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(54) **USE OF A SENSITIZING COMPOSITION FOR AN EXPLOSIVE**

VERWENDUNG EINER SENSIBILISIERUNGSZUSAMMENSETZUNG FÜR EINEN SPRENGSTOFF
 UTILISATION D'UNE COMPOSITION SENSIBILISANTE POUR UN EXPLOSIF

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(56) References cited:
EP-A1- 0 228 354 EP-A1- 0 775 681
WO-A1-89/02881 WO-A1-94/27933
WO-A1-97/30955 WO-A2-2008/026124
AU-B2- 598 162 GB-A- 1 262 973
GB-A- 1 344 148 GB-A- 2 096 590
US-A- 5 074 939

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EP 2 396 288 B1

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DescriptionBACKGROUND OF THE INVENTION

5 **[0001]** This invention relates generally to a sensitizing composition for use with slurry and emulsion explosives (hereinafter collectively referred to as explosives) to provide sensitization through density reduction.

[0002] The term "base emulsion" is used to refer to a water-in-oil emulsion comprising an inorganic oxidizer salt solution, for example ammonium nitrate, as a discontinuous phase and an organic fuel as a continuous phase.

10 **[0003]** A base emulsion component of an emulsion explosive typically has a density in a range 1.3 to 14 g/cc. At these densities, the base emulsion is not "cap sensitive" i.e. it is too dense, and therefore too insensitive, to be detonated to explode by the initiating shock produced by a blasting cap.

[0004] To sensitize the base emulsion, to a cap sensitive composition, a density reducing agent is added to reduce the density typically to within a range 0.9 to 1.1 g/cc.

15 **[0005]** A density reducing agent may be chemical agent for example sodium nitrite, which chemically reacts with the base emulsion to produce density reducing gas bubbles, it may be a mechanical agent, such as a hollow or solid microsphere, or it may be a combination of a chemical and a mechanical agent.

[0006] An example of the microspheres used in a density reducing context is isobutane plastic enclosed micro-balloons, each with a particle diameter in a range 10-150 μm .

20 **[0007]** Microspheres provide an advantage, over gas bubbles created by a chemical agent, in that they do not coalesce to reduce the sensitivity of the emulsion, and their density reducing effect can be more accurately predicted due to their relatively regular unit dimensions. However this advantage is somewhat mitigated by handling difficulties, due to their small particulate size. Consequently, the microspheres easily can become airborne, creating a dust problem, exacerbated in an underground location, and a respiratory irritant.

[0008] The invention at least partially addresses the aforementioned problems.

SUMMARY OF INVENTION

30 **[0009]** The terms "surfactant" and "emulsifier" (hereinafter the terms are used interchangeably) are used to describe an organic compound that exhibits an amphiphilic characteristic, meaning it has both hydrophobic and hydrophilic properties, which enables a surfactant compound to interface between a hydrophobic organic compound and an aqueous solution to form an emulsion.

35 **[0010]** The invention provides the use of a sensitizing composition to sensitize a base emulsion which includes a carrier emulsion, of a liquid non-polar organic fuel, a surfactant and an aqueous solution, and a plurality of microspheres suspended in the carrier emulsion. Sensitizing compositions using gassing agents are known from WO 2008/026124 and WO 89/02881.

[0011] The organic fuel may a mineral oil, a vegetable oil or a wax.

[0012] The surfactant may be any suitable surfactant, for example an SMO (sorbitan mono oleate) or PIBSA (polyisobutylene succinic anhydride) based surfactant.

40 **[0013]** The aqueous solution may include one or more compounds selected from a group of inorganic salts consisting of ammonium, alkali and alkaline earth metal nitrates, chlorates and perchlorates and a group of organic compounds consisting of organic nitrates, for example MMAN (monomethyl ammonium nitrate), and organic chlorides.

[0014] The aqueous solution may contain at least calcium nitrate. Preferably the aqueous solution is a solution of calcium nitrate and a perchlorate salt, for example sodium perchlorate.

45 **[0015]** The sensitizing composition may contain the following components in the following concentration ranges:

- | | | |
|-----|--|----------------------|
| (a) | calcium nitrate: | 40 - 80 % (m/m); |
| (b) | water: | 15 - 45 % (m/m); and |
| (c) | the carrier emulsion and the surfactant: | 4 - 20% (m/m). |

50 **[0016]** The microspheres may be either solid, for example polystyrene spheres or beads of vermiculite, or hollow, for example gas filled micro-balloons of glass, plastic, a resinous material or a carbonaceous material. Preferably, the microspheres are isobutane filled plastic micro-balloons of the type manufactured by Akzo Nobel.

[0017] The microspheres may be present in the sensitizing composition in a range 0.5% - 10%. Preferably the range is 1% - 4% (m/m). More preferably 2% (m/m) of the sensitizing composition comprises microspheres.

55 **[0018]** The average diameter of the microspheres may be in a range 20-160 μm . Preferably the range is 60-80 μm .

[0019] The density of the sensitizer composition may be in a range 0.3 to 1.05 g/cc.

[0020] Optionally, the sensitizing composition may include a chemical gassing agent, for example sodium nitrite, to

provide gas bubbles in the composition which are functionally supplementary to the microspheres.

[0021] The invention further provides a method of producing an explosive composition which includes the steps of:

- (a) providing a base emulsion;
- (b) providing a sensitizing composition which includes a carrier emulsion, of a liquid non-polar organic fuel, a surfactant and an aqueous solution, and a plurality of microspheres suspended in the carrier emulsion; and
- (c) mixing the base emulsion with the sensitizing composition in a respective mass ratio in the range 90:10 to 50:50 to form the explosive composition.

[0022] The term "explosive composition" is used hereinafter to refer to a composition which has been diluted to within a density range of 0.4 - 1.35 g/cc, and thus is sensitized to detonate when initiated, either by booster or cap initiation.

[0023] The base emulsion may have a density above 1.28 g/cc.

[0024] Preferably, the mass ratio of base emulsion to sensitizing composition is 80:20.

[0025] The organic fuel of the base emulsion and the organic fuel of the sensitizing composition may be the same.

[0026] Preferably, the inorganic oxidizer salt solution of the base emulsion includes ammonium nitrate (AN) whilst the aqueous solution of the sensitizing composition includes at least one salt or compound from the following: an ammonium, alkali or alkali earth metal nitrate, chlorate or perchlorate, an organic nitrate and an organic chloride.

[0027] Preferably the aqueous solution includes calcium nitrate. AN may be excluded from the aqueous solution to render the solution thermodynamically stable relatively to the base emulsion.

BRIEF DESCRIPTION OF THE DRAWING

[0028] The invention is further described by way of example with reference to the accompanying drawing which schematically illustrates the process steps in the production of an explosive mixture from the combination of a base emulsion and a sensitizing composition which is in accordance with the present invention.

DESCRIPTION OF PREFERRED EMBODIMENT

[0029] With reference to. Figure 1, an explosive mixture 10 is produced from the combination of a base emulsion 12 and a sensitizing composition 14 which is in accordance with the present invention.

[0030] The base emulsion 12, as hereinabove generally defined, can be any inorganic oxidizer salt solution 16 and organic fuel 18 combination, with a density in a range 1.3 to 1.4 g/cc, emulsified with a suitable emulsifier 20.

[0031] The sensitizing composition 14 comprises a carrier emulsion 22 of a fuel phase 24 and an aqueous phase 26 to which is added the plastic or glass micro-balloons 28.

[0032] The fuel phase 24 is a mixture of an organic hydrocarbon fuel 30, for example a mineral oil, and surfactant 32 such as PIBSA and/or SMO.

[0033] The aqueous phase 26 is an aqueous solution of calcium nitrate. Optionally, another oxidizer salt for example sodium perchlorate, can be included in the aqueous solution.

[0034] The sensitizing composition 14 contains the following components in the following concentrations:

- (a) calcium nitrate: 64 % (m/m);
- (b) water: 20 % (m/m);
- (c) the fuel phase: 14 % (m/m); and
- (d) micro-balloons: 2% (m/m).

[0035] The sensitizing composition 14 is mixed with the base emulsion 12, in situ, in the mass ratio (sensitizing composition to base emulsion) of 20:80, to produce the explosive mixture which has a density within the range 0.9 to 1.1 g/cc.

Claims

1. Use of a composition in the form of an emulsion containing the following components in the following concentration ranges

- (a) calcium nitrate: 40 - 80 % (m/m);

EP 2 396 288 B1

(continued)

- (b) waster: 15 - 45 % (m/m);
(c) a liquid non-polar organic fuel and a surfactant: 4 - 20% (m/m);
(d) microspheres: 0,5-10% (m/m);

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(a) and (b) being present as an aqueous solution and having a density in a range 0.3 to 1.05 g/cc as a sensitizing composition to sensitize a base emulsion comprising a water-in-oil emulsion comprising an inorganic oxidizer salt solution as a discontinuous phase and an organic fuel as a continuous phase.

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2. Use according to claim 1, wherein the organic fuel is a mineral oil, a vegetable oil or a wax.
3. Use according to claim 1 or 2, wherein the surfactant is a sorbitan mono oleate (SMO) or polyisobutylene succinic anhydride (PIBSA) based surfactant.
4. Use according to any one of claims 1 to 3 wherein the aqueous solution includes, in addition to calcium nitrate, one or more compounds selected from a group of inorganic salts consisting of ammonium, alkali and alkaline earth metal nitrates, chlorates and perchlorates and a group of organic compounds consisting of organic nitrates and organic chlorides.
5. Use according to claim 4, wherein the aqueous solution includes a solution of calcium nitrate and a perchlorate salt.
6. Use according to any one of claims 1 to 5, wherein the microspheres are either solid or hollow.
7. Use according to claim 6, wherein the solid microspheres are polystyrene spheres or beads of vermiculite.
8. Use according to claim 6, wherein the hollow microspheres are gas-filled micro-balloons of glass, plastic, or a resinous or carbonaceous material.
9. Use according to claim 8, wherein the microspheres are isobutane filled plastic micro-balloons.
10. Use according to any one of claims 1 to 9, wherein the average diameter of the microspheres is in a range 20-160 μ m.
11. A method of producing an explosive composition which includes the steps of:
 - (a) providing a base emulsion;
 - (b) providing a sensitizing composition according to anyone of claims 1 to 10; and
 - (c) mixing the base emulsion with the sensitizing composition in a respective mass ratio in the range 90:10 to 50:50 to form the explosive composition.
12. A method according to claim 11, wherein the base emulsion has a density above 1.28 g/cc.
13. A method according to claim 11 or 12, wherein the mass ratio of base emulsion to sensitizing composition is 80:20.
14. A method according to any of claims 11 to 13, wherein the base emulsion includes ammonium nitrate (AN) and the aqueous solution of the sensitizing composition includes calcium nitrate.

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Patentansprüche

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1. Verwendung einer Zusammensetzung in Form einer Emulsion, die die folgenden Komponenten in den folgenden Konzentrationsbereichen enthält:
 - (a) Calciumnitrat: 40-80 % (m/m),
 - (b) Wasser: 15-45 % (m/m),
 - (c) einen flüssigen unpolaren organischen Brennstoff und einen oberflächenaktiven Stoff: 4-20 % (m/m),
 - (d) Mikrosphären: 0,5-10% (m/m),

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EP 2 396 288 B1

wobei (a) und (b) als wässrige Lösung vorliegen und eine Dichte in einem Bereich von 0,3 bis 1,05 g/cm³ aufweisen als Sensibilisierungszusammensetzung zum Sensibilisieren einer Basisemulsion, die eine Wasser-in-Öl-Emulsion umfasst, die eine Lösung von anorganischem Sauerstoffträgersalz als diskontinuierliche Phase und einen organischen Brennstoff als kontinuierliche Phase umfasst.

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2. Verwendung nach Anspruch 1, wobei der organische Brennstoff ein Mineralöl, ein Pflanzenöl oder ein Wachs ist.

3. Verwendung nach Anspruch 1 oder 2, wobei der oberflächenaktive Stoff ein oberflächenaktiver Stoff auf Basis von Sorbitanmonooleat (SMO) oder Polyisobutylbernsteinsäureanhydrid (PIBSA) ist.

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4. Verwendung nach einem der Ansprüche 1 bis 3, wobei die wässrige Lösung außer dem Calciumnitrat eine oder mehrere Verbindungen ausgewählt aus einer Gruppe von anorganischen Salzen bestehend aus Ammonium-, Alkali- und Erdalkalimetallnitraten, -chloraten und -perchloraten und einer Gruppe von organischen Verbindungen bestehend aus organischen Nitraten und organischen Chloriden beinhaltet.

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5. Verwendung nach Anspruch 4, wobei die wässrige Lösung eine Lösung von Calciumnitrat und einem Perchloratsalz beinhaltet.

6. Verwendung nach einem der Ansprüche 1 bis 5, wobei die Mikrosphären entweder massiv oder hohl ausgebildet sind.

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7. Verwendung nach Anspruch 6, wobei die massiven Mikrosphären als Polystyrolkugeln oder Vermiculitperlen ausgebildet sind.

8. Verwendung nach Anspruch 6, wobei die hohlen Mikrosphären als gasgefüllte Mikrobällons aus Glas, Kunststoff oder einem harzartigen oder kohlenstoffhaltigen Material gebildet sind.

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9. Verwendung nach Anspruch 8, wobei die Mikrosphären als mit Isobutan gefüllte Kunststoff-Mikrobällons ausgebildet sind.

10. Verwendung nach einem der Ansprüche 1 bis 9, wobei der mittlere Durchmesser der Mikrosphären in einem Bereich von 20 bis 160 µm liegt.

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11. Verfahren zur Herstellung einer Sprengstoffzusammensetzung, umfassend die Schritte:

(a) Bereitstellen einer Basisemulsion,

(b) Bereitstellen einer Sensibilisierungszusammensetzung nach einem der Ansprüche 1 bis 10 und

(c) Vermischen der Basisemulsion mit der Sensibilisierungszusammensetzung in einem geeigneten Massenverhältnis im Bereich von 90:10 bis 50:50, um die Sprengstoffzusammensetzung auszubilden.

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12. Verfahren nach Anspruch 11, wobei die Basisemulsion eine Dichte über 1,28 g/cm³ aufweist.

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13. Verfahren nach Anspruch 11 oder 12, wobei das Massenverhältnis der Basisemulsion zur Sensibilisierungszusammensetzung 80:20 beträgt.

14. Verfahren nach einem der Ansprüche 11 bis 13, wobei die Basisemulsion Ammoniumnitrat (AN) beinhaltet und die wässrige Lösung der Sensibilisierungszusammensetzung Calciumnitrat beinhaltet.

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Revendications

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1. Utilisation d'une composition sous la forme d'une émulsion contenant les composants suivants dans les plages de concentration suivantes

(a) du nitrate de calcium : 40-80 % (m/m) ;

(b) de l'eau : 15-45 % (m/m) ;

(c) un combustible organique non polaire liquide et un tensioactif : 4-20 % (m/m) ;

(d) des microsphères : 0,5-10 % (m/m) ;

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EP 2 396 288 B1

(a) et (b) étant présents sous forme d'une solution aqueuse et ayant une masse volumique dans une plage de 0,3 à 1,05 g/cm³ comme composition sensibilisante pour sensibiliser une émulsion de base comprenant une émulsion d'eau dans l'huile comprenant une solution de sel comburant inorganique en tant que phase discontinue et un combustible organique en tant que phase continue.

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2. Utilisation selon la revendication 1, dans laquelle le combustible organique est une huile minérale, une huile végétale ou une cire.

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3. Utilisation selon la revendication 1 ou 2, dans laquelle le tensioactif est un tensioactif à base de monooléate de sorbitane (SMO) ou d'anhydride polyisobutylène-succinique (PIBSA).

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4. Utilisation selon l'une quelconque des revendications 1 à 3 dans laquelle la solution aqueuse comprend, en plus du nitrate de calcium, un ou plusieurs composés choisis dans un groupe de sels inorganiques constitué par les nitrates, chlorates et perchlorates d'ammonium, de métaux alcalins et de métaux alcalinoterreux et un groupe de composés organiques constitué par les nitrates organiques et les chlorures organiques.

5. Utilisation selon la revendication 4, dans laquelle la solution aqueuse comprend une solution de nitrate de calcium et d'un sel perchlorate.

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6. Utilisation selon l'une quelconque des revendications 1 à 5, dans laquelle les microsphères sont soit pleines soit creuses.

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7. Utilisation selon la revendication 6, dans laquelle les microsphères pleines sont des sphères de polystyrène ou des billes de vermiculite.

8. Utilisation selon la revendication 6, dans laquelle les microsphères creuses sont des microballons de verre, de plastique ou d'une matière en résine ou carbonée remplis de gaz.

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9. Utilisation selon la revendication 8, dans laquelle les microsphères sont des microballons en plastique remplis d'isobutane.

10. Utilisation selon l'une quelconque des revendications 1 à 9, dans laquelle le diamètre moyen des microsphères est dans une plage de 20-160 μm.

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11. Procédé de production d'une composition explosive qui comprend les étapes consistant à :

(a) obtenir une émulsion de base ;

(b) obtenir une composition sensibilisante selon l'une quelconque des revendications 1 à 10 ; et

(c) mélanger l'émulsion de base avec la composition sensibilisante en un rapport massique respectif dans la plage de 90:10 à 50:50 pour former la composition explosive.

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12. Procédé selon la revendication 11, dans lequel l'émulsion de base a une masse volumique au-dessus de 1,28 g/cm³.

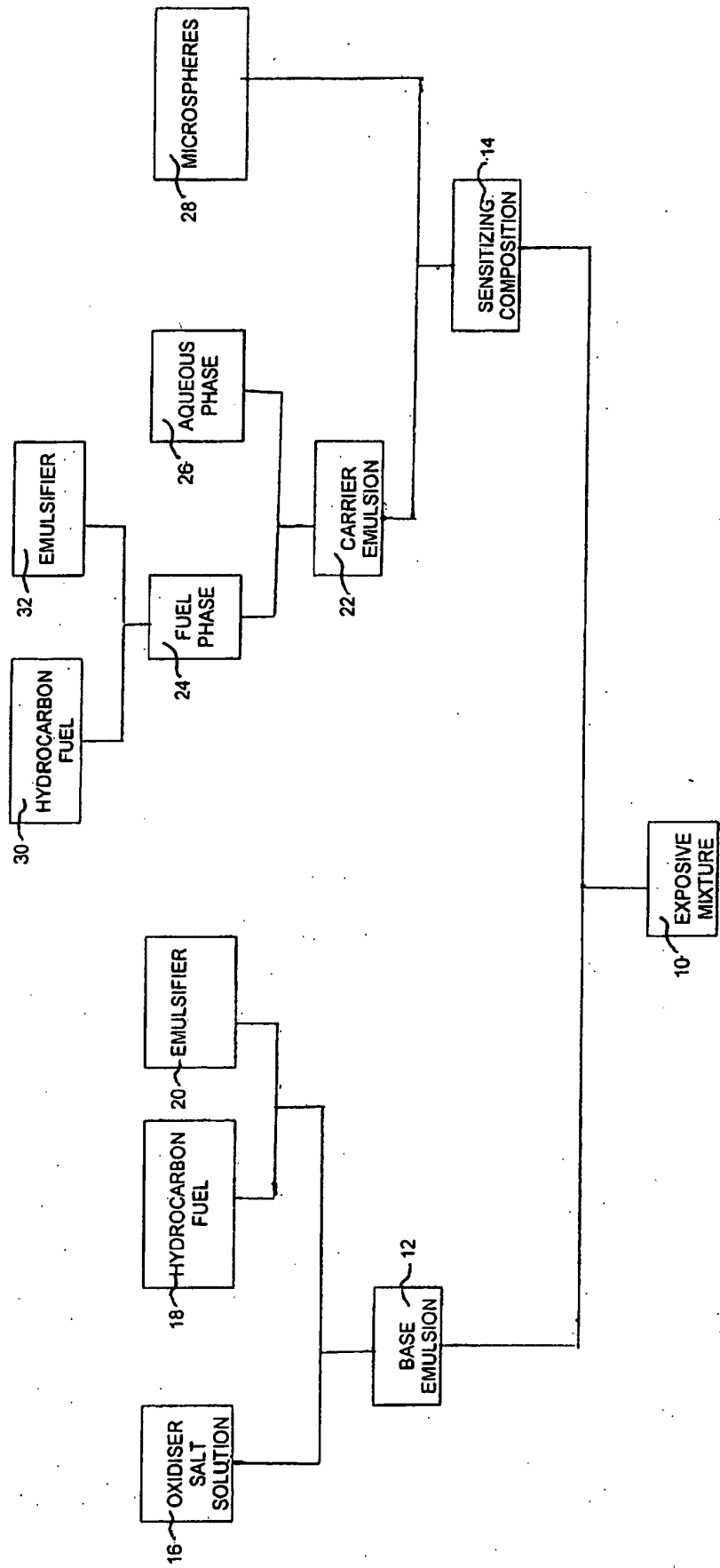
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13. Procédé selon la revendication 11 ou 12, dans lequel le rapport massique de l'émulsion de base à la composition sensibilisante est de 80:20.

14. Procédé selon l'une quelconque des revendications 11 à 13, dans lequel l'émulsion de base comprend du nitrate d'ammonium (AN) et la solution aqueuse de la composition sensibilisante comprend du nitrate de calcium.

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO 2008026124 A [0010]
- WO 8902881 A [0010]