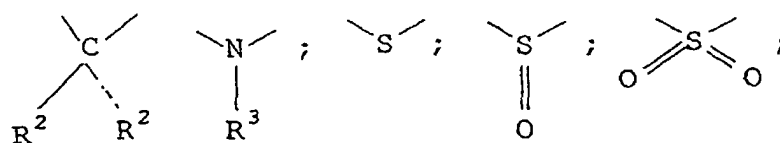
1. Verfahren zur Reduzierung von Veränderlichkeiten in der Sensitometrie unter Zuständen hoher und niedriger Aktivität, worin unter Zuständen hoher Aktivität die Entwicklung eines farbfotografischen Materials verzögert wird und unter Zuständen niedriger Aktivität die Entwicklung beschleunigt wird, worin das farbfotografische Material mindestens eine Silberhalogenid-Emulsionsschicht mit einem zugehörigen Farbstoffbild erzeugenden Kuppler umfasst, und das in einer Schicht davon ein oder mehrere Elektronenübertragungsmittel beinhaltet, die Verbindungen aus folgender allgemeiner Formel freisetzen:

R eine substituierte oder nicht substituierte Alkyl- oder Aryl- oder eine fotografische Ballastgruppe ist, die einen Ringwasserstoff ersetzt;

y ist 0, 1, 2 oder 3;

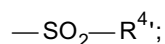
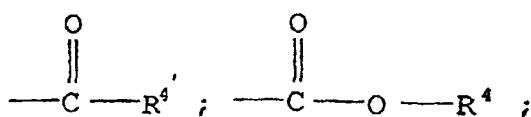
R¹ ein nicht substituiertes oder substituiertes Alkyl ist;

Z sich in dem Ring nicht benachbart zur Ketocarbonylgruppe befindet und eine Gruppe mit einer der folgenden Formeln ist:



R² jeweils eine substituierte oder nicht substituierte Alkyl-, Aryl- oder heterozyklische Gruppe oder eine Carbamoyl-, Carbonamid-, Sulfamoyl-, Sulfonamid-, Ester- oder Säuregruppe ist;

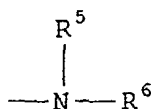
R³ ist H;



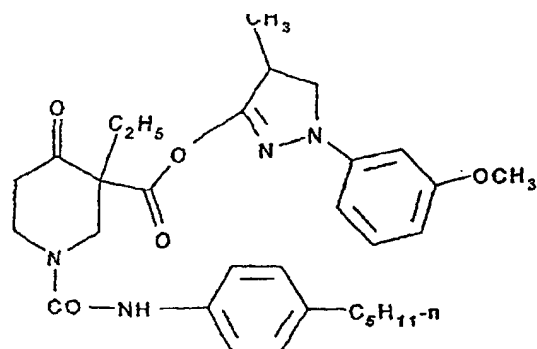
eine substituierte oder nicht substituierte Alkyl-, Aryl- oder fotografische Ballastgruppe ist;

R⁴ ein substituiertes oder nicht substituiertes Alkyl oder Aryl ist;

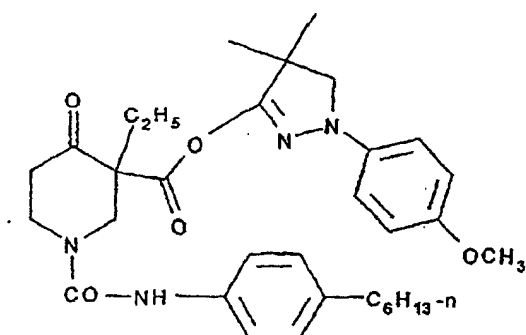
R^{4'} ein substituiertes oder nicht substituiertes Alkyl oder Aryl ist; oder



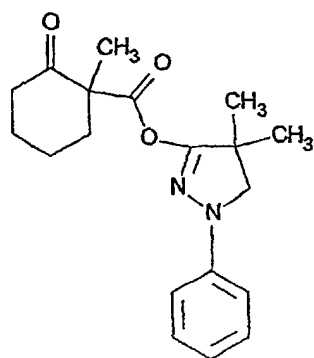
und R⁵ und R⁶ jeweils Wasserstoff oder nicht substituiertes oder substituiertes Alkyl oder Aryl sind; oder die Verbindung eine der folgenden Strukturen hat:



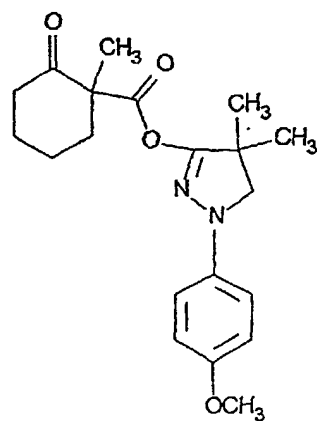
Verbindung 4



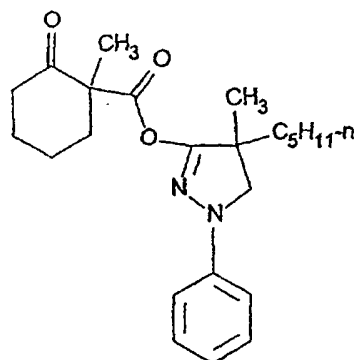
Verbindung 6



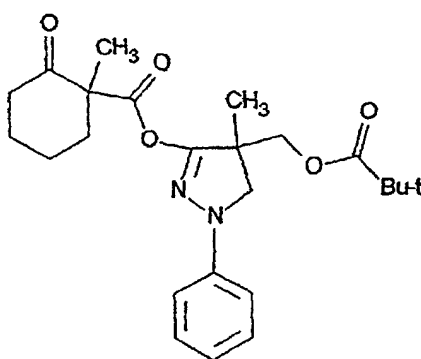
Verbindung 7



Verbindung 8



Verbindung 9



Verbindung 10

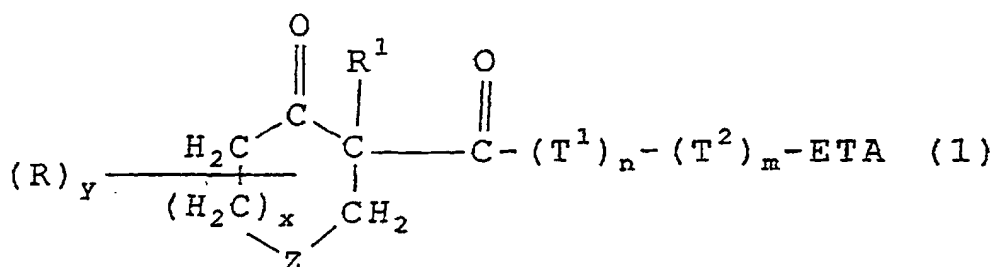
wobei das Verfahren den Schritt der Behandlung des Materials mit einer fotografischen Farbentwicklerzusammensetzung umfasst, die ein Binukleophil enthält.

2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** die Verbindung aus Formel (I) eine ETA-Gruppe der allgemeinen Formel (4) oder (5) aufweist, worin R^9 bis R^{12} wie für Typ (1) definiert sind.
3. Verfahren nach einem der vorausgehenden Ansprüche, **dadurch gekennzeichnet, dass** die Verbindung aus Formel (I) eine ETA-Gruppe der allgemeinen Formel (4) oder (5) aufweist, worin R^9 bis R^{12} wie für Typ (1) definiert sind und in Kombination mit einer Verbindung aus Formel (I) mit einer ETA-Gruppe der allgemeinen Formel (4) oder (5) ist, worin R^9 bis R^{12} wie für Typ (3) definiert sind.
4. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** die Verbindung aus Formel (I) eine ETA-Gruppe der allgemeinen Formel (4) oder (5) aufweist, worin R^9 bis R^{12} wie für Typ (2) definiert sind und in Kombination mit einer Verbindung aus Formel (I) mit einer ETA-Gruppe der allgemeinen Formel (4) oder (5) ist, worin R^9 bis R^{12} wie für Typ (3) definiert sind.
5. Verfahren nach Anspruch 1-4, **dadurch gekennzeichnet, dass** die Farbentwicklungszusammensetzung ein wasserlösliches Elektronenübertragungsmittel enthält.
6. Verfahren nach einem der Ansprüche 1-5, **dadurch gekennzeichnet, dass** das Elektronenübertragungsmittel ein Pyrazolidinon ist.

Revendications

1. Procédé de réduction de la variabilité de la sensitométrie dans des conditions d'activité élevées ou faibles, où lorsque l'activité est importante, on déccélère le développement d'un produit photographique en

couleurs et lorsque l'activité est faible, on accélère le développement, où le produit photographique en couleurs comprend au moins une couche d'émulsion aux halogénures d'argent à laquelle est associé un coupleur formateur d'image de colorant et dont l'une des couches contient un ou plusieurs composé(s) libérant un agent de transfert d'électrons de formule générale :

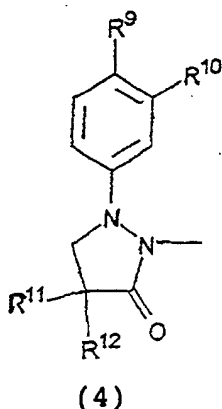


où

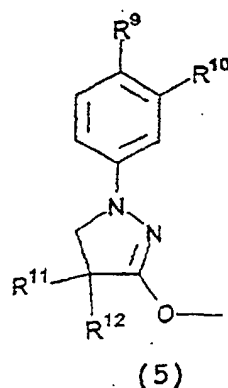
T¹ et T² représentent individuellement des groupes retardateurs pouvant être libérés ;

n et m représentent individuellement 0 ou 1, au moins l'un des nombres n et m étant égal à 1 ;

ETA est un groupe libéré comme agent de transfert d'électrons et est représenté par l'une des formules :



ou



où dans le type (1)

R⁹ et R¹⁰ sont chacun l'hydrogène ou un groupe alkyle en C₁₋₃ ou alcoxy ou un groupe alkyle substitué en C₁₋₇ ou alcoxy,

R¹¹ et R¹² sont chacun l'hydrogène ou un groupe alkyle en C₁₋₃ ou hydroxyalkyle, et où au moins l'un des groupes R⁹ et R¹⁰ n'est pas l'hydrogène, sauf lorsque R¹¹ est un groupe acyloxyalkyle ou aryloxyalkyle, lorsque chacun des groupes R⁹ et R¹⁰ peut être l'hydrogène ;

où dans le type (2)

R⁹ et R¹⁰ sont chacun l'hydrogène ou un groupe alkyle en C₁₋₃ et R¹¹ et R¹² sont chacun un groupe alkyle en C₁₋₃ ou hydroxyalkyle, et

dans le type (3)

R⁹ à R¹² sont chacun l'hydrogène ou un groupe alkyle en C₁₋₁₂ substitué ou non ou alcoxy, où le nombre total des atomes de carbone de R⁹ à R¹² est d'au moins 4 ;

où un ou plusieurs composés de formule (I) comprend(nent) un ETA de type (1) utilisé seul ou une combinaison du type (1) et du type (3) ou du type (2) et du type (3) ;

x est 0, 1 ou 2 ;

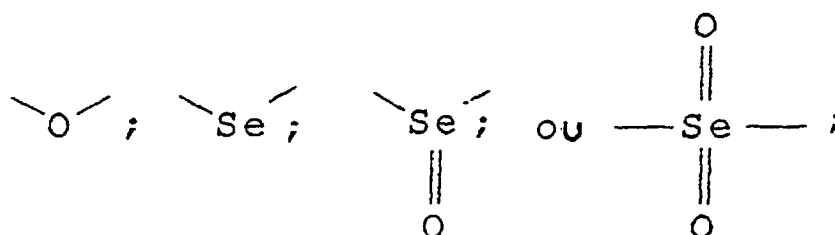
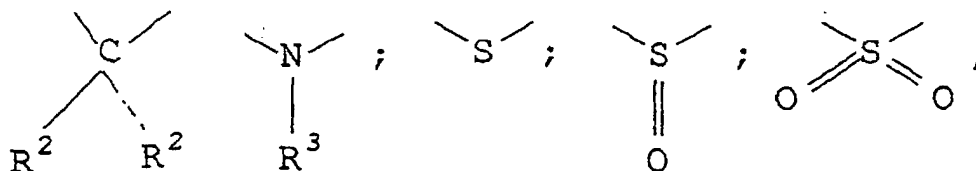
R est un groupe alkyle ou aryle substitué ou non ou encore un groupe ballast photographique remplaçant un

hydrogène cyclique ;

y est 0, 1, 2 ou 3 ;

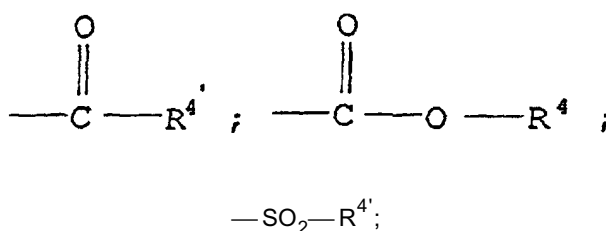
R¹ est un groupe alkyle substitué ou non ;

dans le cycle, Z n'est pas adjacent au groupe céto-carbonyle et est un groupe représenté par l'une des formules suivantes :



chaque groupe R² est individuellement un groupe alkyle, aryle ou hétérocyclique substitué ou non ou un groupe carboxyle, carbonamido, sulfamoyl, sulfonamido, ester ou acide ;

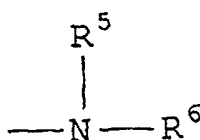
R³ est H ;



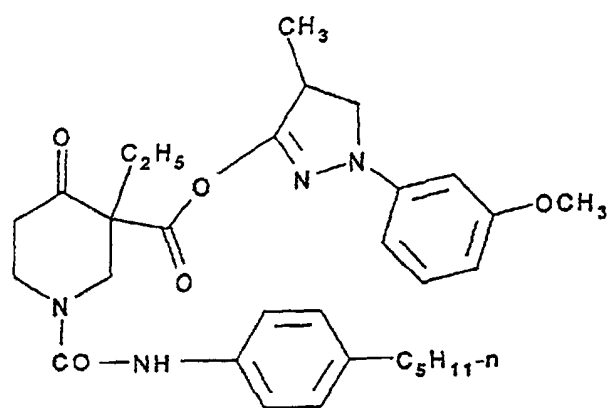
un groupe alkyle ou aryle substitué ou non ou un groupe ballast photographique ;

R⁴ est un groupe alkyle ou aryle substitué ou non ;

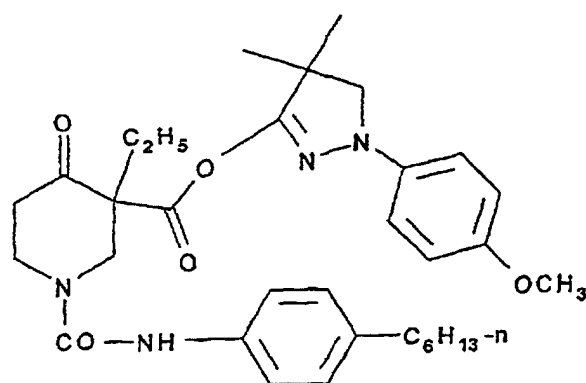
R^{4'} est un groupe alkyle ou aryle substitué ou non, ou



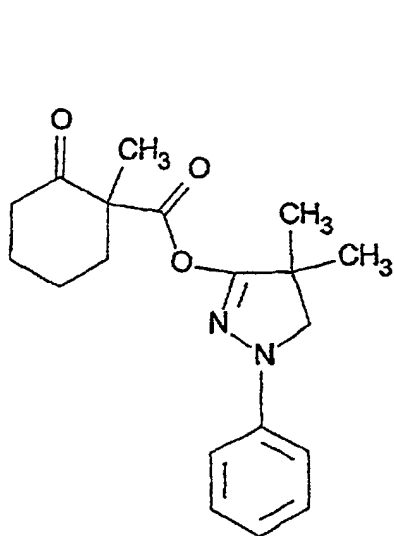
et R⁵ et R⁶ représentent individuellement l'hydrogène ou un groupe alkyle ou aryle substitué ou non ; ou le composé est représenté par l'une des structures :



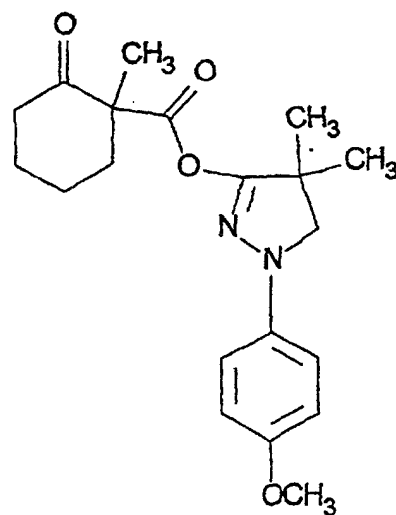
Composé 4



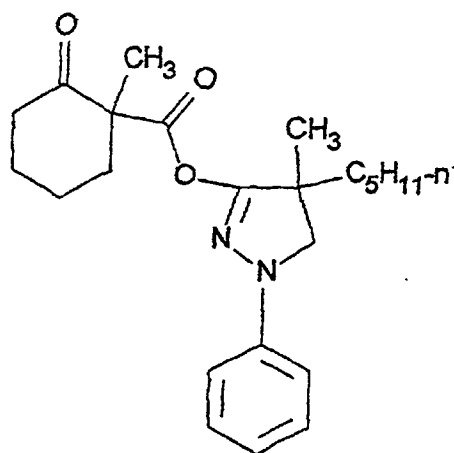
Composé 6



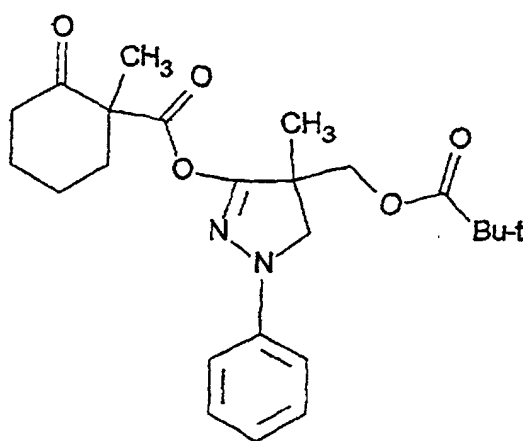
Composé 7



Composé 8



Composé 9



Composé 10

ledit procédé comprend le traitement du produit au moyen d'une composition de développement chromogène photographique contenant un binucléophile.

2. Procédé selon la revendication 1, dans lequel le composé de formule (I) comprend un groupe ETA de formule générale (4) ou (5), où R^9 à R^{12} sont tels que définis dans le type (1).
3. Procédé selon l'une quelconque des revendications précédentes, dans lequel le composé de formule (I) comprend un groupe ETA de formule générale (4) ou (5), où R^9 à R^{12} sont tels que définis dans le type (1) et est combiné à un composé de formule (I) ayant un groupe ETA de formule générale (4) ou (5), où R^9 à R^{12} sont tels que définis dans le type (3).
4. Procédé selon la revendication 1, dans lequel le composé de formule (I) comprend un groupe ETA de formule générale (4) ou (5), où R^9 à R^{12} sont tels que définis dans le type (2) et est combiné à un composé de formule (I) ayant un groupe ETA de formule générale (4) ou (5), où R^9 à R^{12} sont tels que définis dans le type (3).
5. Procédé selon l'une quelconque des revendications 1-4, dans lequel la composition de développement chromogène contient un agent de transfert d'électrons soluble dans l'eau.
6. Procédé selon l'une quelconque des revendications 1-5, dans lequel l'agent de transfert d'électrons est une pyrazolidinone.

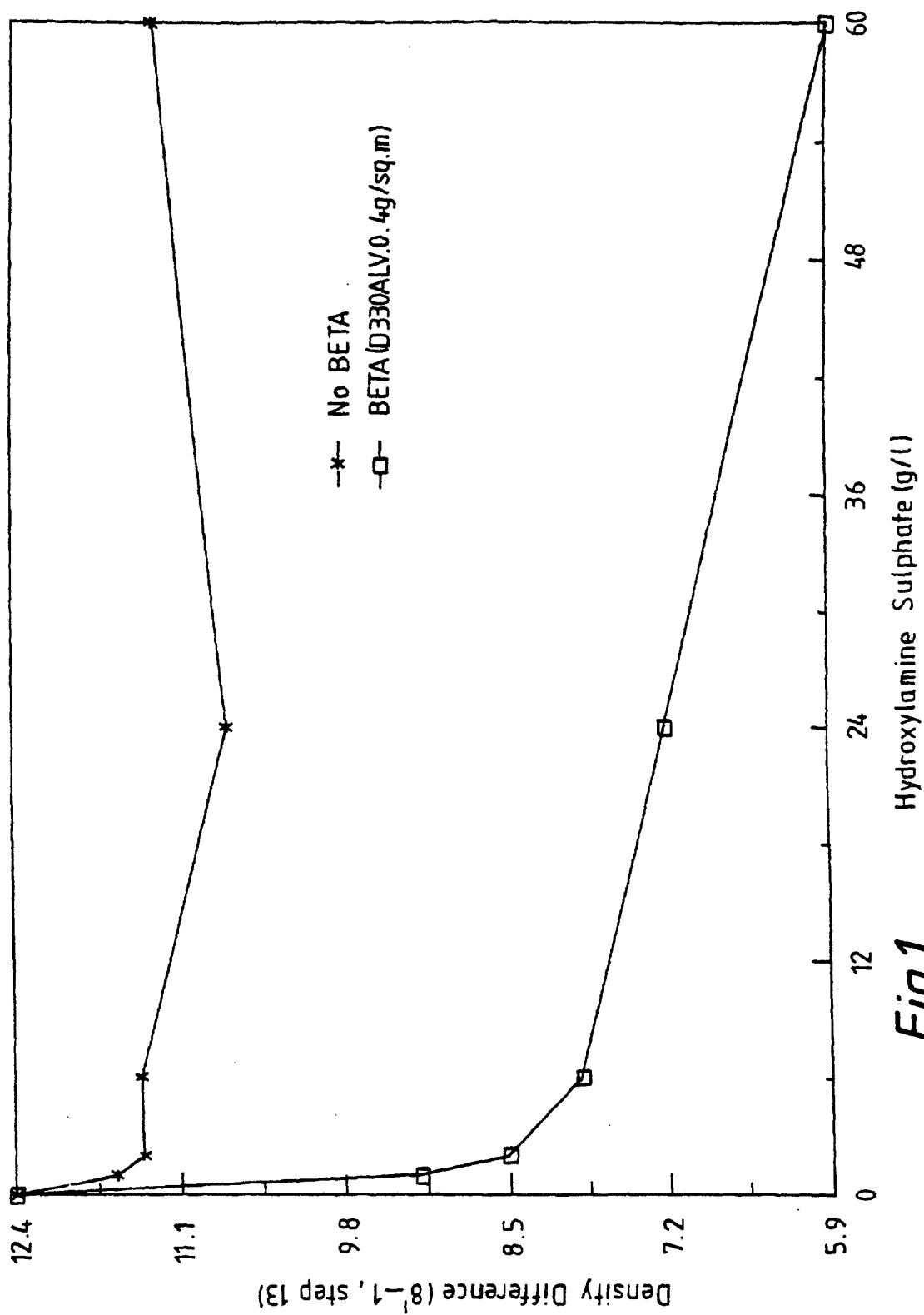
*Fig.1.*

Fig.2.

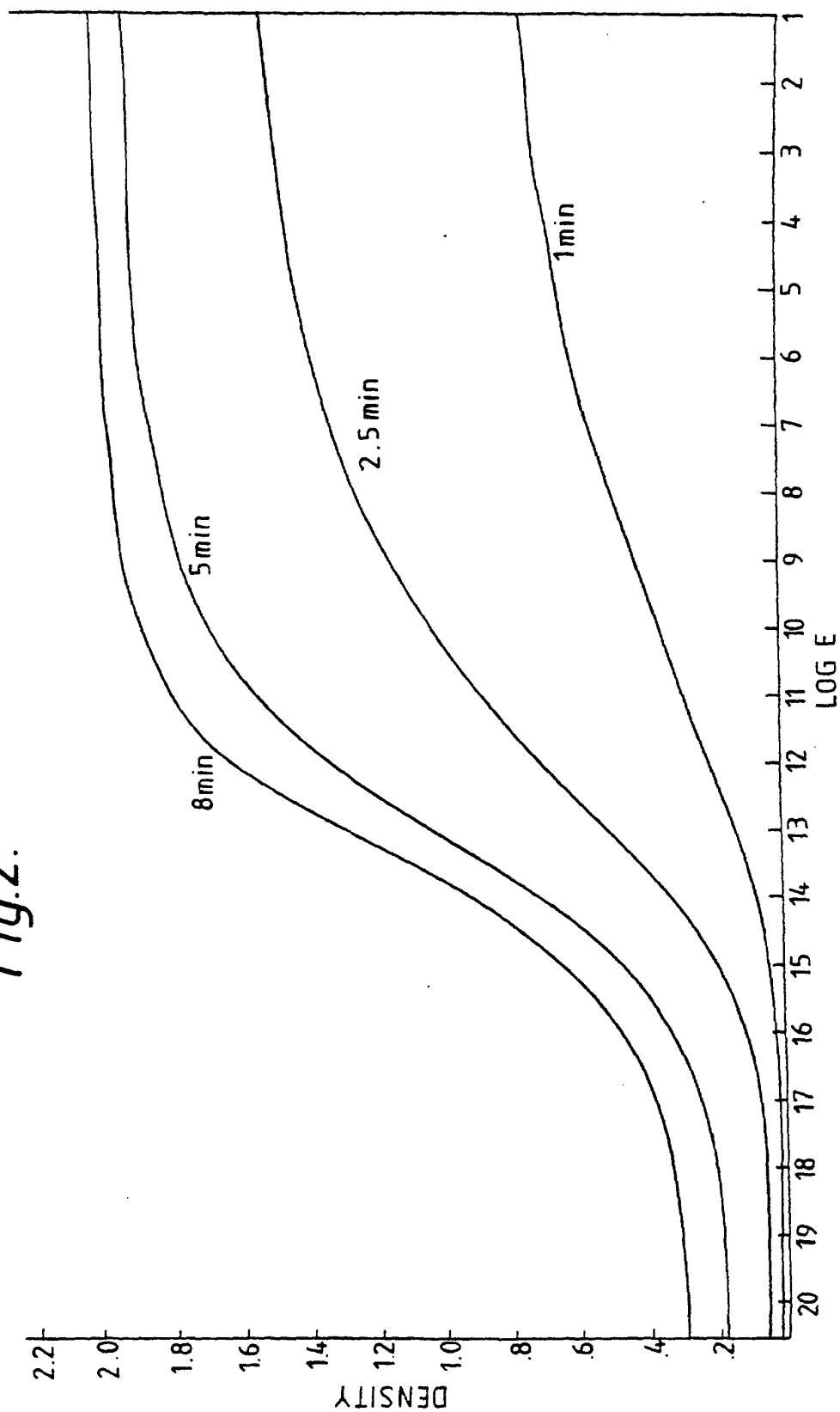
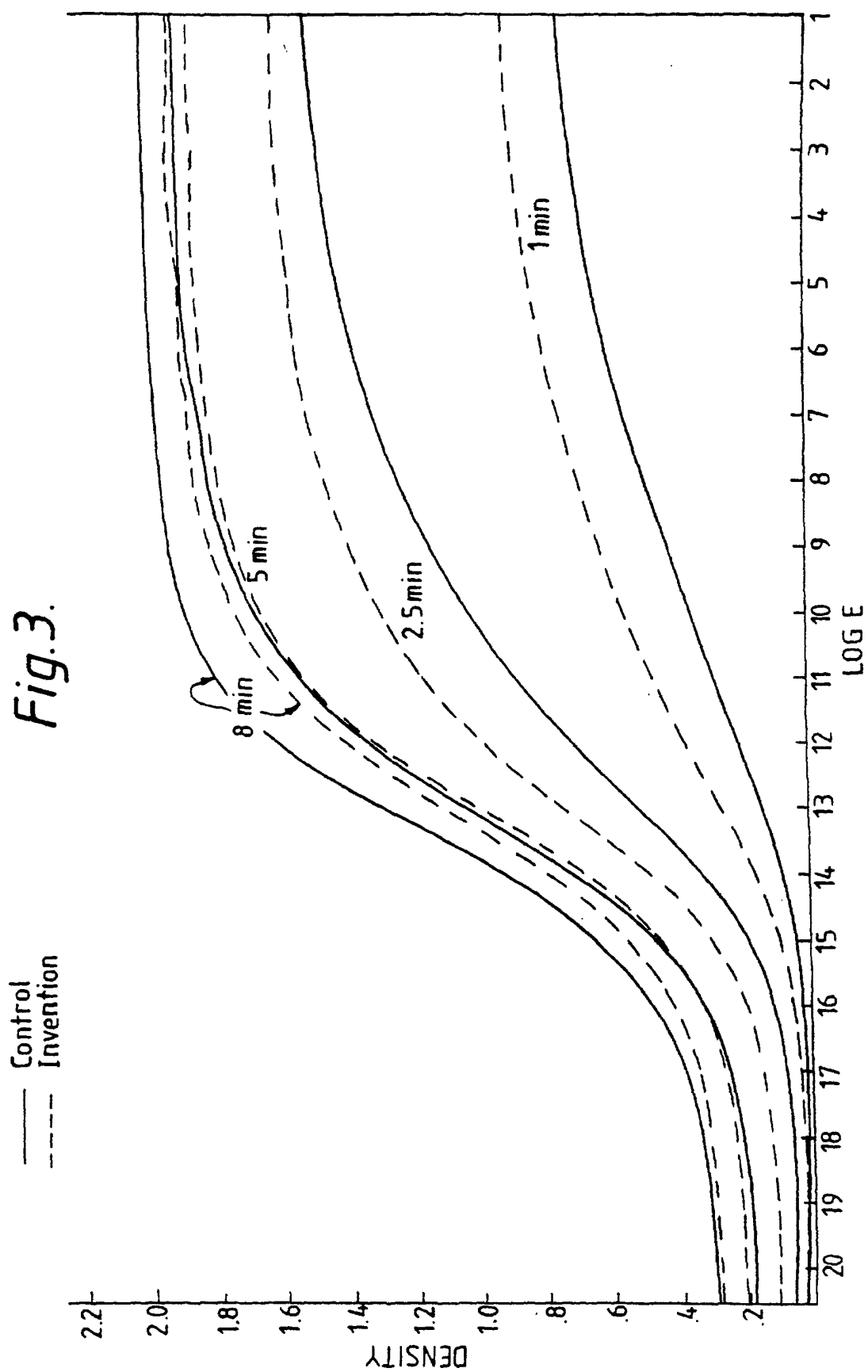


Fig. 3.



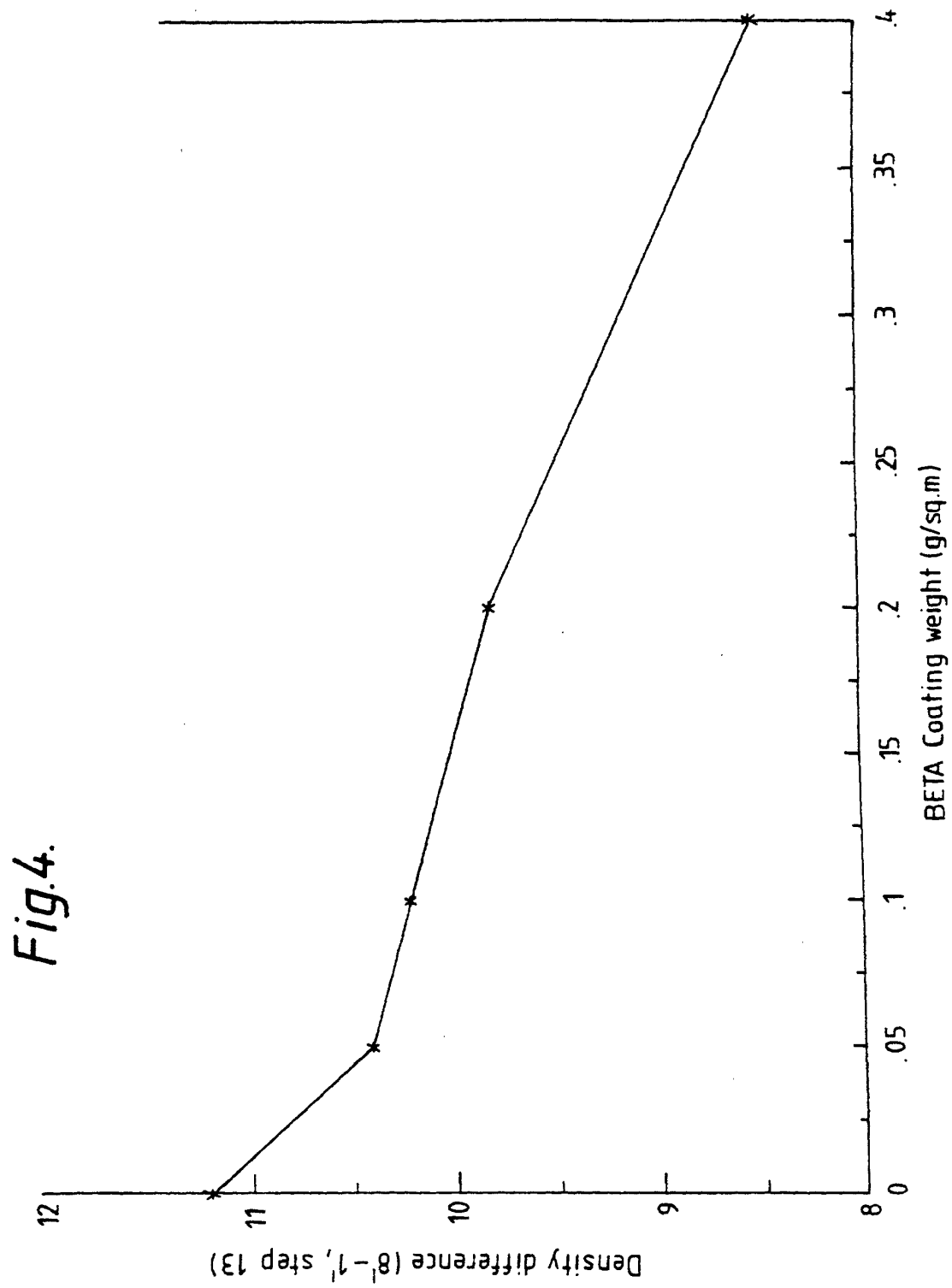


Fig.5.

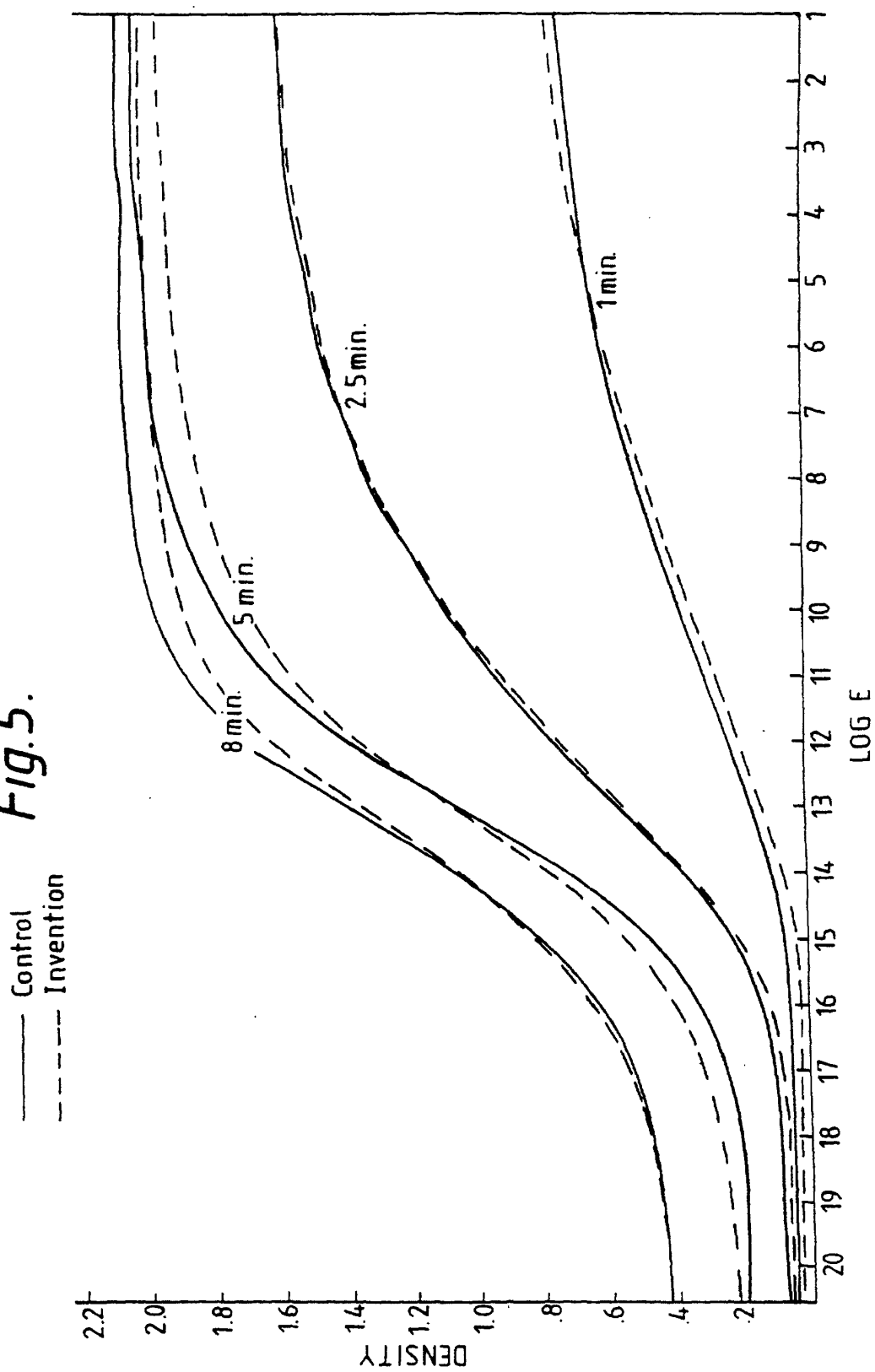


Fig. 6.

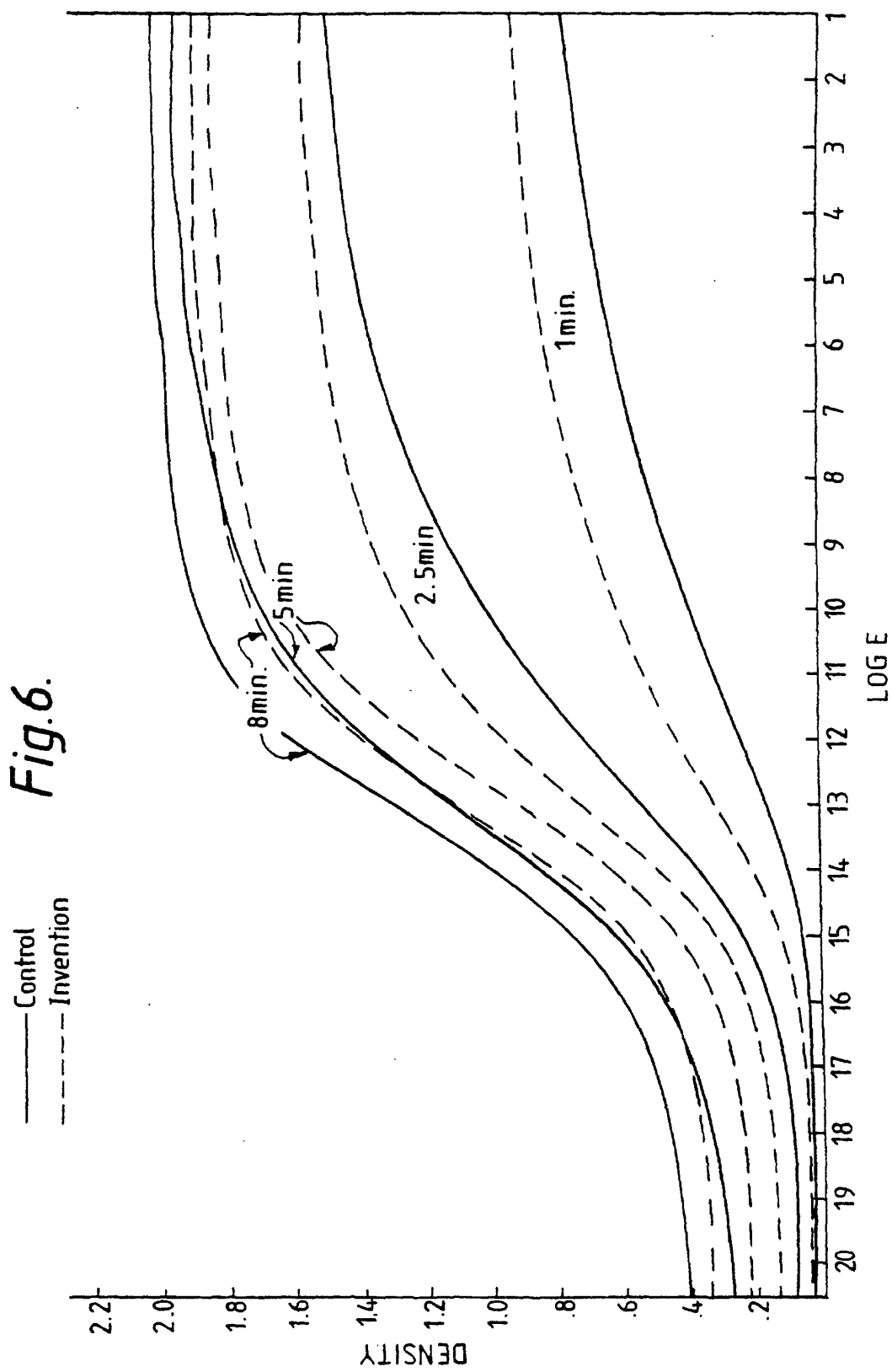


Fig. 7.

