

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 204 372
A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 86200942.0

(51) Int. Cl.⁴: G03C 5/26

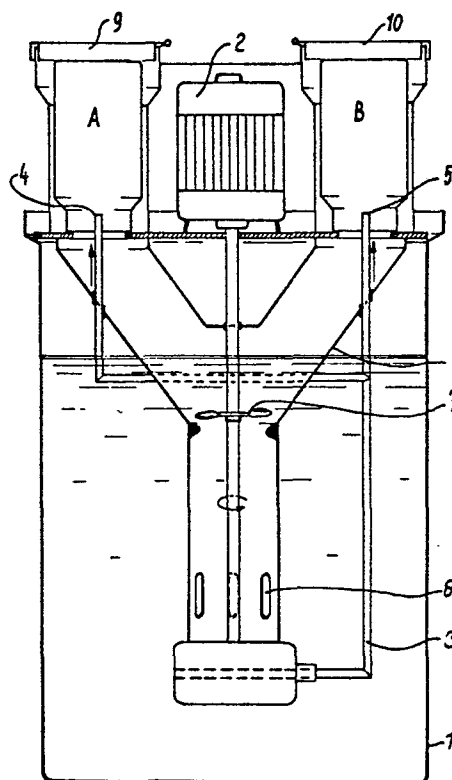
(22) Date of filing: 29.05.86

(30) Priority: 07.06.85 NL 8501659

(43) Date of publication of application:
10.12.86 Bulletin 86/50(84) Designated Contracting States:
DE FR GB IT NL(71) Applicant: **CHEMCO, INC.**
P.O. Box 2
NL-3760 AA Soest(NL)(72) Inventor: **Doesborgh, Alexander Hubertus**
Petrus
Boegmeen 26
NL-3844 KP Harderwijk(NL)(74) Representative: **van der Beek, George Frans**
et al
Nederlandsch Octrooibureau Johan de
Wittlaan 15 P.O. Box 29720
NL-2502 LS 's-Gravenhage(NL)

(54) Method for the preparation of photographic bath concentrates in paste form, method for processing such concentrates to give ready-for-use photographic processing baths, an apparatus suitable for such processing and a pump arrangement appertaining to this apparatus.

(57) Concentrated silver halide processing baths commonly used in the photographic and reprographic industries such as developer baths, regeneration baths, rejuvenation baths etc. having the form of a paste. As essential common component therein a viscosity-increasing and crystal growth-inhibiting agent such as a water-soluble or water-miscible polymer like carboxymethylcellulose, triethylene glycol or polyethylene glycol is present.



EP 0 204 372 A1

Method for the preparation of photographic bath concentrates in paste form, method for processing such concentrates to give ready-for-use photographic processing baths, an apparatus suitable for such processing and a pump arrangement appertaining to this apparatus.

The invention relates to a method for the preparation of concentrated photographic processing baths for photographic materials containing silver halides, such as developers and fixing baths, in a form such that the chemical components are present partially as solids and partially as liquids in the concentrate (such a mixture is commonly referred to as paste).

It is generally known that the concentrations of the various components in a photographic processing bath must lie within relatively narrow limits in order to obtain a product having optimal photographic properties; see, for example, the book by L.F.A. Mason "Photographic Processing Chemistry" (The Focal Press, London, 2nd edition, 1975). The most important solvent for the processing of photosensitive material based on silver halides is water. Most inorganic salts can be readily dissolved therein, while the solubility in water of the organic chemicals usually employed in this sector of photography, such as developing agents and antifogants, is also sufficiently great.

However, a major shortcoming of ready-for-use solutions is that they have a high water content, as a result of which a substantial proportion of the handling, transport and storage costs which must be incurred in order to bring the product from the manufacturer to the user, can be attributed to the water. In view of the fact that the person who carries out the processing of the photographic material normally also has water available, it is obvious to offer to the user a mixture of substances which is such that the photographic bath can be made up in a simple manner therefrom by addition of, or dissolution in, a given quantity of water.

Although in principle it is possible for the user himself to make up photographic baths with the aid of a formula, this presents a number of problems in practice. Industrial preparations are frequently the result of extensive research and development programmes and employ protected and/or difficult-to-obtain base materials, as a result of which such a recipe is not directly freely available. The photographic baths composed in accordance with a published non-protected recipe are often far from optimal as regards photographic properties.

The abovementioned book by L.F.A. Mason, on page 141, deals with the two most important types of composite developers and regeneration baths, namely liquid concentrates and powder mixtures. The liquid concentrates have the advantage of convenience in use; the disadvantages are, inter alia, the relatively high costs of packaging compared to

powders, the need to use water-miscible organic solvents such as diethylene glycol and triethylene glycol, and the danger of freezing under winter conditions.

A powder has the advantage that it permits a very high concentration. The disadvantages are the additional requirements which the chemicals have to meet (they must be solid, non-volatile substances), the formation of dust from the fine material during the dissolution procedure, the need to package chemicals separately and the more troublesome metering and mixing procedures compared to liquids. In the chemical and related industries, dust control furthermore has high priority; working with chemical mixtures which may cause dust therefore has to be avoided from the point of view of industrial hygiene and health.

In modern specialist photographic literature developer concentrates in broth or paste form according to Hübl, such as are described in the old photographic literature, for example the "Ausführliches Handbuch der Photographie" ("Detailed Handbook of Photography"), edited by Prof. Dr. J.M. Eder and Dr. Lüppo-Cramer (third volume, part two, published by Wilhelm Knapp, 1930) on page 123, are no longer encountered. This developer contains, as the developing agent, "glycin" or para-hydroxyphenylaminoacetic acid and is prepared as follows: 50 g of sodium sulphite heptahydrate are dissolved in 80 ml of hot water; thereafter 20 g of "glycin" are added and subsequently 110 g of potassium carbonate are added slowly. During this last procedure, 150 ml of a paste of good stability are formed, with evolution of carbon dioxide. In order to prepare a ready-for-use developer therefrom, 1 part by volume of the paste, which must first be stirred thoroughly, is taken and diluted with 15 parts by volume of water. However, this form of concentrate has, as far as uses are concerned, remained restricted to the glycin paste according to Hübl, since the disadvantages such as the need for stirring up and the somewhat more awkward metering of volumes clearly have not compensated for the advantages. Furthermore "glycin" as a developing agent has for decades been overtaken by other developers, such as the fine-grain developers derived from phenylenediamine. Another important practical disadvantage of the paste form according to Hübl is furthermore the fact that on aging (storage) rather large, hard and difficult-to-dissolve crystals form.

It has now been found that it is very readily possible to convert all silver halide processing baths commonly used in the photographic and reprographic industries, such as developer baths, regeneration baths, rejuvenation baths, stopping baths, fixing baths, bleaching baths, bleach-fixing baths, intensifiers and reducers, into a stable and storable concentrate in paste form. It is essential to use therein a viscosity-increasing and crystal growth-inhibiting agent. It is known from the literature that certain polymeric compounds counteract the agglomeration of crystal through adsorption on the crystal surface. It is also known that substances from certain classes of water-soluble organic solvents bring about a stabilization of the crystal surface, as a result of which processes such as agglomeration are greatly slowed down; see, for example, the book by A.L. Smith (ed.): "Particle Growth in Suspensions" (Academic Press, London, 1973). Organic polymers such as carboxymethylcellulose, gelatine, agar-agar, casein, alginates, polyvinyl alcohol and polyvinylpyrrolidinone or organic water-miscible solvents, such as methylcellosolve, ethylcellosolve, diethylene glycol, triethylene glycol and polyethylene glycol, and their derivatives, appear to prevent the formation of large crystal lumps and thus have a favourable effect on the shelf life and the rate of dissolution of the concentrate. The concentrations achievable are found to be even higher than those achievable via powder mixtures.

Further, it has been found that the content of containers filled with the paste can be totally dissolved in a simple manner, to give a ready-for-use solution, in a device specially developed for the purpose, which can be operated manually or works automatically, via squirting out and transferring into a mixing vessel, with a predetermined quantity of water. According to this aspect of the invention, the objections to the need for homogenization (namely stirring-up) and the difficulties to be expected in metering the paste volumes for the user have all been completely removed.

Figure 1 shows an apparatus according to the invention, whereby it is possible, using a predetermined quantity of water, to squirt empty the containers which have been filled with paste in the factory, and to transfer the contents into a mixing vessel.

The operation of the apparatus may be described as follows:

A quantity of water in accordance with the instructions is introduced into the mixing vessels - (1). Thereafter, the containers (A and B), filled with paste, are introduced into the spaces (9 and 10) intended for the purpose and provided with removable lids. The pump (2) is then switched on as a result of which the water passes through the line - (3) and squirts the paste out of the holders via nozzles (4) and (5), under high pressure. The water/paste mixture drops under gravity into the mixing vessel and in doing so passes a rapidly rotating cutter (7) mounted in a housing (6), which cutter serves the purpose of comminuting any lumps which may still be present in the paste. In the housing (6) there are one or more orifices (8) which provide the connection between the housing (6) and the mixing vessel (1). The abovementioned method prevents excessively large fragments from getting into the mixing vessel. In fact, the very intensive mixing in the housing (6) is intended to comminute lumps and fragments, through dissolution, so rapidly that they can still pass through the orifices in the housing into the mixing vessel. In the mixing vessel, stirring also takes place but this is less intensive than in the abovementioned housing. When the paste has completely dissolved in the mixing vessel, the solution thus obtained can be employed directly as a photographic processing bath.

Finally, the invention relates to a pump arrangement comprising a pump (2), a line (3) connected to the pump housing and provided with one or more orifices (8) on its underside, a cutter (7) mounted on the pump shaft and two spaces (9 and 10) provided with a removable lid, and intended for the containers (A) and (B) filled with paste.

The examples which follow illustrate the invention without limiting it.

Example I

A two-component developer concentrate having the following composition was prepared:

50

55

Component A:

water	300 g
sodium carbonate	300 g
potassium carbonate	500 g
50% strength potassium hydroxide	800 g
sodium sulphite heptahydrate	1,200 g
sodium hydrogen sulphite	600 g
potassium bromide	100 g
carboxymethylcellulose, low viscosity	30 g

Component B:

triethylene glycol	1,000 g
polyethylene glycol	100 g
1,2,3-benzotriazole	2 g
1-phenylpyrazolid-3-one	20 g
hydroquinone	600 g
potassium sulphite	400 g

By diluting these components A and B, each having a volume of about 2 litres, with 25 litres of water, about 30 litres of ready-for-use photographic developer are obtained.

It would have been preferable to combine the components A and B into a single component but this is not possible due to the instability of the 1-phenylpyrazolid-3-one in a strongly alkaline medium.

²⁵ Example II

A two-component fixing concentrate having the following composition was prepared:

³⁰

Component A:

water	300 g
carboxymethylcellulose, low viscosity	15 g
ammonium thiosulphate	2,000 g
sodium sulphite	300 g
boric acid	100 g

Component B:

water	100 g
carboxymethylcellulose, low viscosity	10 g
ammonium thiocyanate	1,500 g
glacial acetic acid	100 g
ammonium acetate	500 g

By diluting these components A and B, each having a volume of about 2 litres, with 25 litres of water, about 30 litres of ready-for-use fixing bath solution are obtained.

It would have been preferable to combine the components A and B into one component; this is however not possible due to the instability of the ammonium thiosulphate at low pH values.

Claims

1. Concentrated photographic processing baths for photographic materials containing silver halides, characterized in that these are in the form of a paste in which paste a crystal growth inhibitor is also incorporated.

2. Concentrated photographic processing baths according to Claim 1, characterized in that this crystal growth inhibitor is a water-soluble organic polymer.

3. Concentrated photographic processing baths according to Claim 1, characterized in that this crystal growth inhibitor is a water-miscible organic solvent.

4. Concentrated photographic processing baths according to Claim 2, characterized in that the water-soluble organic polymer is carboxymethylcellulose.

5. Concentrated photographic processing baths according to Claim 3, characterized in that the water-miscible organic solvent is a mixture of triethylene glycol and polyethylene glycol.

6. Method for the preparation of ready-for-use photographic processing baths for silver halide-containing photographic materials, characterized in that the paste concentrates according to one or more of Claims 1 to 5 inclusive are removed from the containers filled therewith by squirting out with the aid of a predetermined quantity of water and that the product thus obtained is collected.

7. Ready-for-use photographic processing baths, obtained according to the method of Claim 6.

8. Apparatus suitable for the processing of the paste concentrates according to one or more of Claims 1 to 5 inclusive to give ready-for-use photographic processing baths, characterized by, on the one hand, a mixing vessel (1), and, on the other hand, a pump arrangement comprising a pump (2), a line (3) connected to the pump housing and provided with two nozzles (4) and (5), a housing (6) which is provided with one or more orifices (8) on its underside, a cutter (7) mounted on the pump shaft and two spaces (9) and (10) provided with a removable lid, and intended for the containers (A) and (B) filled with paste.

9. Pump arrangement defined according to Claim 8.

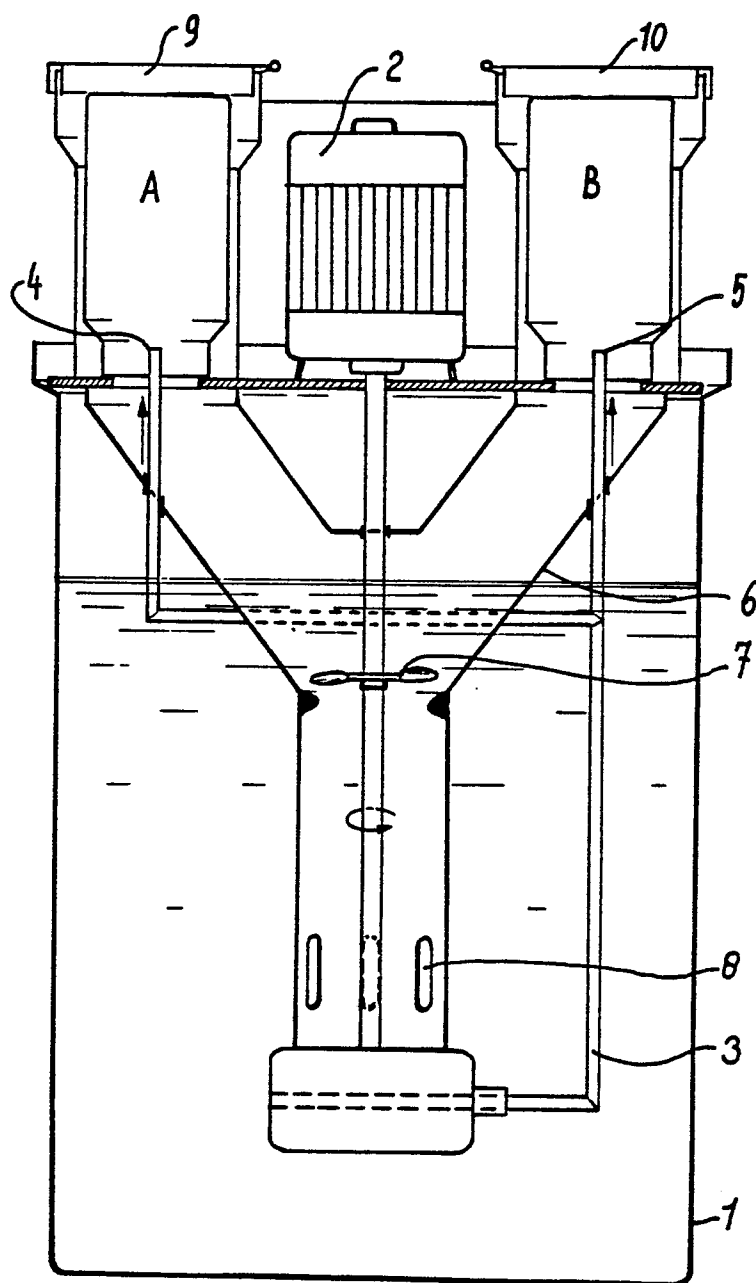
35

40

45

50

55





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.4)
X,Y	DE-A-3 106 775 (P. KLEINSCHMIDT) * Claims 1-3; page 5, paragraphs 3,4 * ---	1-3,5	G 03 C 5/26
Y	FR-A-1 086 655 (L.C. RUDKIN) * Page 1, right-hand column, lines 6-27 * ---	1-4	
A	FR-A-2 286 415 (F. VERONESI) * Page 3, line 6 - page 4, line 10; claims 1-3 * ---	4	
A	US-A-3 785 824 (R.S. FISCH) ---		
A	FR-A-1 575 074 (AGFA GEVAERT) ---		
A	DE-A-1 472 790 (AGFA GEVAERT) * Page 9, lines 1-12; example 2 * ---	5	TECHNICAL FIELDS SEARCHED (Int. Cl.4) G 03 C 5/26 B 01 F 1 B 01 F 3 G 03 C 1 G 03 D 3
A	DE-A-2 043 392 (EASTMAN KODAK) ---		
A	US-A-4 103 358 (L.W. GACKI et al.) ---		
A	GB-A-1 195 496 (AGFA GEVAERT) --- -/-		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 08-09-1986	Examiner PHILOSOPH L.P.
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			



EP 86 20 0942

DOCUMENTS CONSIDERED TO BE RELEVANT			Page 2
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	DE-B-1 077 059 (LEONAR-WERKE) --- -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 08-09-1986	Examiner PHILOSOPH L.P.
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			