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[54] FOGGED, DIRECT-POSITIVE EMULSION CONTAINING COMPOSITE SILVER HALIDE GRAINS PROTECTED WITH SILVER HALIDE LAYER AND THE USE THEREOF IN REVERSAL PROCESS

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[58] **Field of Search** 96/107, 108, 109, 64, 120

[56] **References Cited**
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[57] ABSTRACT

A direct positive photographic image material made up of silver halide grains on which development nuclei are formed by pre-exposure fogging are contained in a supported light-sensitive emulsion with a binding agent. The silver halide grains are covered with a protective layer of a silver salt, which silver salt is soluble in a solvent applied to the emulsion with the developer after imagewise exposure.

The protective coating of silver salt stabilizes the fogged emulsion against sensitivity loss.

10 Claims, No Drawings

FOGGED, DIRECT-POSITIVE EMULSION CONTAINING COMPOSITE SILVER HALIDE GRAINS PROTECTED WITH SILVER HALIDE LAYER AND THE USE THEREOF IN REVERSAL PROCESS

This invention relates to a photographic material and a process for the production of direct positive photographic images by imagewise exposure of a photographic material which contains at least one fogged silver salt emulsion layer whereby the developable fog is eliminated imagewise and a direct positive image is subsequently obtained by photographic development.

Direct positive images are generally produced using silver halide emulsions which have been fogged by exposure to light or fogged by chemical treatment. If the emulsions are then exposed imagewise under certain conditions, the developable fog is destroyed in the exposed areas but remains intact in the unexposed areas so that a direct positive image is subsequently obtained by development. Destruction of the developable fog by imagewise exposure is achieved mainly by making use of the Herschel effect or also by the solarisation effect. In the former case, exposure is carried out with longwave light from the absorption range of silver so that the silver nuclei in the exposed areas are destroyed. In the case of the solarisation effect, exposure is carried out with shortwave light from the absorption range of the silver halide. This also leads to destruction of the developable fog. These two processes have remained of minor practical importance because the usual photographic emulsions have relatively little sensitivity.

As described in the article by E. MOISAR and S. WAGNER in "Berichte der Bunsengesellschaft für physikalische Chemie" 67 (1963) 356–359, the sensitivity of fogged direct positive silver halide emulsions can be increased by incorporating ripening nuclei into the interior of the silver halide grain so that the photoelectrons formed in the primary process, which prevent destruction of the developable fog nuclei on the surface of the grain, are trapped in the interior of the grain. The preparation of such emulsions has been described in German Patent Specification No. 1,169,290. An increase in the sensitivity to light can also be obtained in fogged silver halide emulsions which are free from internal nuclei by adding desensitising dyes in accordance with British Patent Specification No. 723,019.

The light sensitivity of fogged direct positive silver halide emulsions depends on the exposure which is necessary to destroy the developable fog nuclei at the surface of the silver halide grains in the process of imagewise exposure. This in turn depends on the size and number of these fog nuclei. They can be adjusted to their optimum size for any given direct positive silver halide emulsion by known methods of optimising the size and number of fog nuclei. Fogging of direct positive emulsions is generally carried out by means of chemical fogging agents.

If the emulsions are too heavily fogged, the fog nuclei can be adjusted to their optimum size and number by conventional bleaching processes. There are, however, limits to this possibility of increasing the sensitivity of direct positive emulsions since a relatively high degree of fogging is necessary to achieve a sufficiently high density in the direct positive silver image. By degree of fogging is meant the percentage proportion of fogged (and hence developable) silver halide in the layer. This is based on the fact that the maximum density increases monotonously with the maximum number of developable grains.

One disadvantage of the more highly sensitive direct positive emulsions in which the development nuclei on the surfaces of the silver halide grains have an optimum (i.e. relatively small) size lies in the sensitivity of these nuclei to oxidation. The development nuclei are destroyed in storage, especially if the emulsions are stored under moist conditions, so that both the sensitivity and the maximum density obtainable on development are greatly reduced. Stabilisation of the development nuclei by means of the additives commonly used for stabilising the latent image in negative emulsions is not possible in the case of direct positive emulsions because the light sensitivity of direct positive emulsions would also be severely reduced by such additives. The reason for this is that this stabilisation generally renders it more difficult for the development nuclei to be destroyed on imagewise exposure. It is known to stabilise fogged direct positive emulsions by adding gold salts before the emulsions are cast. A certain stabilising effect is thus achieved but the light sensitivity of the direct emulsions is still unduly reduced.

It is among the objects of the present invention to develop photographic materials for the production of direct positive photographic images, which materials should combine high stability in storage with optimum sensitivity to light and should yield direct positive images with sufficient maximum density.

We now have found a photographic material comprising at least one direct positive silver salt emulsion layer in which the silver salt grains have a composite grain structure in which the grains of the direct positive silver salt emulsion which is initially provided on the surface with a developable fog are enveloped with a protective layer of a silver salt.

A further subject of the present invention is a process for the production of direct positive photographic images by imagewise exposure of a photographic material comprising at least one direct positive silver salt emulsion layer in which the silver salt grains have a composite grain structure, accompanied by imagewise destruction of the developable fog and followed by photographic development to give a direct positive image, using a photographic material comprising at least one fogged developable direct positive silver salt emulsion layer in which the fogged silver salt grains are enveloped in a protective layer of a silver salt, development of the exposed layer being carried out with a developer which contains a silver salt solvent at least for the outer protective layer of silver salt.

The thickness of this protective layer of silver salt should be kept as low as possible in order to simplify development of the exposed direct positive silver salt emulsion layers according to the invention, i.e. in order to accelerate the process of dissolving the protective layer of silver salt by the developer to set free the developable nuclei which as a result of exposure are now distributed imagewise. The thickness of this protective layer may, however, vary within wide limits according to the nature of the direct positive emulsion and of the silver salt. The lower limit is necessarily determined by the requirement for a sufficient protective action and the upper limit by the requirement that the protective layer should dissolve sufficiently rapidly in the developer. Thicknesses of between 5 and 100 lattice planes have generally been found sufficient. If the silver salts used are silver halides, thicknesses of between 15 and 50 lattice planes are preferred for the protective layers.

The chemical nature of the silver salt used for the protective layer in principle is not critical. The most suitable silver salt used as protective layer in any given fogged direct positive emulsion can easily be determined by a few simple tests. Its composition may be the same as or different from that of the silver salt of the grain of the fogged direct positive emulsion. It preferably has substantially the same composition. Moreover, it has been found advantageous to use silver bromide as the silver salt for the protective layer. Reference may be made to the direct positive emulsion described in British Patent Specification No. 723,019.

The fogged direct positive silver salt emulsions preferably contain silver halides, e.g. silver chloride and/or silver bromide, if desired with a proportion of silver iodide which is preferably up to 10 mols percent. The direct positive silver salt emulsions are preferably silver bromide or silver iodobromide emulsions. Silver bromide emulsions which have been converted to silver iodide on the surface are particularly suitable.

Silver halide emulsions with silver halide grains which contain ripening nuclei in their interior are preferred. In the case of direct positive emulsions with ripening nuclei in the interior of the grains and a composite grain structure, the grains of the direct positive emulsion according to the invention then have at least three layers, namely the core, which is chemically ripened on the surface, the shell, which has a developable fog on the surface, and the outer protective layer which envelops and protects the fogged silver halide shell. These fogged and enveloped emulsions may contain the usual dyes used for optically sensitizing direct positive emulsions. The emulsions of the present invention constitute direct positive emulsions which have excellent stability both as regards their sensitivity and their maximum density. Samples of emulsion according to the invention have practically the same sensitivity and maximum density when freshly prepared and after prolonged storage under tropical conditions.

The binding agents used for the emulsion layer may be the usual hydrophilic film-forming substances, e.g. proteins in particular gelatin, alginic acid or its derivatives such as esters, amides or salts, cellulose derivatives such as carboxymethylcellulose and cellulose sulfates, starch or derivatives thereof or hydrophilic synthetic binders such as polyvinyl alcohol, partly saponified polyvinyl acetate, polyvinyl pyrrolidone, etc.

The hydrophilic binders in the layers may be mixed with other synthetic binders in a dissolved or dispersed form, such as homopolymers or copolymers of acrylic or methacrylic acid or derivatives thereof such as esters, amides or nitriles or vinyl polymers such as vinyl esters or vinyl ethers.

The fogged silver salt emulsions are applied to the usual layer supports such as glass or foils of cellulose esters such as cellulose acetate or cellulose acetobutyrate or polyester foils, in particular foils or polyethylene terephthalate or polycarbonate, particularly those based on bis-phenylolpropane.

Baryta paper supports or paper supports which have been backed with polyolefines such as polyethylene or polypropylene may also be used as layer supports.

The fogged silver halide emulsions according to the invention preferably have a narrow grain size distribution and are preferably fine grained emulsions as described in German Patent Specification No. 1,169,290.

Fogging of the silver halide grains in the photographic direct positive emulsions according to the invention is carried out in known manner by treatment with reducing agents, preferably in the presence of water-soluble salts of metals which are more electropositive than silver. Suitable reducing agents are e.g. tin-(II) salts such as tin-(II)chloride, hydrazine compounds, sulfur compounds such as thiourea dioxide, phosphonium salts e.g. tetra-(hydroxymethyl)phosphonium chloride or formamidine sulfinic acid. Suitable compounds of metals which are more electropositive than silver are, for example, salts of gold such as potassium chloroaurate or gold-(III) chloride, rhodium salts, platinum salts, palladium salts such as ammonium hexachloropalladate and iridium salts such as potassium chloroiridate.

The concentration of reducing agents and noble metal salts used for fogging may vary within wide limits. It is generally sufficient to employ concentrations of about 0.0005 to about 0.06 milliequivalents of reducing agent and about 0.001 to about 0.01 millimols of the noble metal salt per mol of silver halide as described in German Offenlegungsschrift No. 1,547,790. If the emulsions are too heavily fogged, they may subsequently be treated with a bleaching agent in known manner to adjust them to the optimum light sensitivity.

Fogging may also be carried out by the known method of silver salt digestion according to WOOD described in J.phot.Science, 1 (1963), page 163, carried out at pAg values of between 2 and 5 and pH values above 6.5.

According to a particularly preferred embodiment of this invention, the fogged direct positive silver halide emulsions used contain ripening nuclei in the interior of the silver halide grain. As described in the publication by E. MOISAR and S. WAGNER in "Berichte der Bunsengellschaft für physikalische Chemie" 67 (1963)356–359, the photoelectrons formed in the primary process, which prevent the destruction of developable fog nuclei at the surface of the grain, are thereby trapped in the grain interior. The preparation of such emulsions with a composite grain structure has been described in German Patent Specification No. 1,169,290 and in German Offenlegungschrift No. 1,597,488. The formation of ripening nuclei in the interior of the grain is carried out in known manner, e.g. by chemical sensitisation using noble metal compounds, in particular gold salts or iridium salts, or sulfur compounds such as thiosulphate or a combination of noble metal salts and sulfur compounds.

Other direct positive emulsions which are suitable for this invention have been described in German Patent Specifications Nos. 606,392 and 642,222 and in British Patent Specifications Nos. 581,773 and 655,009. The emulsions may also contain mercury salts or thallium salts as described in German Offenlegungschrift No. 1,622,256.

The protective layer which envelops the fogged silver halide shell is preferably applied by precipitation but it may also be applied by a process of redissolving and crystallisation by mixing the fogged emulsion with a finely grained emulsion and leaving it to undergo physical ripening. The coarser grains then grow at the expense of the smaller grains and the fine grained emulsion is deposited on the fogged, more coarsely grained emulsion.

The direct positive silver salt emulsions according to the invention which have fogged nuclei situated under the surface of the grains can be optically sensitised in the usual manner using either desensitisers or the sensitising dyes commonly used for negative emulsions.

Suitable desensitisers which are capable of acting as electron traps are usually compounds in which the sum of the anodic and cathodic polaragraphic half wave potential is positive. Compounds of this kind have been described in U.S. Patent Specification Nos. 3,501,305; 3,501,306 and 3,501,307. The sensitisers described in German Patent Specification No. 1,153,246 and in U.S. Patent Specification No. 3,314,796 are also suitable. Reference may also be made to the imidazoquinoxaline dyes, e.g. those described in Belgian Patent Specification No. 660,253.

The emulsions may contain the usual stabilisers, e.g. homopolar or salt-type compounds of mercury which contain aromatic or heterocyclic rings (such as mercaptotriazoles), simple mercury salts, sulfonium mercury double salts and other mercury compounds. Azaindenes are also suitable stabilisers, particularly tetra- or penta-azaindenes and especially those which are substituted with hydroxyl or amino groups. Compounds of this kind have been described in the article by BIRR, Z.Wiss.Phot. 47, 2–58 (1962). Other suitable stabilizers are e.g. heterocyclic mercapto compounds such as phenylmercapto tetrazole, quaternary benzothiazole derivatives, benzotriazole and the like.

The emulsions may be hardened in the usual manner, for example with formaldehyde or halogenated aldehydes which contain a carboxyl group, such as mucobromic acid, diketones, methanesulfonic acid esters, dialdehydes and the like.

Photographic materials which contain at least one of the direct positive silver salt emulsion layers according to the invention may be used for various photographic purposes, e.g. as materials with steep gradation for reprographic purposes, as direct positive X-ray films, for the production of direct positive colored images, e.g. by the silver dye bleaching process or dye diffusion process, or for the production of photographic color images by conventional processes of chromogenic development.

The materials according to the invention may also be used for color intensifying processes or for the production of bubble images according to German Offenlegungsschrift 2,201,849.

After exposure, the material according to the invention is processed in the usual manner. The usual black-and-white or color-forming developers may be used for development but they must contain a solvent for the external protective layer of silver salt. Suitable solvents for this purpose are e.g. sulfites, thiocyanates or thiosulfates, particularly of alkali metals, ammonium or alkaline earth metals, or organic solvents such as triethanolamine. The concentration of solvent required in the developer varies from 0.03 g to 130 g per litre of developer according to the nature of the silver salt of the protective layer and the dissolving power of the solvent. The optimum quantity can easily be determined by a few simple tests.

The examples given below demonstrate that the loss of sensitivity in storage is largely eliminated by displacing the fog nuclei into the interior of the grain in accordance with the invention. Furthermore, in the case of spectrally sensitised emulsions, the reduction in maximum density which is frequently observed after storage of such emulsions is greatly attenutated by the application of a protective shell in accordance with the invention.

EXAMPLE 1

a. Preparation of a comparison emulsion

720 ml of a 3-molar $AgNO_3$ solution and 720 ml of a 3-molar KBr solution are fed into a solution of 40 g of gelatin in 800 ml of water at 55°C by means of dosing pumps at the rate of 240 ml per hour each, the pAg being adjusted to about 7.5. 32 g of gelatin and 64 ml of water are added after precipitation. The emulsion is washed with water in the usual manner and then ripened at 50°C for 1 hour after addition of 26 ml of a 10^{-2} molar solution of $Na_3[Au(S_2O_3)_2]$. The emulsion is then left to solidity and washed. 2.22 Litres of a 3 molar $AgNO_3$ solution and 2.22 litres of a 3 molar KBr solution are then run into this emulsion at 65°C at the rate of 740 ml per hour from dosing pumps, the pAg being adjusted to about 7.5. 220 g of gelatin and 440 ml of water are added after precipitation. The emulsion is washed in the usual manner and then contains 8.7 % of Ag in the form of silver halide. After washing, the emulsion is fogged by treating it for 2 hours with 0.57 μ mol of formamidine sulfinic acid per mol of AgBr and 3.5 μ mol of $H[AuCl_4]$ per mol of AgBr at 60°C.

b. Preparation of the emulsion according to the invention

A layer of silver bromide is precipitated on the surface of the grains of the above described comparison emulsion by feeding 40 ml of a 3-molar $AgNO_3$ solution and 40 ml of a 3-molar KBr solution into 360 g of the comparison emulsion at 50°C by way of dosing pumps at the rate of 92 ml per hour, the pAg value being adjusted to about +7.5. The emulsion is then left to solidify and washed in the usual manner. The protective layer precipitated on the surfaces of the grains has a thickness of about 30 lattice planes.

c. Processing of the emulsion

The comparison emulsion and the emulsion according to the invention are diluted with a 10% gelatin solution using a proportion by weight of emulsion to gelatin solution of 1:1 and the diluted emulsions are cast to form films (silver application 3.2 g/m^2).

Samples of these two light sensitive materials were stored in a heating cupboard (60°C, 40% relative humidity) while other samples of these materials were stored at 20°C for two days. After exposure to a 500 Watt incandescent lamp from a distance of 1.5 m behind a grey wedge, the samples were developed in the following developer at 20°C for 13 minutes:

Sodium sulfite	100 g
Hydroquinone	15 g
Potassium carbonate	26 g
1-Phenylpyrazolidone-3	1 g
Water up to 1 litre	

The emulsions were then fixed and washed in the usual manner. Positive step wedges were obtained in all cases.

The results of the sensitometric test are summarised in the Table below. The loss in sensitivity on storage in a heating cupboard under the conditions specified above is entered in the second column of the Table as a percentage of the sensitivity of the freshly prepared sample. The sensitivity was determined according to DIN 4512, sheet 4.

Table 1

Sample	Loss in sensitivity after storage in heating cupboard in % of sensitivity of fresh sample
Comparison emulsion	54%
Emulsion according to the invention	0%

EXAMPLE 2

a. Preparation of a comparison emulsion

720 ml of a 3-molar $AgNO_3$ solution and 720 ml of a 3-molar KBr solution are introduced into a solution of 40 g of gelatin in 800 ml of water at 55°C at the rate of 320 ml per hour by way of dosing pumps, the pAg being adjusted to about +7.5. 32 g of gelatin and 64 ml of water are added after precipitation. The emulsion is washed in the usual manner and ripened for 1 hour at 50°C after the addition of 76 ml of a 10^{-2} molar solution of $Na_3[Au(S_2O_3)_2]$. When the emulsion has solidified it is washed with water.

4.5 Litres of a 3-molar $AgNO_3$ solution and 4.5 litres of a 3-molar KBr solution are introduced into this emulsion at 50°C. at the rate of 1600 ml per hour by way of dosing pumps, the pAg being adjusted to about 7.5. 450 g of gelatin and 900 ml of water are added after precipitation. After being washed in the usual manner, the emulsion contains 8.8% of Ag. The emulsion is then fogged by treating if for 80 minutes at 60°C with 0.57 μ mol of formamidine sulfinic acid per mol of AgBr and 2.3 μ mol $H[AuCl_4]$ per mol of AgBr.

b. Preparation of the emulsion according to the invention

The pAg value in 380 g of the comparison emulsion described above is raised to +9.5 by the addition of a 0.3 molar solution of KI at 50°C. A layer of silver bromide is then precipitated on the emulsion grains by introducing 35 ml of a 3-molar $AgNO_3$ solution and 35 ml of a 3-molar KBr solution by way of dosing pumps at a rate of 140 ml per hour at 50°C, the pAg being adjusted to about +7.5. The emulsion is then left to solidify and washed in the usual manner.

c. Processing of the emulsions

The comparison emulsion and the emulsion according to the invention are processed as described in Example 1.

The results of the sensitometric measurements are summarised in the following Table in which the columns have the same meaning as in the table of Example 1.

Sample	Loss in sensitivity after storage in heating cupboard in % of sensitivity of fresh sample
Comparison emulsion	57%
Emulsion according to the invention	11%

EXAMPLE 3

a. Preparation of a comparison emulsion

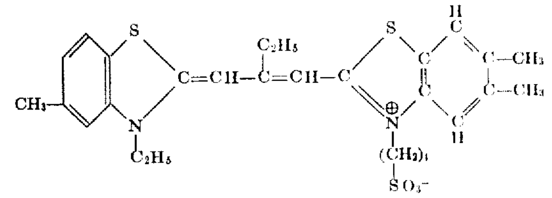
As in Example 2.

b. Preparation of the emulsion according to the invention

35 ml of a 3-molar $AgNO_3$ solution and 35 ml of a 3-molar KBr solution are introduced into 380 g of the comparison emulsion described above at 50°C by means of dosing pumps at a rate of 140 ml/hour, the pAg being adjusted to about +7.5. The emulsion is then solidified and washed.

c. Processing

100 g of the emulsion according to the invention are mixed with 100 ml of a 10% gelatin solution and 17 ml of a 0.1% solution of the compound of the following formula



in dimethylsulfoxide at 40°C and cast on a layer support of cellulose acetate (silver application 3.2 g of Ag in the form of silver halide per m²).

The analogous procedure was adopted for the comparison emulsion. The sensitising dye shown above has been described in German Patent Specification No. 1,072,765.

Samples taken from both these light sensitive materials were stored in a heating cupboard for 2 days (60°C, 40% relative humidity) and other samples of these materials were stored at 20°C for 2 days.

After exposure to a 500 Watt incandescent lamp from a distance of 1.5 m behind a grey wedge and a red filter (Agfa-Gevaert L 622), the samples were developed as described in Example 1.

The results of the sensitometric measurements are summarised in the table below. The column 2 has the same meaning as in the table in Example 1. The maximum densities are compared in the third column of the table.

Sample	Loss in sensitivity after storage in heating cupboard in percent of sensitivity of fresh sample	Reduction of D_{max} after storage in heating cupboard in % of D_{max} of fresh sample
Comparison emulsion	21%	69%
Emulsion according to the invention	3	4%

What we claim is:

1. A light-sensitive photographic material comprising a supported direct positive silver halide emulsion layer containing silver halide grains of composite structure, the said grains comprising a core of silver halide which is chemically sensitized, the said core is coated by a silver halide shell which at the surface contains spontaneously developable fog and an outer protective layer of silver halide which envelops the shell and covering the developable nuclei protects the nuclei from desensitization the thickness of said protective layer is between 5 and 100 lattice planes of silver halide.

2. A process for the production of direct positive photographic images comprising the steps of

a. preparing a light-sensitive photographic material comprising a supported direct positive silver halide emulsion layer containing silver halide grains of composite structure, the said grains comprising a core of silver halide which is chemically sensitized the said core is coated by a silver halide shell which at the surface contains spontaneously developable fog and an outer protective layer of silver halide which is covering the developable nuclei protecting the nuclei from densitization the thickness of said protective layer is between 5 and 100 lattice planes of silver halide;

b. imagewise exposure and

c. development of the exposed layer with a developer solution containing a solvent for the silver halide of the said protective layer.

3. The photographic material of claim **1**, wherein the soluble silver salt is silver bromide which may contain up to 10% of silver iodide.

4. The photographic material of claim **1**, wherein the silver halide grains with development nuclei are the product of fogging the silver halide grains with a reducing fogging agent in the presence of a compound of a metal selected from the group consisting of gold and a metal more electropositive than silver.

5. The photographic material of claim **1**, wherein the emulsion is optically sensitized.

6. The process of claim **2**, wherein the protective layer has a thickness of 15 to 50 lattice planes.

7. The process of claim **2**, wherein the silver halide is silver bromide or silver iodobromide with an iodide content of up to 10 mols percent.

8. The process of claim **2**, wherein the developer contains a silver halide solvent selected from the group consisting of sulfite ions, thiocyanate ions, thiosulfate ions and triethanolamine.

9. A light-sensitive photographic material comprising a supported direct positive silver halide emulsion layer containing silver halide grains of composite structure having spontaneously developable nuclei on the surface of the grain, the said surface containing the spontaneously developable nuclei being enveloped by a covering layer consisting essentially of a soluble silver salt so as to be protected from desensitization the thickness of the said protective layer is between 5 and 100 lattice planes of silver halide.

10. The photographic material of claim **1**, wherein the protective layer has a thickness of 15 to 50 lattice planes.

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