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3,528,810

PROCESS FOR THE PRODUCTION OF DIRECT POSITIVE IMAGES BY THE SILVER SALT DIFFUSION PROCESS

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No Drawing. Continuation-in-part of application Ser. No. 545,257, Apr. 26, 1966. This application Dec. 13, 1966, Ser. No. 601,318

Claims priority, application Germany, May 8, 1965, A 49,159

Int. Cl. G03c 5/54, 1/02

U.S. Cl. 96—29 8 Claims

ABSTRACT OF THE DISCLOSURE

The invention relates to an improvement of the silver salt diffusion process by the use of light-sensitive silver salts which can be processed with neutral or acid developer solutions and in the case of certain transfer materials can even be developed with water.

This is a continuation in part of application Ser. No. 545,257 filed on Apr. 26, 1966, now abandoned.

In the silver salt diffusion process, a light-sensitive silver halide material is exposed and further processed in contact with a transfer material which generally contains development nuclei, with a conventional alkaline developer. In this process, the silver halide of the light-sensitive layer diffuses from the unexposed and undeveloped parts of that layer into the transfer layer where it is reduced on the development nuclei to form a positive image. This process has gained great importance in practice. However, owing to the use of the alkaline developers, it has certain disadvantages, especially on account of the yellowing of the positive copies produced. This yellowing is mainly due to the presence of alkalis from the developer which remains in the transfer layer containing the positive silver image.

It is among the objects of the present invention to improve the known silver salt diffusion process in such a manner that the use of alkaline developer baths is avoided.

It has now been found that processing by the silver salt diffusion process is possible without alkaline development baths if light-sensitive layers are used which contain light-sensitive silver salts of aliphatic carboxylic acids. the aliphatic chain of which is substituted with an organo thio-

ether grouping, instead of the light-sensitive silver halides customarily employed. The light-sensitive silver salts of the present invention are more soluble in water at pH values between 1 and 7 than are the conventional silver halides and are capable of being developed at a pH between 1–7.

The minimum solubility of the said silver salts in water at a pH between 1 and 7 is 0.2 g./l. of silver in the form of the silver salt. Suitable silver salts of the thio-substituted aliphatic carboxylic acids are described in Belgian patent specification 668,340 so far as they meet the above conditions. Especially suitable are silver salts of the following formula:

$$R—(S)_n—X—COOAg$$

in which

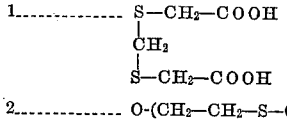
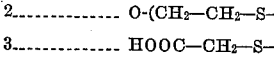
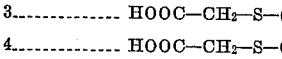
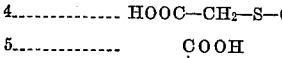
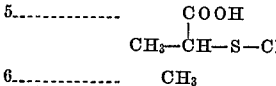
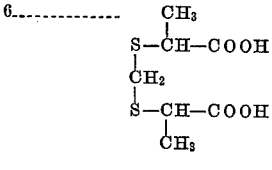
n=1 or 2, preferably 1,

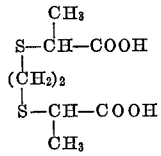
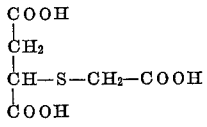
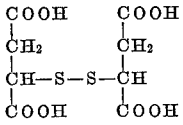
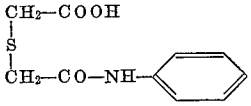
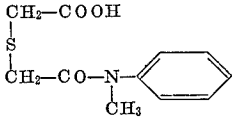
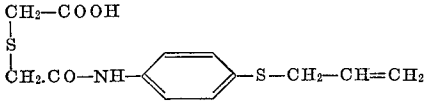
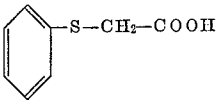
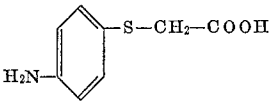
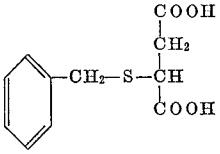
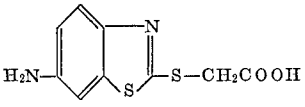
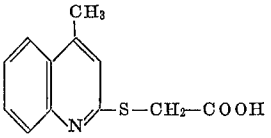
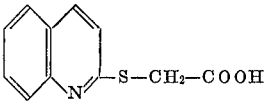
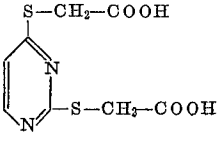
R=alkyl with preferably up to 3 C-atoms, aryl such as phenyl or naphthyl preferably phenyl, or heterocyclic rings such as diazolyl, oxazolyl, triazolyl, thiadiazolyl, oxadiazolyl, tetrazolyl, azaindenyl preferably tetra- or pentaazaindenyl, benzthiazolyl, naphthothiazolyl, benzoxazolyl, naphthoxazolyl, pyridyl, quinolyl, pyrimidinyl, quinoxalinyl, quinazolinyl, which radicals may in turn be substituted, for example, by alkyl preferably with up to 3 C-atoms, aryl such as phenyl or naphthyl, hydroxyl, alkoxy, aroxy such as phenoxy, acyl in particular acetyl, amino, alkylamino the alkyl groups of which have up to 5 carbon atoms, acylamino with preferably acyl groups derived from aliphatic carboxylic acids, for example, acetyl, or aryl-substituted amino preferably a phenylamino, mercapto groups, mercapto groups substituted with alkyl having up to 6 carbon atoms, a phenyl, a naphthyl or a heterocyclic radical, halogen such as chlorine or bromine, sulfo groups or carboxyl groups nitro and the like; R can be further substituted by at least one grouping

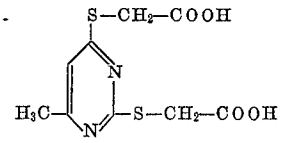
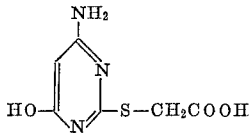
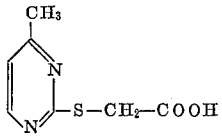
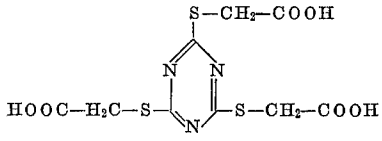
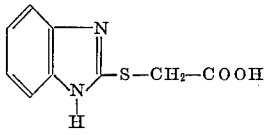
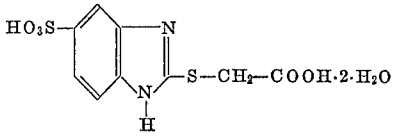
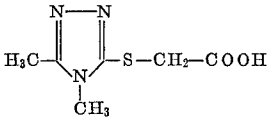
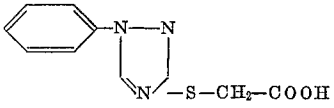
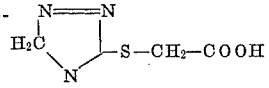
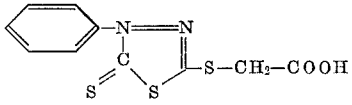
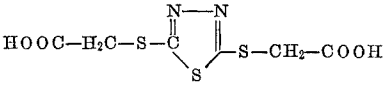
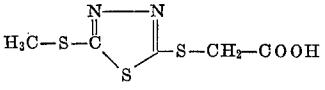
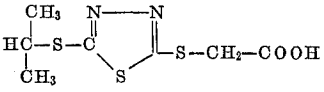
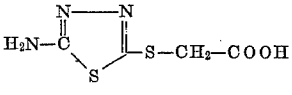
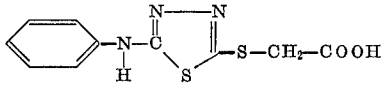
$$—(S)_n—X—COOAg$$

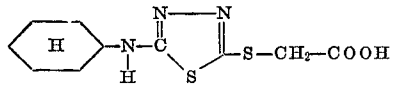
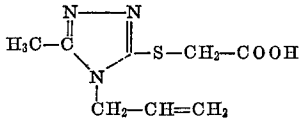
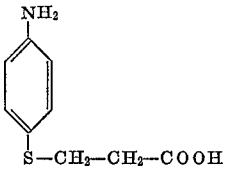
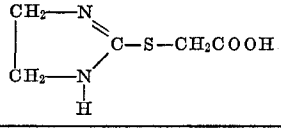
X=a branched or unbranched alkylene chain, preferably with up to 3 carbon atoms in the chain, in which the alkylene may be substituted, e.g., with aryl such as phenyl, hydroxyl, alkoxy or halogen such as chlorine.

The aliphatic acids, the aliphatic chain of which is substituted with an organo thioether group, are called in the following simply "thiocarboxylic acids." Suitable acids of this kind, which are to be used according to the invention, include the following:

1		Beilstein, vol. 3, page 249.
2		44°.
3		Beilstein, vol. 3, 3rd supp. vol. part 1, page 417.
4		Beilstein, vol. 3, page 253.
5		Beilstein, vol. 3, page 291.
6		Do.

7		Beilstein, vol. 3, 3rd supp: vol. part 1, page 511;
8	$HOOC-CH-(NH_2)-CH_2-S-CH_2-COOH$	J. Am. Chem. Soc. vol. 66, page 1758 (1944);
9		Beilstein, vol. 3, 3rd supp. vol. part 2, page 924.
10		Beilstein, vol. 3, page 439.
11		Beilstein, vol. 12, page 485. 103–104° C.
12		114° C.
13		102° C.
14		Beilstein, vol. 6, page 313.
15		198° C.
16		Beilstein, vol. 6, page 453.
17		200° C.
18		120–120.5° C;
19		91° C.
20		270° C; (decomposition).

21		169° C.
22		230-234° C. (decomposition).
23		196° C.
24		Beilstein, vol. 26, page 128.
25		Beilstein, vol. 23, 2nd Supp. vol., page 321.
26		296° C. (decomposition).
27		165° C.
28		184-85° C.
29		156° C.
30		Beilstein, vol. 27, 1st supp. vol., page 612.
31		159° C.
32		150° C.
33		Uncrystallized.
34		260° C. (decomposition).
35		192° C.

36		158° C.
37		177° C.
33		122-123° C.
39		184° C.

Particularly suitable are the silver salts of carboxymethylthiomalic acid, S-phenyl-thioglycollic acid, S-triazolyl-thioglycollic acid, S - thiadazolyl(2, or 5) thioglycollic acid, thiodiglycollic acid, bis-(beta-carboxy-methylthio) ethyl ether, and substitution products in which these compounds have further substituents on the R and X portions selected in accordance with the general definition set out above.

The compounds may be prepared by the processes described in the publications referred to in the table. Where no publication is referred to, the compounds may be prepared from the corresponding mercaptans and organic halogen compounds or halogen carboxylic acids in alkaline solution by processes similar to those described in Houben-Weyl, vol. 9, pages 103 to 113. The compounds can be isolated in the form of free acids or as alkali metal salts. The compounds can be purified by recrystallisation from or by solution and reprecipitation from water or alcohol.

The silver salts are prepared from solutions of the thiocarboxylic acid and a soluble silver salt such as silver nitrate. In many cases it has proved advantageous to react the components with a slight molar excess of the thiocarboxylic acid. It is possible, however, to react equimolar quantities of the components.

The reaction takes place in an aqueous solution of the reaction components, preferably in the presence of a protective colloid such as gelatin, polyvinyl alcohol, or derivatives of alginic acid such as salts, e.g., sodium alginate, or esters. Depending on the type of thioaliphatic carboxylic acid used, the components can be reacted in a molar ratio about 1:1. That molar ratio relates to the number of carboxyl groups. Thus, an acid which contains two carboxyl groups can be reacted with 2 mols of water-soluble silver salt such as silver nitrate. Acids which contain 3 or more carboxyl groups are preferably reacted with at least 2 mols of silver salt.

The silver salts according to the invention may also be employed in admixture with one another or with conventional silver halides.

The type of water-permeable binding agents which can be used include those which are known to be satisfactory for dispersing silver halides. These colloids comprise preferably gelatin which however can be wholly or partially replaced by other film-forming natural or synthetic materials such as proteins for instance albumin or casein, alginic acids or derivatives thereof such as alkali salts of alginic acid, esters of alginic acids in particular esters with lower aliphatic alcohols preferably glycols such as propylene glycol, carboxyalkylcellulose such as carboxymethylcellulose, alkylcellulose, such as methylcellulose or hydroxyethylcellulose, starch, starch ethers or esters such as esters with lower aliphatic alcohols having up to 5 carbon atoms or alkyl ethers the ether group of which has up to 5 carbon atoms, carraghenates, polyvinylalcohol, partially saponified polyvinylacetate, polyvinyl pyrrolidone and the like.

The light-sensitive silver salt emulsions contain between 1 and 80, preferably 2 and 25 g. of silver ni the form of the silver salt of the thiocarboxylic acid per liter of emulsion. The final light-sensitive layers contain between 0.05 and 10 preferably between 0.2 and 2 g. of silver in the form of the silver salt of the thiocarboxylic acid per square meter. The thickness of the layers is between 0.5 and 30μ, preferably 6–15μ.

According to a preferred embodiment of the present invention, the light-sensitive silver salt emulsion contains additionally a light-sensitive silver halide, particularly silver chloride and/or silver bromide in amounts of 0.1–25 mol percent, preferably 0.5–5 mol percent based on the light-sensitive silver salt of the thiocarboxylic acid.

The light-sensitive emulsions can be chemically sensitized by any of the accepted procedures. The emulsions can be treated with salts of the noble metals such as ruthenium, rhodium, palladium, iridium and platinum.

Suitable compounds are well known in the art. The emulsions can also be sensitized with gold salts as described by R. Koslowsky, Z. wiss. phot. 46, 65–72 (1951).

The emulsion can also be chemically sensitized with reducing agents such as stannous salts, polyamines, sulfur compounds, such as described in the U.S. Pat No. 1,574,944, polyethylene oxides and the like.

The emulsion can also be optically sensitized with the ordinary sensitizing dyes, cyanines or merocyanines. The emulsions and the light-sensitive emulsion layers have a pH of between 1 and 6, preferably between 2.5 and 5.

Since the light-sensitive silver salts of thiocarboxylic acids to be used for the process according to the invention are soluble in aqueous acids, such acids can be used as the silver salt solvent for the process according to the invention instead of the usually employed thiosulfates or sulfites. The acids only need to meet the requirement that under the processing conditions they must not form a silver salt which is more sparingly soluble than the light-sensitive silver salts of the emulsion layer. Thus, for example, hydrohalic acids such as hydrochloric acid cannot be used. Suitable acids are, for example, inorganic acids such as sulfuric acid, nitric acid, organic acids such as acetic acid, citric acid, adipic acid and the like. It is also possible to use as the acid component thiocarboxylic acids the silver salts of which may be contained as light-sensitive substance in the emulsion layer.

Unexpectedly such light-sensitive layers are stable on storage. This is presumably due to the fact that the silver salts and acids are present in solid form in the layer. Upon wetting the layer during processing small quantities of the two components are dissolved so that they can diffuse into the transfer layer and be reduced there. In cases where acid-containing emulsion layers are used, the acids are added in quantities of 0.001 to 10 g., preferably 0.1 to 3 g. per m.^{2}, depending on the basicity in the given case and on the binding agent used.

Materials of the usual composition may be used for the transfer materials for the process of the invention. The type of support used is not critical; it is preferred to use paper, which may carry a baryta-coating as customarily employed. Transparent supports of cellulose esters or polyesters, especially polyethylene glycol terephthalate, may also be used. The papers may be lacquered or coated with synthetic film-forming polymers, e.g., with polyethylene. The usual binders are suitable for the transfer layer, for example, gelatin, alginic acid or its derivatives such as alkali metal salts, esters, especially with propylene glycol, starch ethers, especially alkyl ethers containing alkyl groups with up to 5 C-atoms, polyvinyl alcohol, polyvinyl acetate, carboxyalkyl celluloses, especially carboxyl methyl celluloses, hydroxyethyl celluloses, galactomannane and poly-N-vinyl-pyrrolidone.

The transfer layers also contain development nuclei on which the silver salts which are transferred from the unexposed areas of the light-sensitive layer can be reduced. The development nuclei may be made up of substances known for this purpose, e.g., finely divided metals such as silver, gold or the like or metal compounds such as sulfides or selenides, e.g., silver sulfide, cadmium sulfide, zinc sulfide, nickel sulfide or the like. The nuclei must, of course, be sparingly soluble under the conditions of processing. It is also possible to apply in combination with or instead of the development nuclei, substances which are capable of reducing the transferred silver salt under the conditions of processing.

Developers which may be used in the process according to the invention are any which are capable of reducing the silver salts of thiocarboxylic acids under the conditions of processing, bearing in mind especially the relatively low pH values. There may be used, for example, developers of the pyrazolidone-(3) series, preferably 1-phenyl-pyrazolidone-(3) or its derivatives, and in addition, 3-aminopyrazolines, e.g., 1-p-aminophenyl-(3)-aminopyrazoline or its derivatives as described, for example, in British specification 768,071, 4-aminopyrazolones or its derivatives, as described e.g., in British patent specification 768,071, 1-phenyl-3-carbonamido-4-amino-pyrazolone-(5), 1-phenyl-3-methyl-4-aminopyrazolone-(5), oxytetronic acid or derivatives such as ascorbic acid or similar products or salts of heavy metals in a reduced state or valency such as ferrous salts, e.g., ferrous citrate. The most suitable as developers are the first mentioned substances.

The following are examples of suitable developers of the 3-pyrazolidone series:

1-phenyl-3-pyrazolidone
1-m-toluyl-3-pyrazolidone
1-p-toluyl-3-pyrazolidone
1-phenyl-4-methyl-pyrazolidone
1-phenyl-5-methyl-3-pyrazolidone
1,4-dimethyl-3-pyrazolidone
4-methyl-3-pyrazolidone
4,4-dimethyl-3-pyrazolidone
1-phenyl-2-acetyl-3-pyrazolidone
1-phenyl-4,4-dimethyl-3-pyrazolidone
1-(4-bromophenyl)-3-pyrazolidone

The above developers may also be used in combination with each other or with other known developers.

The developers may be used as aqueous solutions with pH values between about 1 and 7 or they may be incorporated in the transfer layer. The processes according to the invention may, of course, also be carried out in such a manner that the developers are present in the aqueous treatment bath and the transfer layer.

If the developers are added to the transfer layer, the amount in the dry layer should preferably be 0.01 to 2.5 g. per m.^{2} of transfer layer. Aqueous solutions suitable for development preferably contain 0.1 to 50 g., in particular 0.5 to 20 g. of developer per liter. The light-sensitive layer may also contain reducing substances provided these do no fog the silver salts on storage.

It is a preferred embodiment of the process according to the invention to use transfer layers which contain the developers. If the solvents for silver salts are also present in the transfer layer or in the light-sensitive silver salt emulsion layer, the treating bath can be water. The considerable advantages of such a process are obvious. In this embodiment, it is only necessary to moisten the exposed silver salt emulsion layer and then bring it into contact with the dry transfer layer. Moistening of the transfer material may entail certain disadvantages because there is the risk of the developer being prematurely dissolved out of the layers. As soon as the two layers are in contact, the developer diffuses from the transfer layer into the exposed silver salt emulsion layer and develops the silver salt at the exposed portions of the layer. Simultaneously the silver salts in the unexposed areas are dissolved ind transferred into the transfer layer, where they are reduced at the development nuclei to form a positive silver image.

In certain cases it might be advantageous to apply a second layer onto the nucleated layer of the transfer material, in order to retard diffusion of the not yet developed silver salts from the exposed areas into the transfer layer. In that case the developer compounds are added preferably to the upper layer.

Diffusion of the soluble silver salts is retarded by the outer layer in the transfer material, which does not contain any nuclei, and adequate development is thus achieved in the exposed portions of the light-sensitive silver salt emulsion layer. Similar effects are achieved by suitable choice of binding agents of the light-sensitive layer and the transfer layer.

To the transfer layer and the silver salt emulsion layer there may, in addition, be added additives usual for achieving a desired image tone or for stabilization. For this purpose there may be used, for example, heterocyclic mercapto compounds such as 1-phenyl-mercaptotetrazole and 1-phenyl-3-mercapto-triazole-1,2,4 or azaindenes as described in the article by Birr in Z. wiss. phot., vol. 47 (1952), pages 2 to 8. 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene is especially suitable. In addition, other known additives may be added both to the transfer layer and to the emulsion layer in order to improve the properties of the layers. Such additives are, for example, salts of metals such as copper, zinc, cadmium or lead. Suitable toners, especially blue toners, are described in British patent specifications 753,434, 783,793, 867,174, 922,479, 962,976, 950,668 and 972.954 and in U.S. Pats. Nos. 2,987,396, 3,053,657, 3,062,643, 3,068,029 and 3,017,270.

The layers may be hardened by any suitable hardener, such as formaldehyde and halogen substituted aliphatic acids such as mucobromic acid.

To carry out the process according to the invention one may use apparatus usual for the silver salt diffusion process, but it is preferable to use those in which only the light-sensitive layer is moistened.

The process according to the invention can be accelerated by heating during development and transfer.

EXAMPLE 1

Light-sensitive material

33 g. of carboxymethylthiomalic acid (compound 9), are added in the form of a 10% aqueous solution to 1 liter of a 6% aqueous gelatin solution. The solution is acidified with 15 ml. of a 25% aqueous sulfuric acid and

the corresponding silver salt is then precipitated at 40° C. by the addition of 18.6 g. of silver nitrate in the form of a 10% aqueous solution.

To the finished emulsion are added per liter, 3 ml. of a 0.01% methanolic solution of eosin as sensitizer, 5 ml. of a 40% aqueous formaldehyde solution and 10 cc. of a 30% aqueous saponin solution. The resulting mixture is cast in the usual manner onto a paper support to form a layer of a thickness such that the finished material contains 0.5 g. of silver per m.².

Instead of the carboxymethylthiomalic acid, one may also use the following compounds in the quantities given.

	G.
S-phenylthioglycollic acid (compound 4)	20.2
S-[4-amino-6-hydroxypyrimidinyl-(2)]-thioglycollic acid (compound 22)	24.3
S-[4-allyl-5-methyl-1,2,4-triazolyl-(3)]-thioglycollic acid (compound 37)	27
S-[4-aminophenyl-(1)]-β-thiopropionic acid (compound 38)	23.8

The thiocarboxylic acid derivatives may be added either in the solid form or in the form of 5 to 10% aqueous solutions to the binder, if necessary after addition of the necessary quantity of alkali, e.g., aqueous sodium hydroxide, to dissolve it.

Transfer material

To a 3% aqueous solution of hydroxyethyl cellulose are added 5 ml. of a colloidal yellow silver solution in gelatin. This solution is used for coating a paper raw material of weight 70 g. per square meter to produce a coating of about 20 mg. of Ag nuclei per m.². Instead of hydroxyethylcellulose, carboxymethylcellulose can be used.

Processing

The light-sensitive layer is imagewise exposed. The exposed material and the transfer material are then passed through a 0.5% aqueous solution of 1-phenylpyrazolidone-(3). Thereafter the light-sensitive layer and the nucleated layer of the transfer material are placed into intimate contact with each other. After a brief contact time of about 10 seconds, the layers are separated. A positive, non-reversed black silver image of the original is formed in the transfer layer.

EXAMPLE 2

Light-sensitive material

By the addition of a 10% aqueous solution of 10.2 g. $AgNO_3$ to 1 liter of a 6% aqueous gelatin solution which contains 10 g. of thiodiglycollic acid (compound 4), the corresponding silver salt is precipitated.

To the above emulsion are then added 25 ml. of a 10% aqueous sulfuric acid and 5 cc. of a 40% aqueous formaldehyde solution and 10 cc. of a 30% aqueous saponin solution. The resulting mixture is applied in the usual manner onto a paper support. The prepared material contains, per m.², 0.7 g. of silver in the form of the thiodiglycollic acid salt.

Instead of the thiodiglycollic acid, the following compounds may be used in the given quantities:

	G.
S-[6-methylpyrimidinyl-(2,4)-]-dithioglycollic acid (compound 21)	18.1
S-[2-methylmercapto-1,3,4-thiadiazolyl-(5)]-thioglycollic acid (compound 32)	14.7
S-[1-phenyl-1,2,4-triazolyl-(3)]-thioglycollic acid (compound 28)	15.2

The above substances may be added in the manner indicated in Example 1.

Transfer layer

A formalin-hardened gelatin layer is applied to a paper support (85 g. per square meter of raw paper) as described in Example 2. The layer should contain between 2 and 25 mg. of colloidal nickel sulfide per m.² as development nuclei.

ZnS is also suitable as development nuclei, which may be present in quantities between 1 and 100 mg./m.². Mixtures of different metal sulfides can also be used as nuclei.

Over the layer of nuclei is applied, by a method analogous to that described in Example 2, a sodium alginate layer which contains 1-phenylpyrazolidone in quantities between 0.2 and 1.2 g.

The sodium alginate can be replaced, for example, by starch ethers such as starch ethyl ether or plant products such as binding agents from carob bean flour, for example, the product marketed by Henkel Cie. under the trade name Wakal, or galactomannane such as that sold under the trade name Meypro-Guar by Meyhall Chemical AG, Kreuzlingen of Switzerland.

The nuclei-containing layer may also contain, in addition to the usual additives, wetting agents, optical brighteners and substances which influence the image tone, such as heterocyclic mercapto compounds, e.g., 1-phenylmercaptotetrazole.

Processing

The silver salt emulsion layer is imagewise exposed, moistened with water and brought into contact with the dry transfer layer. After separation of the two materials a positive image of the original is obtained in the transfer layer. The contact time is about 5 seconds.

EXAMPLE 3

33 g. of carboxymethylthiomalic acid (compound 9) and 1.0 g. of sodium chloride are added in the form of a 10% aqueous solution to a liter of a 6% aqueous gelatin solution. The solution is acidified with 15 ml. of a 25% aqueous sulfuric acid and the corresponding silver salts are then precipitated at 40° C. by the addition of 21 g. of silver nitrate in the form of a 10% aqueous solution.

A light-sensitive layer is prepared and further processed as described in Example 1.

A positive transfer image with improved density is obtained.

We claim:

1. In the silver salt diffusion process of imagewise exposing a supported light-sensitive silver salt emulsion layer, developing the exposed layer and transferring the silver salt from the unexposed and undeveloped portions of the light-sensitive layer to a transfer layer where the transferred silver salts are reduced to a positive silver image, the improvement according to which at least 75 mol percent of the silver salt is a light-sensitive silver salt of an aliphatic carboxylic acid the aliphatic chain of which is substituted with an organo thioether group, which salt is soluble in water at a pH between 1 and 7 in an amount of at least 0.2 g. silver in the form of the silver salt per liter and capable of being developed at a pH between 1 and 7, and the developing is effected at said pH.

2. The combination of claim 1, wherein the light-sensitive silver salt has the following formula:

$$R—[(S)_n—X—COO\ Ag]_m$$

wherein

m=1–3;

n=1 or 2;

R stands for alkyl having up to 3 carbon atoms, a radical of the benzene of naphthalene series or a heterocyclic ring of the group consisting of diazolyl, oxazolyl, triazolyl, thiadiazolyl, oxadiazolyl, tetrazolyl, azaindenyl, benzthiazolyl, naphthothiazolyl, benzoxazolyl, naphthoxazolyl, pyridyl, quinolyl, pyrimidinyl, quinoxalinyl, and quinazolinyl;

X represents an alkylene chain having up to 3 carbon atoms in the chain.

3. The combination of claim 2, wherein the silver salt emulsion layer has a pH of between 1 and 6.

4. The combination of claim 1, wherein the development is performed with a developer of the pyrazolidone-(3) series, the 3-aminopyrazoline series, the 3-aminopyrazolone series or ascorbic acid.

5. The combination of claim 4, wherein the development is performed with 1-phenyl-pyrazolidone-(3).

6. The combination of claim 1, wherein the transfer layer comprises a supported layer development nuclei contained in said layer and a second layer overcoating said supported layer and containing the developer compound.

7. The combination of claim 1, wherein the light-sensitive silver salt is a silver salt of an S-[phenyl]thioglycollic acid, an S-[triazolyl]-thioglycollic acid, an S-[thiadiazolyl]-thioglycollic acid, a thiodiglycollic acid or a bis-[β-(carboxy-methylthio)-ethyl]-ether.

8. The combination of claim 1, wherein the light-sensitive silver salt is essentially the silver salt of carboxymethylthiomalic acid.

References Cited

UNITED STATES PATENTS

3,330,663 7/1967 Weyde et al. ---------- 96—94

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96—94