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IMAGE-RECEIVING MATERIAL FOR USE IN SILVER SALT DIFFUSION TRANSFER PHOTOGRAPHY

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ABSTRACT OF THE DISCLOSURE

An image-receiving material containing a specific amine compound such as bis-(β-hydroxyethyl) amine, tris-(β-hydroxyethyl) amine, or N-β-hydroxyethyl piperidine in at least one of either its receiving layer or an adjacent layer. The amine compound serves to enhance the activity of a development nucleus contained in the receiving layer.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to an image-receiving material for use in a silver salt diffusion transfer photographic process.

Description of the prior art

The diffusion transfer photographic process utilizing a silver salt such as silver halides has previously been known. In this photographic process, finely divided particles of a photosensitive silver salt such as silver halides are dispersed in a hydrophilic binder such as gelatin, and the resultant dispersion is coated on a support to form a light sensitive photographic layer. The light sensitive photographic layer is exposed to light imagewise, and then developed by contact with a processing liquid containing a developing agent. The silver halide that was exposed in the photosensitive layer is reduced (developed) to silver. Concurrently or subsequently, the photographic material is brought into contact with a processing liquid containing a solvent for the silver halide, such as sodium thiosulfate or potassium thiocyanate, whereupon the unexposed silver halide reacts with the solvent for the silver halide to form a water-soluble silver complex compound. When a receiving material that has a receiving layer comprising a catalyst (physical development nucleus) for the reduction of the water-soluble silver complex compound dispersed in the hydrophilic binder is brought into intimate contact with the photosensitive layer, the silver complex compound formed in the photosensitive layer diffuses together with the processing liquid containing the solvent for silver halide, and moves from the photosensitive layer to the receiving layer where it is reduced to silver by the action of the development nucleus. When

the receiving surface is seen as a whole, a silver image is formed as if the image were transferred from the photosensitive layer to the receiving layer.

The development nuclei usually used in the silver salt diffusion transfer photographic process include, for example, sparingly water-soluble metal sulfides, metal selenides, or colloidal heavy metals or noble metals. Such a substance is dispersed in a polymeric material, such as gelatin or polyvinyl alcohol, which allows an alkaline liquid to penetrate, and the resulting dispersion is coated on a support such as paper, film or a metal plate to produce an image-receiving material. Needless to say, the development nucleus of the receiving material should have a high activity and receiving materials utilizing a highly active development nuclei can be used favorably as high speed diffusion transfer photographic materials. U.S. Pat. 2,698,237 discloses that when a water-soluble metal salt is mixed with a water-soluble sulfide in finely divided silicon dioxide, the precipitate of a water-soluble metal sulfide is obtained and this product has a very high activity as a development nucleus. This known development nucleus, however, has the defect that during the storage of the receiving material it gradually loses its activity.

SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to provide an image-receiving material in which the activity of a development nucleus contained therein is markedly enhanced and in which the enhanced activity hardly decreases during storage for long periods of time.

The present invention provides an image-receiving material for use in a silver salt diffusion transfer photographic process which contains a compound of the following general formula in at least one of either its receiving layer or an adjacent layer:

$$R_2—\underset{\displaystyle R_1}{N}—C_nH_{2n}OH$$

wherein n is an integer of 1 to 5, and each of R_1 and R_2 is a member selected from the group consisting of a hydrogen atom, an alkyl group having not more than 5 carbon atoms, a substituted alkyl group having not more than 5 carbon atoms in which at least one of the hydrogen atoms is substituted with a hydroxyl group or a halogen atom, a substituted alkyl group having not more than 5 carbon atoms in which at least one of the hydrogen atoms is substituted with an amino group,

$$—C(NH_2)=NH$$

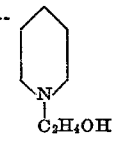
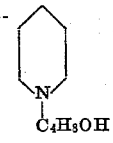
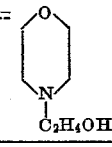
group, an acyl group and an allyl group, or R_1 and R_2 are bonded directly or through another atom to form a hetero ring together with the nitrogen atom.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Specific examples of the compound of the above formula that is useful in the photographic material of the invention are as follows:

Nos.	Compound	Structural formula
1	β-Hydroxyethylamine	$H_2NCH_2CH_2OH$
2	N-methyl-β-hydroxyethylamine	$CH_3NHCH_2CH_2OH$
3	N,N-dimethyl-β-hydroxyethylamine	$(CH_3)_2NCH_2CH_2OH$
4	N-ethyl-β-hydroxyethylamine	$C_2H_5NHCH_2CH_2OH$
5	N,N-diethyl-β-hydroxyethylamine	$(C_2H_5)_2NCH_2CH_2OH$
6	N-methyl-N-ethyl-β-hydroxyethylamine	$CH_3(C_2H_5)N\cdot CH_2CH_2OH$
7	N-n-pentyl-β-hydroxyethylamine	$C_5H_{11}NHCH_2CH_2OH$
8	Bis-(β-hydroxyethyl)amine	$HN(CH_2CH_2OH)_2$
9	N,N-bis-(β-hydroxyethyl)methylamine	$CH_3N(CH_2CH_2OH)_2$
10	N,N-bis-(β-hydroxyethyl)-β-chloroethylamine	$ClCH_2CH_2N(CH_2CH_2OH)_2$
11	N,N-bis-(β-hydroxyethyl)-n-pentylamine	$C_5H_{11}N\cdot(CH_2CH_2OH)_2$
12	N,N-bis-(β-hydroxyethyl)-n-butylamine	$C_4H_9N(CH_2CH_2OH)_2$
13	Tris-(β-hydroxyethyl)amine	$N(CH_2CH_2OH)_3$
14	N-isopropyl-β-hydroxyethylamine	$C_3H_7NH\cdot CH_2CH_2OH$
15	N-β-hydroxyethyl acetamide	$CH_3CO\cdot NH\cdot CH_2CH_2OH$
16	N-t-butyl-β-hydroxyethylamine	$C_4H_9NH\cdot CH_2CH_2OH$
17	N-allyl-β-hydroxyethylamine	$CH_2=CHCH_2NH\cdot CH_2CH_2OH$
18	N-allyl-N-ethyl-β-hydroxyethylamine	$CH_2=CHCH_2(C_2H_5)N\cdot CH_2CH_2OH$

TABLE—Continued

Nos.	Compound	Structural formula
19	β-Hydroxyethylurea	$H_2N{\cdot}CO{\cdot}NH{\cdot}CH_2CH_2OH$
20	N-vinyloxyethyl-β-hydroxyethylamine	$CH_2{=}CHOCH_2CH_2NHCH_2CH_2OH$
21	N-3-hydroxyethylguanidine	$HN{=}C(NH_2){\cdot}CH_2CH_2OH$
22	Hydroxymethylamine	$H_2N{\cdot}CH_2OH$
23	γ-Hydroxypropylamine	$H_2N{\cdot}CH_2CH_2CH_2OH$
24	N,N-dimethyl-1-methyl-3-hydroxypropylamine	$(CH_3)_2{\cdot}N{\cdot}CH(CH_3)CH_2CH_2OH$
25	5-hydroxypentylamine	$H_2N{\cdot}C_5H_{10}OH$
26	N-β-hydroxyethyl piperidine	
27	N-δ-hydroxybutyl piperidine	
28	N-β-hydroxyethyl morpholine	

In the present invention, the above-described substance is incorporated in at least one of a receiving layer or an adjacent layer of the image-receiving material used in the silver salt diffusion transfer photographic process. According to the conventional silver salt diffusion transfer process, the receiving material is composed of a support, a receiving layer provided thereon, and an adjacent layer including a sub layer for increasing the adhesion of the receiving layer to the support and a stripping layer (provided for rendering both the photographic material and the receiving layer separable from each other after the diffusion transfer treatment) or a protective layer (provided for preventing scratch injury or contamination of the image surface). Each of these layers contains as a binder a hydrophilic film-forming polymeric material such as gelatin, polyvinyl alcohol or polyvinyl pyrrolidone. There is no particular restriction on the support which can be, for example, cellulose diacetate film, cellulose triacetate film, polystyrene paper, polyethylene laminate paper or baryta-coated paper.

The above-mentioned compound affects the action of the development nucleus. The amount of the compound to be incorporated in the receiving layer or adjacent layer is 1 to 200 moles por mole of the development nucleus, and best results are obtained when the amount is 10 to 100 moles per mole of the development nucleus.

The compound is generally added to a solution or dispersion of the compound which forms the receiving layer or the adjacent layer at any stage until the coating of the solution. If desired, a solution of the compound may be applied before or after the coating of the receiving layer or the adjacent layer, so that the compound is caused to penetrate into the layer. In short, the requirement is that the compound is finally present in the receiving layer or the adjacent layer.

On storing for prolonged periods of time, the receiving material of the invention hardly suffers from a reduction in the activity of the development nucleus, and even if there is a reduction, it is slight so that the desired object can still be well achieved.

All of the above-exemplified compounds and others which correspond to the general formula given above have an action of preventing the deterioration of the receiving material that may occur with the passage of time. However, bis-(β-hydroxyethyl)-amine, tris-(β-hydroxyethyl)-amine, N-β-hydroxyethyl piperidine, and N-β-hydroxyethyl guanidine especially exhibit superior results.

The invention will further be described by the following examples and comparative example, which are presented for illustrative, rather than limitative, purposes.

COMPARATIVE EXAMPLE

Preparation of comparative sample

Solution A of the following mixture was coated on the surface of baryta paper at the coating weight of 25 cc./m.²

Solution A

Distilled water	cc.	1,000
Cadmium acetate (dihydrate)	g.	2.8
Lead acetate (trihydrate)	g.	0.9
Zinc nitrate (hexahydrate)	g.	5.5
Silicic anhydride [Santocel C, product of Monsanto Chemical Co.]	g.	30
Aqueous solution of sodium sulfide (3% by weight)	cc.	9.5
Aqueous solution of saponin (6% by weight)	cc.	20

The coating was dried, and on top of it, Solution B of the following mixture was coated, followed by drying.

Solution B

Distilled water	cc.	1,000
Sodium salt of carboxymethyl cellulose	g.	10
Aqueous solution of saponin (6% by weight)	cc.	20

The resultant receiving material was used as a comparative sample.

EXAMPLE 1

Preparation of Sample 1

A receiving material (Sample 1) was prepared by the same procedure as set forth in the Comparative Example except that a solution of the following formulation was used instead of Solution A.

Distilled water	cc.	1,000
Cadmium acetate (dihydrate)	g.	2.8
Lead acetate (trihydrate)	g.	0.9
Zinc nitrate (hexahydrate)	g.	5.5
Santocel C	g.	30
Aqueous solution of sodium sulfide (3% by weight)	cc.	9.5
Aqueous solution of saponin (6% by weight)	cc.	20
β-Hydroxyethylamine (Compound 1)	g.	15

EXAMPLES 2 TO 11

Receiving materials (Samples 2 to 11) were prepared in the same way as set forth in the comparative example

using each of the compounds indicated in the following table instead of the Compound 1 used in Example 1.

Examples	Compounds (Nos.)	Amount (g.)	Sample No.
2	Bis-(β-hydroxyethyl)amine (8)	18	2
3	Tris-(β-hydroxyethyl)amine (13)	20	3
4	N,N-bis-(β-hydroxyethyl)-n-butylamine (12).	4	9
5	n-ethyl-β-hydroxyethylamine (4)	18	5
6	5-hydroxypentylamine (25)	20	6
7	N-β-hydroxyethyl piperidine (26)	17	7
8	N,N-bis-(β-hydroxyethyl)-β-chloroethylamine (10).	10	8
9	N-β-hydroxyethyl guanidine (21)	20	9
10	N-β-hydroxyethyl acetamide (15)	10	10
11	N-allyl-β-hydroxyethylamine (17)	12	11

EXAMPLES 12 AND 13

Receiving materials (Samples 12 and 13) were prepared by the same procedure as set forth in the comparative example except using a coating solution of the following formulations respectively instead of Solution B used in Example 1.

Examples	Formulation of the coating solution	Amount	Sample No.
12	Sodium salt of carboxymethyl cellulose	10 g.	12
12	Tris-(β-hydroxyethyl)amine (Compound 13).	20 g.	12
12	Aqueous solution of saponin (6% by weight).	20 cc.	12
12	Distilled water	1,000 cc.	12
13	Gum arabic	10 g.	13
13	N-β-hydroxyethyl morpholine (Compound 28).	15. g.	13
13	Aqueous solution of saponin (6% by weight).	20 cc.	13
13	Distilled water	1. 000 cc.	13

One half of each of the samples obtained above was forcibly deteriorated by allowing to stand for 24 hours in an atmosphere at 50° C. and a relative humidity of 80%.

Each of the treated samples was superposed on a silver salt diffusion transfer photosensitive material which had been exposed imagewise so that the receiving layer of the receiving material came into intimate contact with the photosensitive layer of the photographic sensitive material. Between the image receiving layer and the exposed photosensitive layer, a processing liquid of the following composition was spread.

COMPOSITION OF THE TREATING LIQUID

	G.
Water	1,860
Sodium salt of carboxymethyl cellulose	117
Sodium sulfite anhydride	78
Sodium hydroxide	74.6
Sodium thiosulfate (crystals)	14.5
Citric acid	38.5
Hydroquinone	52

Both materials were brought into contact with each other for 15 seconds and then separated from each other. It was found that a silver image transferred from the photographic material and was formed on the surface of the receiving layer of the receiving material. The maximum density of the image was measured and the following results were obtained.

The following table shows the results both for forcibly deteriorated samples and non-deteriorated samples. The degree of forcible deterioration can be estimated by $100\Delta D/D_1$, where ΔD is a difference between D_1 which is the maximum density of the transfer image formed on the non-deteriorated sample, and D_2 which is the maximum density of the transfer image of the forcibly deteriorated sample.

Sample	Maximum transfer density D_1	Maximum transfer density D_2	Decrease in density, $\Delta D = D_1 - D_2$	Percentage decrease in density (percent), $100 \times \Delta D/D_1$
Comparison	1.46	0.76	0.70	48.0
1	1.42	1.04	0.38	26.7
2	1.50	1.30	0.20	13.3
3	1.40	1.30	0.10	7.1
4	1.44	1.10	0.34	23.6
5	1.47	1.07	0.40	27.2
6	1.36	0.99	0.37	27.2
7	1.42	1.22	0.20	14.1
8	1.40	1.05	0.35	25.0
9	1.50	1.20	0.30	20.0
10	1.40	0.95	0.45	32.1
11	1.46	1.06	0.40	27.4
12	1.42	1.12	0.30	21.1
13	1.46	1.11	0.35	24.0

It is seen from the above table that the comparative sample which did not contain the compound of the invention has a percentage decrease in density of 48% which shows that it tends very much to deteriorate in the course of time, whereas the Samples 1 to 13 which contained the amine compound of the invention have a percentage decrease in density of less than 32%. Especially, Sample 3 which contained tris-(β-hydroxyethyl) amine had a percentage decrease in density of only 7.1, and indicated the most outstanding prevention of deterioration with the passage of time.

It was also found that the amine compound used in the present invention serves to prevent the processing composition from remaining attached to the surface of the receiving material when the receiving material was separated from the photosensitive material after the diffusion transfer process.

What we claim is:

1. An image-receiving material for use in the diffusion transfer process, said material comprising a development nucleus material and an amine compound of the following general formula in at least one of either its receiving layer or an adjacent layer:

$$R_2\text{—}N(R_1)\text{—}C_nH_{2n}OH$$

wherein n is an integer of 1 to 5, and each of R_1 and R_2 is a member selected from the group consisting of (1) a hydrogen atom, (2) an alkyl group having not more than 5 carbon atoms, (3) a substituted alkyl group having not more than 5 carbon atoms in which at least one of the hydrogen atoms is substituted with a hydroxyl group or a halogen atom, (4) a substituted alkyl group having not more than 5 carbon atoms in which at least one of the hydrogen atoms is substituted with an amino group, (5) —$C(NH_2)$=NH group, (6) an acyl group, and (7) an allyl group, or R_1 and R_2 are bonded directly or through another atom to form a hetero ring together with the nitrogen atom.

2. An image-receiving material of claim **1** wherein the amount of the amine compound is 1 to 200 moles per mole of a development nucleus material contained in the image-receiving material.

3. An image-receiving material of claim **2** wherein the amount of the amine compound is 10 to 100 moles per mole of the development nucleus material.

4. An image-receiving material of claim **1** wherein the amine compound is selected from the group consisting of

β-hydroxyethylamine,
N-methyl-β-hydroxyethylamine,
N,N-dimethyl-β-hydroxyethylamine,
N-ethyl-β-hydroxyethylamine,
N,N-diethyl-β-hydroxyethylamine,
N-methyl-N-ethyl-β-hydroxyethylamine,
N-n-pentyl-β-hydroxyethylamine,
bis-(β-hydroxyethyl)amine,
N,N-bis-(β-hydroxyethyl)methylamine,
N,N-bis-(β-hydroxyethyl)-β-chloroethylamine,
N,N-bis-(β-hydroxyethyl)-n-pentylamine,

N,N-bis-(β-hydroxyethyl)-n-butylamine,
tris-(β-hydroxyethyl)amine,
N-isopropyl-β-hydroxyethylamine,
N-β-hydroxyethyl acetamide,
N-t.-butyl-β-hydroxyethylamine,
N-allyl-β-hydroxyethylamine,
N-allyl-N-ethyl-β-hydroxyethylamine,
β-hydroxyethylurea,
N-vinyloxyethyl-β-hydroxyethylamine,
N-β-hydroxyethyl guanidine,
hydroxymethylamine,
γ-hydroxypropylamine,
N,N-dimethyl-1-methyl-3-hydroxypropylamine,
5-hydroxypentylamine,
N-β-hyldroxyethyl piperidine,
N-δ-hydroxybutyl piperidine, and
N-β-hydroxyethyl morpholine.

5. An image-receiving material of claim 4 wherein the amine compound is bis-(β-hydroxyethyl) amine, tris-(β-hydroxyethyl) amine, N-β-hydroxyethyl piperidine, or N-β-hydroxyethyl guanidine.

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