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Schober

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[54] **PHOTOGRAPHIC ACTIVATING BATH**

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[58] **Field of Search** ..... 96/50 R, 95

[56] **References Cited**

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[57] **ABSTRACT**

Improved photographic activating baths containing at least one low-molecular weight, aliphatic alcohol give improved image density for photographic films containing developing agents.

5 Claims, No Drawings

PHOTOGRAPHIC ACTIVATING BATH

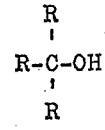
This invention relates to a photographic activating bath.

It is known to add a developer substance to photographic films and to initiate development by treatment with an aqueous alkaline bath, the so-called activating bath. The main constituents of an activating bath are a compound for activating the developing process, usually a caustic alkali, and a preservative. In addition to caustic alkalis, sodium carbonate, potassium carbonate, aluminates, phosphates or organic bases can also be used. Sodium sulfite is generally used as a preservative. Other additives can be present, such as stabilizers, development accelerators and wetting agents.

Activation processes are advantageous because they are simple in their operation; results are obtained quickly; and the solutions can be made stable to oxidation. Activating baths are also efficient because only a limited quantity of developer substance in the photographic materials is available.

There are disadvantages, however, when activating baths are used in photographic processing. In many instances considerable loss in image density is noted when compared with the density achieved by normal photographic processing. For this reason, these processes have been used for the processing of photographic paper where very low densities are sufficient. The loss in density is believed to be caused primarily by the fact that the developer substances of the hydrophilic type diffuse out of the photographic films into the aqueous activating bath too rapidly, without being photographically active; whereas, conversely, when hydrophobic developer substances are used, the activation by aqueous alkaline solutions takes place too slowly and too incompletely. In both instances, the developer substances are not fully utilized by the activating process as a result of the too large or too small solubility, making losses in density unavoidable. In addition, a nonuniform density distribution is frequently observed at the same exposure. This is attributable to a nonuniform diffusion of the developer.

The above disadvantages have been overcome by a photographic activating bath for activating light-sensitive silver halide materials having developer substances incorporated in them, the activating bath comprising an aqueous solution of an alkaline substance, a preservative and one or more watermiscible alcohols of the formula



where R is H, alkyl (C_1–C_{12}), aryl, vinyl, Ch_3O—$(CH_2.)_n$—, HO—$[C(R_1)_2]_n$—; R_1 is H or alkyl; and n is 1–4; in quantities of 10–60 percent by weight.

Especially suitable water-miscible alcohols are the low-molecular-weight, monovalent, aliphatic alcohols, e.g., methanol, ethanol, propanol and butanol. The alcohols can be used alone or in mixtures. A useful mixture of alcohols is ethanol and tertiary butanol.

The mode of operation of the alcohol-containing activating bath can probably be explained in that the diffusion of the hydrophilic developer substances out of the photographic films is retarded and swelling is reduced; whereas, on the other hand, an improved solubility for compounds of the hydrophobic type is displayed so that hydrophobic developer substances can be used optimally for the activation process.

This result is surprising and unexpected since it is known that the addition of alcohols to developer solutions in quantities of up to 10 percent by weight has little effect on the sensitometric values, whereas high concentrations, such as are used according to the invention, lead to marked fogging of the light sensitive material.

Activating baths within the scope of the invention may contain some 5–60 grams/liter of alkali, 2–60 grams/liter of alkali sulfite and 100–600 milliliters/liter of a watermiscible alcohol. Preferably, the pH of the activating solution should be located between 10 and 13. The activator solutions described can be applied to the exposed photographic material by known methods, e.g., by immersion, washing the material with a roller or by spraying. Subsequent to the activation process, the photographic material can be fixed and washed in the usual manner. If a longer storage stability is not necessary, a stabilizing bath can follow the activating bath. In the stabilizing bath, the unexposed silver halide is converted into a light-insensitive, light-stable, complex compound so that the washing process can be dispensed with. The activator solutions described are suitable for activating all photographic silver halide materials which contain the developer substances in the light sensitive emulsion film or in an auxiliary layer such as an undercoated layer. Silver chloride, silver bromide and silver iodide emulsions are suitable, as well as emulsions containing mixtures of these halides.

As developer substances, all known compounds of the hydrophilic and hydrophobic types may be contained in the photographic films. Examples of suitable hydrophilic compounds are hydroquinone, catechol, hydroquinone sulfonate and chlorohydroquinone. Suitable as hydrophobic compounds are butylhydroquinone, propyl gallate, and compounds the functional group or groups of which are inactivated by suitable protecting groups, for example, ester, ether or similar groups. Examples of such compounds are described in Offenlegungschrift No. 1,929,223 (German).

The activating baths have a number of advantages. The most important advantage is that they exhibit increased activation when compared with the known baths, that is, they facilitate an optimum utilization of the developer substances contained in the film so that when these baths are used materials with superior density values are obtained.

Moreover, the activating baths are advantageous in that they reduce the swelling of th photographic films, which leads to obtaining materials with improved dimensional stability in processing. As a result of the reduced swelling, shorter drying times are necessary. The activating baths also exhibit very favorable effects on the diffusion of the developer substances so that uniformly developed silver images are obtained. The alcohol-containing activating bath increase the covering power of the developed silver more strongly than alkaline aqueous solutions, resulting in an additional saving of silver.

The invention will be illustrated by the following examples:

EXAMPLE 1

To 1 liter of a 5% solution of gelatin were added 15 grams of each of the following developer substances:

Sample 1: hydroquinone

Sample 2: catechol Sample 3: chlorohydroquinone

Sample 4: propyl gallate

The addition of these substances can take place as solids or as aqueous alcoholic solutions. The gelatin solution is then cast on a transparent polyester film base so that a solid coating of 1.5 grams of developer substance per square meter results. On this substrate, a silver chloride-silver bromide emulsion is applied, which contains 70 mol-percent of chloride and 30 mol-percent of bromide. The silver coating amounts to 9 grams/ square meter.

Subsequently, a protective gelatin film is applied and hardened in the usual manner. After drying, the material is contact exposed with an incandescent light (30 watt) at a distance of 1.5 meters in aa vacuum printing frame. For comparison, a sample strip of the light-sensitive material is treated with a conventional aqueous activating bath A and another strip is treated with an alcohol-containing activating bath B.

Aqueous activator bath A consists of:

NaOH	6.0	grams
Sodium sulfite anhydrous	2.0	grams
Potassium bromide	2.0	grams
Benzotriazole	0.1	gram
Water make up to	1	liter

Alcohol-containing bath B consists of:

NaOH	6.0	grams
Sodium sulfite anhydrous	2.0	grams
Potassium bromide	2.0	grams
Benzotriazole	0.1	gram
Allyl alcohol	200	centimeters[3]
Water make up to	1	liter

The treatment of the sample strips takes place under the same conditions, 10 seconds at 20°C.

The results are compiled in the following table:

Table 1

Sample Number	Activator Bath A 10 sec. at 20°C.		Activator Bath B 10 sec. at 20°C.	
	D max	fog	D max	fog
1	1.2	0.04	4.2	0.15
2	1.3	0.05	3.8	0.05
3	0.6	0.05	2.9	0.05
4	0.8	0.05	2.5	0.15

From the table it is clearly evident that considerably higher density values can be obtained with developer substances of the hydrophobic type using the alcohol-containing bath B of the invention than with the conventional bath A.

EXAMPLE 2

A light-sensitive material produced according to Example 1 is used except that as developer substances, the following compounds are added to the basecoat:

Sample 1: hydroquinone sulfonate (15 grams)

Sample 2: 15 grams of the monoester of hydroquinone with α-triethylaminoacetic acid chloride (compound 1 of Offenlegungschrift No. 1,929,223).

One of each of the sample strips of the materials exposed under the conditions given in Example 1 is again treated for 30 seconds at 20°C. with a conventional activating bath A and with an alcohol-containing activating bath B of the invention.

Bath A:

NaOH	20.0	grams
Sodium sulfite anhydrous	2.0	grams
Potassium bromide	2.0	grams
Benzotriazole	0.1	gram
Water make up to	1	liter

Bath B:

NaOH	20.0	grams
Sodium Sulfite anhydrous	2.0	grams
Potassium bromide	2.0	grams
Benzotriazole	0.1	gram
Ethanol	360	centimeters[3]
Tertiary-Butanol	40	centimeters[3]
Water make up to	1	liter

The following results were obtained:

Table 2

Sample Number	Activator Bath A 30 sec. at 20°C.		Activator Bath B 30 sec. at 20°C.	
	D max	fog	D max	fog
1	0.4	0.04	4.3	0.15
2	0.1	0.05	3.6	0.20

From the table it is evident that with developer substances of the hydrophilic type and with developer precursor compounds considerably better density values can be achieved on using the alcohol-containing bath B of the invention.

EXAMPLE 3

Four samples of the material produced and exposed according to Example 1, in each case, are treated with the conventional bath A given in Example 1 and, for comparison therewith, with baths in which 200 cm^3 of the water in bath A is replaced by 200 cm^3 of various alcohols or mixtures of alcohols.

Bath B contains	200 cm^3 of allyl alcohol
Bath C contains	200 cm^3 of ethanol
Bath D contains	200 cm^3 of tert.-butanol
Bath E contains	200 cm^3 of ethylene glycol
Bath F contains	180 cm^3 of ethanol and 20 cm^3 of tert.-butanol
Bath G contains	180 cm^3 of ethanol and 20 cm^3 of dodecyl alcohol

Treatment is carried out for 10 seconds at 20°C. and the results are compiled in Tables 3 and 4.

Table 3

Activator bath 10 sec. at 20°C.	Sample 1 D max	Sample 1 fog	Sample 2 D max	Sample 2 fog
A	1.2	0.04	1.3	0.5
B	4.2	0.15	3.8	0.05
C	3.3	0.04	3.6	0.15
D	3.4	0.05	3.8	0.10
E	2.3	0.04	2.7	0.05
F	3.3	0.04	4.2	0.12
G	3.1	0.05	3.4	0.05

Table 4

Activator bath 10 sec. at 20°C.	Sample 3 D max	Sample 3 fog	Sample 4 D max	Sample 4 fog
A	0.6	0.05	0.8	0.05
B	2.9	0.05	2.5	0.15
C	3.3	0.05	1.4	0.10
D	3.3	0.05	2.1	0.10
E	2.4	0.05	1.2	0.08
F	3.4	0.05	2.3	0.20
G	3.6	0.06	1.7	0.15

EXAMPLE 4

Two test strips of the material produced and exposed as in Example 2, in each case, are treated with the activating bath A and, for comparison therewith, with baths according to the invention in which 400 cm^3 of the water in bath A is replaced by 400 cm^3 of various alcohols or mixtures of alcohols.

Bath B contains	400 cm^3 of ethanol
Bath C contains	400 cm^3 of isopropanol
Bath D contains	400 cm^3 of tert.-butanol
Bath E contains	100 cm^3 of benzyl alcohol 100 cm^3 of methanol 200 cm^3 of acetone
Bath F contains	400 cm^3 of methylglycol
Bath G contains	360 cm^3 of ethanol 40 cm^3 of tert.-butanol

Treatment is carried out for 30 seconds at 20°C. and the results are given in Table 5.

Table 5

Activator bath 30 sec. at 20°C.	Sample 1 D max	Sample 1 fog	Sample 2 D max	Sample 2 fog
A	0.4	0.04	0.10	0.05
B	3.8	0.10	3.3	0.20
C	4.3	0.10	2.8	0.20
D	2.0	0.10	1.8	0.20
E	3.8	0.15	3.2	0.25
F	4.0	0.15	2.7	0.20
G	4.3	0.15	3.5	0.20

Much higher densities are obtained with alcoholcontaining baths B–G than with the conventional aqueous activating bath A.

We claim:

1. A photographic activating bath for activating light-sensitive silver halide materials having developer substances incorporated in them, the activating bath consisting essentially of an aqueous solution of an alkaline substance selected from the group consisting of caustic alkali, sodium carbonate, potassium carbonate, aluminates and phosphates, an alkali metal sulfite preservative and at least one water-miscible alcohol of the formula

$$\begin{array}{c} R \\ | \\ R\text{-}C\text{-}OH \\ | \\ R \end{array}$$

where r is H, alkul (C_1–C_{12}), aryl, vinyl, $Ch_3O-(CH_2)_n-$, $HO-[C(R_1)_2]_n-$; R_1 is H or alkyl; and n is 1–4; in quantities of 10–60 percent by weight.

2. A photographic activating bath according to claim 1 wherein said alcohol is methanol, ethanol, propanol, or butanol.

3. A photographic activating bath according to claim 1 wherein the bath contains a mixture of ethanol and tertiary-butanol.

4. A photographic activating bath according to claim 1 which comprises 5 to 60 grams/liter of alkali, 2 to 60 grams/liter of preservative and 100 to 600 milliliters/-liter of said alcohol.

5. A photograhic activating bath according to claim 1 having a pH between 10 and 13.

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