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[54] **SILVER SALT DIFFUSION ALKALINE
BATH OF TRISODIUM PHOSPHATE
AND A POLYALCOHOL**

[72] Inventors: **Werner Liebe; Harald von Rintelen**, both of Leverkusen, Germany; **Gerard Laurens Vanreusel, Hove; Camille Angelina Vandeputte, Mortsel**, both of Belgium

[73] Assignee: **Agfa-Gevaert Aktiengesellschaft**, Leverkusen, Germany

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[56] **References Cited**

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Primary Examiner—Norman G. Torchin

Assistant Examiner—John L. Goodrow

Attorney—Connolly and Hutz

[57] **ABSTRACT**

The modification of the silver salt diffusion process comprises exposure of a supported silver halide emulsion layer containing a photographic developer and development of the exposed layer with an alkaline Trisodiumphosphate bath while in contact with a nucleated image-receiving layer. The stability of the bath is improved by incorporating water-soluble aliphatic polyalcohols or polyamines.

2 Claims, No Drawings

SILVER SALT DIFFUSION ALKALINE BATH OF TRISODIUM PHOSPHATE AND A POLYALCOHOL

The invention relates to an improvement in the silver salt diffusion process, wherein the photographic materials comprising at least one silver halide emulsion layer which contains photographic developers are developed with an alkaline bath.

French Pat. No. 879,995 describes the silver salt diffusion process for the direct production of positives in which the unexposed, and hence undevelopable silver halide of a silver halide emulsion layer which has been exposed to form an image is dissolved during development and is then developed to give a positive image in another image receiving layer which is in close contact with the silver halide emulsion layer. The development is carried out in the presence of development nuclei which are incorporated in this layer. The terms negative and positive are here used only in a relative sense, i.e., direct negatives can also be obtained from a negative original by the same process.

In the conventional silver salt diffusion process, the development baths used have substantially the usual compositions, i.e., developer substances in an alkaline aqueous solution. Owing to the sensitivity to oxidation of the developer substances, the lifetime of such development baths is limited. To overcome this disadvantage, the silver salt diffusion process has been modified so that the photographic developer substance is added to at least one of the photographic layers of the material used, in particular to the silver halide emulsion layer. When using such materials, a so-called activator bath is used for the development. This activator bath contains alkali as the main reagent, in addition to the other conventional additives such as stabilizers, toning agents etc.

These activator baths usually contain trisodium phosphate as the alkaline substance because of its resistance to carbon dioxide. The utility of trisodium phosphate baths, however, is limited since trisodium phosphate undergoes crystallization. Needle-shaped crystals of this substance are very easily deposited on the surface of the activator bath so that the conducting elements and applicator rollers in the processing apparatus as well as the photographic materials become contaminated.

It is the object of the invention to provide activator baths which are stable for as long as possible and will not contaminate the apparatus and materials by crystallization of the substances contained in the bath.

We now have found a silver salt diffusion process for the production of photographic images by exposure of a photographic material which contains at least one supported silver halide emulsion layer which emulsion layer contains one or more photographic developer substances, and development of this exposed material by treating it is an alkaline bath in contact with an image receiving layer which contains development nuclei, wherein the alkaline bath contains trisodium phosphate as alkaline substance and water-soluble aliphatic polyalcohols or polyamines.

Aliphatic polyalcohols which contain three to six carbon atoms and at least three hydroxyl groups are especially suitable. The following are examples of suitable compounds of this type: glycol, glycerol, mannitol, sorbitol, sugars such as saccharose or glucose, dipropylene triamine and triethylene tetramine. The alkaline baths of the present invention are referred to hereinafter as activator baths.

The above mentioned substances are added to the activator baths in quantities of between 5 and 50 g. preferably between 15 and 30 g. per liter of bath liquid. When using sugars, it is advisable to use quantities at the lower end of the given range since at higher concentrations the finished photographic material becomes sticky.

Mixtures of the polyalcohols or polyamines may, of course, also be used. If desired, this substance may be applied together with aliphatic amino alcohols such as ethanolamine or diethanolamine. Glycerol or mannitol or sorbitol has proved to be particularly suitable.

The activator baths otherwise have the usual composition. The following recipe may be used as a general guide:

1 to 10 g. of a sequestering agent

60 to 100 g. of trisodium phosphate

35 to 50 g. of an alkali metal sulfite

0.1 to 1 g. of a stabilizer, such as potassium bromide

10 to 100 mg. of a polyalcohol or polyamine water up to 1 l.

Other additives such as agents for preventing or reducing the formation of sludge of silver of silver compounds may, of course, also be added to the activator bath.

Other silver salt solvents such as sodium thiosulfate may also be used in quantities of about 5 to 75 g. according to the particular kind of silver salt diffusion process which is being used. The quantity required depends on whether the silver salt solvent is entirely, or partly present in the photographic layers.

The optimum concentration of additives for a particular purpose can easily be determined by a few simple tests customarily employed in the art.

The light-sensitive photographic materials suitable for the invention have the usual composition. They contain at least one supported silver halide emulsion layer preferably on a paper support. The silver halides used may be silver chloride, silver bromide or mixtures of these silver halides, if desired together with small quantities of silver iodide of up to 10 mols percent. The silver halide emulsion layer contains a photographic developer substance.

The usual developer substances may be used, for example aromatic phenols, particularly those of the dihydroxybenzene series; furthermore, aminophenol or aminonaphthol compounds or developers of the phenylene diamine type. Developers of the 3-pyrazolidone group have proved to be particularly suitable, in particular those of the 1-phenyl-3-pyrazolidone series. 1-Aryl-3-aminopyrazolines described in German Pat. No. 946,606 are also effective, especially those compounds which contain an amino group attached to the aryl group. 4-aminopyrazolones as mentioned in German Pat. No. 955,025 are also suitable.

So-called masked photographic developers are particularly useful. In these developers, photographically active groups are rendered inactive by substituents which are split off before development. The light-sensitive layers are therefore very stable upon storage. Developers of this type have been described in German Pat. Nos. 1,025,264; 1,038,913; 1,056,472; 1,159,758; 1,200,679; 1,203,129; and 1,203,605 and in British Pat. No. 812,673.

In a preferred embodiment, the light-sensitive material contains hydroquinone and 1-phenyl-pyrazolidone-3 as developer substances.

The image receiving materials also, in principle, have the usual composition. They contain development nuclei for the deposition of the transferred silver halide. These development nuclei are arranged either in a separate layer or in the layer support itself. Suitable nuclei are finely divided noble metals, especially of heavy metals, e.g., silver sulfide or nickel sulfide.

The image receiving layer may also be arranged on a separate support, for example, on paper or on the same support as the silver halide emulsion layer. In the latter case, both layers are on the same side of the support and the image receiving layer is preferably the uppermost layer. In this case, it is advisable to arrange a white pigmented intermediate layer between the image receiving layer and the light-sensitive layer.

Conventional apparatus may be used for processing.

The activator baths according to the present invention are also suitable for processing exposed silver halide emulsion layers which contain developers by the two-bath process (activator bath and stabilizer bath) or multibath processes (activator bath, stabilizer bath, fixing bath and washing).

EXAMPLE 1

Image receiving material

A baryta layer is applied to support of paper (80 g. per m.²) using the following solution:

6 g. of a 50 percent aqueous slurry of barium sulfate

20 ml. of a 10 percent aqueous gelatin solution

8 ml. of a 50 percent aqueous emulsion of polyvinyl acetate water up to 100 ml.

The baryta layer is dried and then covered with an image receiving layer of the following solution (ready for casting):

- 4.5 g. of propylene glycol alginate
- 12.5 mg. of silver sulfide in the form of an aqueous colloidal solution
- 20 ml. of a 50 percent aqueous gelatin solution
- 1.5 ml. of a 30 percent aqueous solution of potassium bromide
- 1.2 ml. of a 30 percent aqueous solution of saponin
- 7.5 g. of sodium thiosulfate
- 30 mg. of the mercaptotriazole blue toner according to Example 1 of German Pat. No. 1,153,247 filled up with water up to 300 ml.

The layer is applied in such a thickness that it contains approximately 1.1 g. of sodium thiosulfate per m².

Another layer of the following casting solution is applied on the layer described above:

- 5.0 g. of formaldehyde bisulfite
- 5.0 g. of hydroquinone
- 3.5 g. of sodium alginate
- 10 g. of sodium thiosulfate
- 0.8 ml. of a 30 percent aqueous potassium bromide solution
- 8 ml. of a 30 percent aqueous saponin solution made up to 350 ml. with water.

This layer is applied in such a thickness that it contains approximately 0.6 g. of sodium thiosulfate per m².

Light-sensitive material

A light-sensitive photographic material which has a silver chloride gelatin emulsion layer on a paper support is used. The layer has been hardened with formaldehyde. It contains 0.8 g. of silver in the form of silver chloride, 850 mg. of hydroquinone and 200 mg. of 1-phenyl-pyrazolidone-3- per m².

Processing

The image receiving layer described above is brought into contact with the exposed silver chloride emulsion layer and developed in the following activator bath in a conventional processing apparatus:

Glycerol	25 ml.	
Sodium thiosulfate	1.5 g.	
sodium sulfite anhydrous		50 g.
trisodium phosphate anhydrous		30 g.
1-phenyl-3-pyrazolidone		1.2 g.
sodium hydroxide		1.5 g.
potassium bromide		1 g.
3-methyl-4-allyl-5-mercapto-1,2,4-triazole		30 mg.
water		0.8 l.

The copies obtained when using the usual contact times of about 5 to 10 seconds have an excellent neutral black image tone.

EXAMPLE 2

Light-sensitive material

The material consists of a silver chloride gelatin emulsion layer on a layer support of paper. The emulsion layer contains 500 mg. of hydroquinone, 150 mg. of 1-phenylpyrazolidone-3 and 0.8 g. of silver in the form of silver chloride per m².

A layer of hydroxyethyl starch ether is applied to the emulsion layer to improve the contact with the image receiving layer during processing. This layer contains 200 mg. of binder and 40 mg. of hydroquinone per m².

10 Image receiving layer

A thin gelatin layer which contains the following substances per m² is applied on a paper support:

15 Gelatin	1.1 g.
glycerol sulfite	1.6 g.
nickel sulfide nuclei	5 mg.
hydroquinone	300 mg.
potassium metabisulfite	1.5 g.
1-phenyl-5-mercaptotetrazole	5 mg.

20 Processing

The above image receiving layer is brought into contact with the exposed silver chloride emulsion layer and developed in the following activator bath in a conventional processing apparatus:

25 Trisodium phosphate . 12H ₂ O	82 g.
sodium sulfite anhydrous	35 g.
potassium bromide	1 g.
sodium thiosulfate anhydrous	7 g.
1-phenyl-5-mercaptotetrazole	50 mg.
30 ethylene diaminetetracetic acid	1 g.
sorbitol	25 g.
made up with water to	1 l.

After contact times of about 10 seconds (which are customarily employed in practice) copies which have a neutral black image tone are obtained.

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We claim:

1. In a silver salt diffusion process for the production of photographic images by exposure of a photographic material which contains at least one supported silver halide emulsion layer, which emulsion layer contains one or more photographic developer substances, and development of the exposed layer by treating it with an alkaline bath in contact with an image receiving layer which contains development nuclei, the improvement wherein the alkaline bath contains trisodium phosphate as an alkaline substance and a polyalcohol selected from the group consisting of glycerol, mannitol and sorbitol.

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2. An improved aqueous alkaline bath of the type containing trisodium phosphate as an alkaline agent for carrying out the process according to claim 1, wherein the improvement comprises additionally containing a water-soluble aliphatic polyalcohol selected from the group consisting of glycerol, mannitol and sorbitol.

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