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HIGHLY SENSITIVE DIRECT POSITIVE PHOTOGRAPHIC MATERIAL WITH EXTREMELY STEEP GRADATION

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ABSTRACT OF THE DISCLOSURE

Very high contrast images are made by silver salt diffusion method with a light-sensitive silver halide emulsion in which 10–40 mol percent of the silver halide is silver bromide, the remainder being silver chloride, and the emulsion contains a material that keeps it from hardening by aldehyde, the emulsion being coated on a thin hardened gelatin intermediate layer which in turn is coated on a supported hardened gelatin transfer layer containing development nuclei and blue toner. The emulsion can be slightly fogged.

This invention relates to a three-layer photographic material for the production of direct positive images with extremely steep gradation by the silver salt diffusion process.

The action of direct positive films can be based on various principles, for example on the Herschel effect. Films of this type consist of chemically fogged or pre-exposed silver halide emulsions, which produce a positive image by a subsequent image-wise exposure with red or infrared light.

Also, the phenomenon which is known as solarisation, according to which silver halide emulsions with increasing light exposure pass through a maximum in the density curve, can be used for the production of positive images. Another photographic effect which is known as the Villard effect can likewise serve for the production of direct positive images. In this case, the light-sensitive photographic layers are pre-exposed with X-rays and subsequently exposed with normal light to form an image.

Yet another fundamentally different possibility of obtaining positive images consists in the reversal development, in which the silver formed in the first development is bleached and dissolved out, the remaining silver halide is uniformly after-exposed with diffused light and once again developed.

All these processes have disadvantages, such as very long exposure times (Herschel effect, solarisation effect) or complicated processing (Villard effect, reversal development).

Positive images can be produced in a relatively simple manner by the so-called silver salt diffusion process. In this process, generally a negative paper with a light-sensitive layer is employed together with a transfer material which contains a layer with reducing agents or development nuclei. These layers are processed by both layers being developed in contact with one another in the presence of silver salt solvents. The undeveloped silver salt of the emulsion layer is dissolved in complex form and diffuses into the image-receiving or transfer layer, where it is deposited on the development nuclei. Processes for silver salt diffusion have also been proposed in which a two-layer material is employed. In this case, the so-called nucleus layer and the light-sensitive layer containing the silver halide are cast one above the other. After the development and diffusion of the silver complexes into the nucleus layer disposed therebeneath, the light-sensitive emulsion layer is rinsed off.

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It is also known to use two-layer materials with a reversed layer arrangement, in which the light-sensitive layer is situated beneath the transfer or nucleus layer. The nucleus layer containing the final silver image is transferred to a second support to complete the processing of such an arrangement.

However, all the prior known processes yield silver images which have soft to medium hard gradations after the development. By gradation is meant the characteristic curve or H and D-curve of an emulsion. For the reproduction of line or screen originals, however, it is necessary to employ a film with extremely steep gradation, since the sharpness of a record reproduced on a photographic layer is largely dependent on the gradation of the light-sensitive layer. The required extremely steep gradation which is not a normal property of the emulsion being used, can only be produced by a special "litho development" with a paraformaldehyde bisulphite developer.

It is among the objects of the present invention to provide a light-sensitive material which yields after exposure and processing direct positive silver images with an extremely steep gradation. Other objects and advantages of the photographic material and the process, some of which are referred to specifically hereinafter, will be evident to those skilled in the art to which this invention pertains.

It has now been found possible to produce direct positive images with extremely steep gradation in a relatively simple manner by the silver salt diffusion process if a three-layer material is employed which has the following layer arrangement and the following layer composition:

(1) Support.—For this purpose, conventional transparent or opaque materials can be used, such as paper, cellulose ester, polystyrene polycarbonates, especially of bis-phenylol alkanes, or polyesters particularly those of ethylene glycol and terephthalic acid. The support can, if desired, be provided in the usual way with a subbing layer.

(2) The layer containing the silver-precipitating development nuclei is coated on the support. Suitable nuclei are, for example, colloidally dispersed noble metals, such as silver, gold, etc., or sulfides or selenides of various metals, e.g., of silver, zinc, cadmium or sodium. Gelatine is used as the layer-forming binding agent. The layer thickness should be between 0.5 and 3μ, advantageously 1–2μ. The concentration of the nuclei, for example of silver sulfide, should correspond to 0.8–2 mg., advantageously about 1.2–1.6 mg., of silver per square meter.

For producing a neutral image tone and for increasing the gradation, so-called blue toners are added, which are known per se, for example, imidazoles, triazoles, tetrazoles, preferably those with mercapto groups like phenyl mercaptotetrazole. Suitable compounds are disclosed in German Patents Nos. 887,733, 890,755; German Auslegeschrift 1,062,112, 1,064,807, 1,070,029, 1,153,247; French Patent No. 1,140,526; British Patent Nos. 706,333, 922,479; U.S. Patent No. 2,704,721 and Belgian Patents Nos. 542,151 and 574,756. It is also possible to employ for this purpose quaternary ammonium salts and thioethers. The necessary amount of blue toners, for example, 1-phenyl mercaptotetrazole, is between 5 and 25 g./g. of silver, advantageously 13–20 g., based on the silver in the transfer layer containing the development nuclei.

The nucleus layer is well hardened in the usual way, for example, by the addition of formalin, mucochloric acid or glyoxal, so that its softening or melting point lies above 100° C. preferably between 100° and 120° C. No softening of the layer should occur below 100° C.

(3) Onto this nucleus layer is cast an intermediate layer of gelatine, which likewise is hardened in the same manner. The thickness of this layer should amount to approximately ⅓ up to at most 3 times the thickness of the nucleus layer and it is provided to facilitate the washing away of the emulsion layer which is necessary during the processing, and more especially to protect the silver image in the nucleus layer from mechanical damage. It is preferred to use intermediate layers which are of the same thickness as the nucleus layer, or thinner than it by approximately the factor 0.3.

(4) The light-sensitive gelatino-silver halide emulsion is applied as the uppermost layer, the light-sensitive silver halide containing 10–40 mol percent of silver bromide and 90–60 mol percent of silver chloride, advantageously of 20–35 mol percent of silver bromide and 65–80% of silver chloride. Preferred are emulsions, which are slightly fogged. Particularly suitable are emulsions uniformly fogged to a degree that they yield a silver density of about 0.3–0.5 when developed with the following developer at 20° C. for 3 minutes:

Water	ml	700
Anhydrous Na_2SO_3	g	80
Hydroquinone	g	15
KBr	g	2
1-phenyl-3-pyrazolidone	g	1
Caustic soda	g	10

With such highly sensitive emulsions it is possible to obtain γ values greater than 10.

The emulsions can be prepared by known processes. They are rinsed and ripened up to maximum sensitivity. In order to produce an increased sensitivity, the emulsion may contain sulphur sensitizers, for example, thiosulphate or thiourea, or reduction sensitizers, such as tin salts. Noble metals, such as gold, palladium, ruthenium, rhodium and iridium, can also be added. The emulsion may further contain other chemical sensitizers, such as onium salts, e.g. ammonium, sulphonium and phosphonium salts, as well as polyethylene oxides. Optical sensitization is effected with known sensitizing dyes such as cyanines and merocyanines.

In order to improve the keeping qualities stabilizers against the formation of fog, such as tetrazoles, triazoles, azaindenes and mercapto compounds, as well as mercury salts can be added to the emulsion.

The emulsion layer is not hardened. In order to avoid the diffusion of hardening agents from the nucleus or intermediate layer into the emulsion layer and hardening the latter, primary amino compounds which are photographically inert and which are capable of preventing the hardening of the gelatine layer by aldehyde compounds, such as formaldehyde, are added to the emulsion. Preferred are aliphatic compounds having up to 5 carbon atoms in particular derivatives of carbonic acid, such as urea in a concentration of 1 to 5 grams per kilogram of emulsion or guanidine, or degraded gelatine. By degraded gelatine is meant natural gelatin which has been treated with acids or alkalis and which has an average molecular weight of between some hundreds and 10,000. The hardening can also be largely prevented by adjusting the pH value of the emulsion to a value between 3 and 5, advantageously 3.5 to 4.5. The light-sensitive layer has a softening or melting point of between 30 and 50° C.

The usual caustic alkali baths with a developer combination of 1-phenyl-3-pyrazolidone and hydroquinone, or monomethyl-p-aminophenol and hydroquinone, are suitable as developers, it being necessary for these developers to contain a solvent for the silver halide, e.g., sodium thiosulphate or sodium sulphite, in quantities of about 10–20 g./1.

The materials are processed in known manner and the unhardened negative layer, after exposure and development, is rinsed off with warm water having a temperature of between 30 and 60° C.

Example 1

A fine-grain gelatino-silver chlorobromide emulsion with 30 mol percent of bromide and 70 mol percent of chloride and a content of 1.5 g. of urea per kg. of emulsion ready for casting, is produced by the usual methods (see, for example, P. Glafkides "Photographic Chemistry," vol. I, Fountain Press, London, 1958), washed and ripened up to maximum sensitivity. The ratio between silver and gelatine is 1:1. If the emulsion is cast on to a conventional support casting thickness about 8μ), exposed and developed, it yields a γ value of 4.1 after 3 minutes of developing the the following developer:

	Grams
Monomethyl-p-aminophenol	7.5
Anhydrous sodium sulphite	40.0
Hydroquinone	3.5
Anhydrous sodium carbonate	30.0
Potassium bromide	3.0

Made up with water to 1 liter.

The same emulsion is applied with a thickness of about 5μ onto a hardened gelatine layer with a thickness of about 0.5μ, which had been coated on a supported hardened gelatine layer containing development nuclei consisting of Ag_2S and blue toners in a layer thickness of about 1μ. The resulting photographic element is exposed and developed for 3 minutes in a developer with the composition as indicated below. After washing off the emulsion layer with warm water, a γ value higher than 15 is obtained in the hardened gelatine layer which had contained the development nuclei, with a fogging value of 0.07, the maximum density being higher than 3.

The developer has the following composition:

Water	ml	700
Anhydrous Na_2SO_3	g	80
Hydroquinone	g	15
KBr	g	2
1-phenyl-3-pyrazolidone	g	1
Caustic soda	g	10
$Na_2S_2O_3 \cdot 5H_2O$	g	15

Instead of 1 g. of 1-phenyl-3-pyrazolidone, it is also possible to use 2.5 g. of monomethyl-p-aminophenol, but the development time then has to be somewhat increased.

Since the positive layer is very thin, a period of time of 1–3 minutes is required for drying the film in a moderate air stream. The total processing time until the developed and dry film is obtained is at most about 5–8 minutes.

Example 2

A gelatino-silver chlorobromide emulsion the silver halide of which consists of 20 mol percent of bromide and 80 mol percent of chloride and which contains 1.5 g. of urea per kg. is prepared as indicated in Example 1. That emulsion is applied onto the hardened gelatine layer of a multilayer element consisting of the hardened gelatin layer coated on another hardened gelatin layer which contains development nuclei consisting of silver and blue toners.

The film is exposed and developed for 3 minutes in the second mentioned developer of Example 1 and the emulsion layer is rinsed off. The resulting silver image has a γ value of about 15, the maximum density being higher than 3. The fogging value is 0.07.

The silver halide emulsion of Example 2 which contains 20 mol percent of silver bromide is half as sensitive as the emulsion of Example 1.

Example 3

The light-sensitive three layer photographic element is produced as described in Examples 1 and 2, the silver halide of the light-sensitive layer consisting of 90% of silver chloride and 10% of silver bromide. The film is exposed and developed for 3 minutes in the second mentioned developer of Example 1. Thereafter the emulsion layer is washed off. The resulting silver image in the layer which had contained the development nuclei has a γ value of 12, the maximum density being higher than 3. The photographic material of Example 1 is 4 times as sensitive as the material of this example. The fogging of the material of the present example is 0.06.

We claim:

1. A light-sensitive photographic element consisting essentially of

(I) an unhardened silver halide gelatin emulsion layer having a softening point of between 30 and 50° C. and a pH-value of between 3 and 5, the silver halide of which consist of 10–40 mol percent of silver bromide and 90–60 mol percent of silver chloride, the emulsion layer additionally containing a compound having a primary amino group capable of preventing hardening of the gelatin in the layer, the emulsion layer being coated on an

(II) intermediate layer consisting essentially of hardened gelatin, superimposed on a

(III) nucleus layer the binding agent of which consists essentially of hardened gelatin having a softening point of above 100° C., the thickness of the nucleus layer being 0.5–3 microns and between ⅓ to 3 times the thickness of the intermediate layer, the nucleus layer containing blue toner and development nuclei in an amount corresponding to 0.8–2 mg. silver per square meter, the nucleus layer being coated on

(IV) a sheetlike support.

2. A light-sensitive photographic element as defined in claim **1**, wherein the nucleus layer contains development nuclei in an amount corresponding to 1.2–1.6 mg. silver per square meter and 1-phenylmercaptotetrazole as blue toner in an amount of between 13–20 g. per g. of silver.

3. A light-sensitive photographic element as defined in claim **1**, wherein the silver halide gelatin emulsion layer contains 1–5 g. urea as hardening preventing agent per kg. of the emulsion.

4. A process for the production of direct positive photographic images of exteremely high contrast, comprising the steps of

(a) exposing an object to be reproduced to a light-sensitive photographic element which consists of

(I) an unhardened silver halide gelatin emulsion layer having a softening point of between 30 and 50° C. and a pH-value of between 3 and 5,

the silver halide of which consists of 10–40 mol percent of silver bromide and 90–60 mol percent of silver chloride, said emulsion layer additionally containing a compound having a primary amino group capable of preventing hardening of the gelatin in the layer, the emulsion layer being coated on an

(II) intermediate layer consisting essentially of hardened gelatin, superimposed on a

(III) nucleus layer the binding agent of which consists essentially of hardened gelatin having a softening point of above 100° C., the thickness of the nucleus layer being 0.5–3 microns and between ⅓ to 3 times the thickness of the intermediate layer, the nucleus layer containing blue toner and development nuclei in an amount corresponding to 0.8–2 mg. silver per square meter, the nucleus layer being coated on

(IV) a sheetlike support,

(b) developing the exposed photographic element in an aqueous caustic developing bath containing a developer compound and a silver halide solvent,

(c) washing off the exposed and developed layer (I) with warm water and

(d) drying the resulting direct positive image.

5. A process as defined in claim **4**, wherein the nucleus layer of the light-sensitive photographic element contains development nuclei in an amount corresponding to 1.2–1.6 mg. silver per square meter and 1-phenylmercapto tetrazole as blue toner in an amount of between 13–20 g. per g. of silver.

6. A process as defined in claim **4**, wherein the silver halide gelatin emulsion layer of the light-sensitive photographic element contains 1–5 g. urea as hardening preventing agent per kg. of the emulsion.

References Cited

UNITED STATES PATENTS

2,635,048	4/1953	Land	96—29
2,834,676	5/1958	Stanley et al.	96—29
3,020,155	2/1962	Yackel et al.	96—29
3,311,473	3/1967	Foster et al.	96—29

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