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(54) Method of making direct-positive images.

(57) Method of making direct-positive images, comprising image-wise exposing a light-sensitive silver halide element comprising a support and at least one internal latent image-type silver halide emulsion layer, and developing the exposed element with a developer comprising 10 to 50 g of hydroquinone per litre in the presence of at least one development nucleator and in the presence of density-stabilizing amounts of organic non-aromatic onium salt.

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BACKGROUND OF THE INVENTION

Field of the invention.

The present invention relates to a method of making direct-positive images by development in the presence of a development nucleator of photographic light-sensitive silver halide elements, said images having a satisfactory maximum density even when exhaustion of the hydroquinone surface-type developer is in progress.

In silver halide photography a photographic method, according to which a positive image is made without the use of a negative image or an intermediary process producing a negative image, is called a direct-positive method. A photographic light-sensitive element and a photographic emulsion for use according to such photographic method are called direct-positive element and direct-positive emulsion respectively.

A variety of direct-positive photographic methods are known. The most useful methods are the method, which comprises exposing prefogged silver halide grains to light in the presence of internal or external electron acceptors and developing them, and the method, which comprises subjecting a silver halide emulsion containing silver halide grains that have light-sensitive specks mainly inside the grains to an image-wise exposure and developing the exposed emulsion in the presence of a development nucleator. The present invention relates to the latter method. A silver halide emulsion comprising light-sensitive specks mainly inside the grains and which forms latent images mainly inside the grains is referred to as internal latent image-type silver halide emulsion, and thus is distinguished from silver halide grains that form latent images mainly at the surface of the grains.

It is known to develop a latent image that has been formed mainly inside the grains by means of a so-called internal developer, but the method, element, and emulsions used in accordance with the present invention are not concerned with that type of development, but rather with the type of development using a so-called surface developeror surface-type developer.

Description of the Prior art :

Methods for making a direct-positive image by development of an exposed internal latent image-type silver halide emulsion in the presence of a development nucleator by means of a surface developer, and photographic emulsions and photographic light-sensitive elements used in such methods have been disclosed in i.a. GB-A 1,011,062, 1,151,363, 1,195,837, in JA Patent Publication No. 29,405/68, in US-A 2,456,953, 2,497,875, 2,497,876, 2,588,982, 2,592,250, 2,675,318, 3,227,552, 3,761,276, and 4,540,655.

In the internal latent image-type method for making a direct-positive image, the development nucleator may be incorporated into a developer, but it is usually incorporated into the photographic emulsion layer or in another layer of the photographic light-sensitive element. Development nucleators that can be used in the above-described method for making a direct-positive image include hydrazine and derivatives thereof as described in i.a. "Zeitschrift für Wissenschaftliche Photographie" by Arens, vol. 48, (1953) p.48, DD-A 5024, DE-A 3,021,423, in US-A 2,563,785, 2,588,982, 3,227,552, 4,245,037, 4,374,923, 4,540,655 , in Research Disclosure 23,510, p. 346-348, in EP-A 416,174, and in PCT/EP 90/01433 and the literature referred to in these documents.

The fogging action of development nucleators in internal latent-type silver halide emulsions is triggered only when the pH of the developer used is sufficiently high i.e. at least 10.5. To reach satisfactory results in particular with respect to maximum density (Dmax) it is customary to increase the pH to values as high as 12 to 13 or even more. Also for rapid processing purposes a higher pH value has to be recommended. However, an increase of the pH of the developer to such high values leads to an increased susceptibility of the solution to aerial oxidation. The oxidation gives rise to substantial changes in the photographic characteristics and in particular it leads to a reduction in Dmax.

Different solutions for this problem have been described earlier. In EP-A 416,174 the use of density-increasing amounts of a compound chosen from the class consisting of formic acid, oxalic acid, glyoxylic acid, or salts thereof and/or of a compound chosen from the class consisting of polyethylene glycols is recommended for addition to the photographic element and/or the developer.

Although it is possible to get sufficiently high maximum densities when exposed photographic elements are developed in a fresh developer, the problem of low maximum densities appears as soon as exhaustion of said developer takes place. This is due to oxidation products generated by aerial oxidation and/or multiple development work. In US-P 4,540,655 the use of increased amounts of developing agent i.e. more than 25 g of hydroquinone has been proposed to get a stable developer. In order to realize the same effect without necessarily increasing the hydroquinone content of the developer, 0.02 to 1.00 mol of density-preserving substituted phenol derivative and 0.025 to 0.500 mol of alkanolamine can be added per liter of developer as described in EP Application N° 91201725.8, which corresponds to the US Serial N° .

Yet, the maximum density obtained in an exhausted developer is still too low.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a method of making direct-positive images by development in the presence of a development nucleator of photographic light-sensitive silver halide elements, said images having a satisfactory maximum density even when exhaustion of the hydroquinone surface-type developer is in progress.

It is also an object of the present invention to provide such a method of making direct-positive images having a satisfactory maximum density by development in a hydroquinone surface-type developer without necessarily increasing the hydroquinone content thereof.

Other objects of the present invention will become apparent from the detailed description given hereinafter.

DETAILED DESCRIPTION OF THE INVENTION

It has been established unexpectedly that by developing - in the presence of development nucleator - exposed photographic light-sensitive silver halide elements comprising an internal latent image, direct-positive images having a satisfactory maximum density can be obtained, even after multiple development work and/or aerial oxidation, when for said development work use is made of a hydroquinone surface-type developer - in other words an exhausted developer - and development is carried out in the presence of density-stabilizing amounts of organic non-aromatic onium salt. It has even been established that the presence of organic non-aromatic onium salt during development with a fresh hydroquinone surface-type developer leads to direct-positive images having a higher maximum density than images developed in the absence of said onium salt.

It has thus been found that the above objects have been accomplished by a method of making direct-positive images, said method comprising the steps of:

- image-wise exposing a photographic light-sensitive silver halide element comprising a support and at least one internal latent image-type silver halide emulsion layer, and
- developing said exposed silver halide element with a hydroquinone surface-type developer comprising 10 to 50 g, preferably 20 to 40 g, of hydroquinone per litre in the presence of at least one development nucleator, preferably e.g. of the class of the hydrazines and derivatives thereof, and in the presence of density-stabilizing amounts of organic non-aromatic onium salt, preferably tetraalkylated ammonium salt.

By the term "density-stabilizing" as used herein is meant that the level of Dmax obtained by developing an image-wise exposed light-sensitive silver halide element comprising at least one internal latent image-type silver halide emulsion layer in the presence of at least one development nucleator with a fresh hydroquinone surface-type developer comprising 10 to 50 g of hydroquinone per litre is maintained substantially even when exhaustion of the developer is in progress owing to oxidation products generated by aerial oxidation and/or multiple development work.

In the description hereinafter details are given about i.a. the organic non-aromatic onium salt and the development nucleators that can be used in the method of the present invention and in the elements of use therein.

The organic non-aromatic onium salt should be present during development of the exposed photographic element and can be incorporated for that purpose into e.g. the light-sensitive silver halide emulsion layer or into a hydrophilic colloid layer in water-permeable relationship therewith or alternatively it can be incorporated into the developer bath or into a separate bath. Mixtures of two or more organic non-aromatic onium salts can be used as well.

Suitable organic non-aromatic onium salts are i.a. ammonium, sulphonium, and phosphonium salts, the cation of which carries covalently linked aliphatic and/or alicyclic hydrocarbon groups. Suitable representatives are e.g. trimethylsulfonium iodide and tetramethylphosphonium iodide.

Preferred organic non-aromatic onium salts are the quaternary ammonium salts and in particular the tetraalkylated ammonium salts. Especially preferred tetra-alkylated ammonium salts are the tetra-alkylated ammonium halides e.g. tetra-n-butylammonium bromide.

The organic non-aromatic onium salt may be added to the light-sensitive silver halide emulsion layer or to a hydrophilic colloid layer in water-permeable relationship therewith in an amount ranging from 0.01 g to 100 g per mol of silver halide. The organic non-aromatic onium salt may also be added to the hydroquinone surface-type developer in an amount ranging from 0.2 to 5 g of organic non-aromatic onium salt per 1.

The development nucleators may be any of the compounds known for that purpose. Suitable development nucleators are i.a. :
sulphur compounds e.g. thiourea dioxide, phosphonium salts e.g. tetra(hydroxymethyl)phosphonium chloride, hydroxylamine, bis-(p-aminoethyl)-sulphide and water-soluble salts thereof, reductic acid and derivatives thereof e.g. 4,4,5,5-tetramethyl-reductic acid, kojic acid, ascorbic acid, 2-hydroxy-1,3-cyclohexanedione, 2-acetoxy- 1,2-di(2-pyridyl)-ethanone, 2-hydroxy-1,2-di(2-pyridyl)-ethanone, reactive N-substituted cycloammonium quaternary salts, and those of the preferred class of hydrazines and derivatives thereof e.g. 1-diphenyl-hydrazine hydrochloride and 1,2-dipyridyl-hydrazine hydrochloride, which have been described in detail in EP-A 416,174, a lot of novel phenyl-substituted hydrazine compounds described in Application PCT/EP 90/01433, hydrazine compounds described in EP Application N° 91201725.8, which corresponds to the US Serial N° , and especially 1-formyl-2-phenyl hydrazine. Mixtures of at least two of the above-mentioned development nucleators can be used advantageously.

Nucleating amounts of the development nucleators are present during development of the photographic element and can be incorporated for that purpose e.g. into the light-sensitive silver halide emulsion layer or into a hydrophilic colloid layer in water-permeable relationship therewith. Alternatively, they can also be added to the developing bath or to a separate bath.

When used in the silver halide emulsion layer the development nucleators are present in a concentration of 10^{-4} mol to 10^{-1} mol per mol of silver halide.

Prior to the coating of the composition that will form the photographic layer comprising at least one development nucleator, the development nucleator(s) can be dissolved in an organic solvent and added to said composition. For instance, 1.3×10^{-3} mol of the development nucleator is added in the form of a 3.0 % solution in methanol per mol of silver.

According to an embodiment of the present invention the development nucleator(s), preferably of the hydrazine-type, can be added in dispersed form to the hydrophilic colloid composition that will form said emulsion layer or said hydrophilic colloid layer. When these hydrazines are present in dispersed form in a hydrophilic colloid layer, preferably in the internal latent image-type silver halide emulsion layer, the direct-positive images obtained upon development have a very fine grain.

The development nucleator(s) can be incorporated into the hydrophilic colloid composition that will form said emulsion layer or said hydrophilic colloid layer by dissolving them first in at least one water-immiscible, oil-type solvent or oil-former, adding the resulting solution to an aqueous phase containing a hydrophilic colloid, preferably gelatin, and a dispersing agent, passing the mixture through a homogenizing apparatus so that a dispersion of the oily solution in an aqueous medium is formed, mixing the dispersion with a hydrophilic colloid composition e.g. a gelatin silver halide emulsion, and coating the resulting composition in the usual manner to produce a system in which particles of development nucleator(s), surrounded by an oily membrane, are distributed throughout the gel matrix. The dissolution of the development nucleator(s) in the oil-former may be facilitated by the use of an auxiliary low-boiling water-immiscible solvent, which is removed afterwards by evaporation.

The development nucleator(s) can be dispersed in hydrophilic colloid compositions with the aid of at least one known oil-former e.g. an alkyl ester of phthalic acid. The oil-formers can be used in widely varying concentrations e.g. in amounts ranging from about 0.1 to about 10 parts by weight and preferably from 0.5 to 2 parts by weight relative to the amount of the development nucleator(s) dispersed therewith.

It may be useful to combine the oil-former with at least one auxiliary solvent that is insoluble or almost insoluble in water and has a boiling point of at most 150 ° C, such as a lower alkyl acetate e.g. ethyl acetate.

In the direct-positive photographic light-sensitive element according to the present invention, it is preferred that the development nucleator(s) be incorporated into at least one internal latent image-type silver halide emulsion layer. However, the development nucleator(s) can also be incorporated into a hydrophilic colloid layer that stands in water-permeable relationship with an internal latent image-type silver halide emulsion layer. Such a hydrophilic colloid layer can be any layer that makes part of the direct-positive photographic light-sensitive element according to the present invention. It can thus be i.a. a light-sensitive layer, an intermediate layer, a filter layer, a protective layer, an antihalation layer, an antistress layer, a subbing layer, or any other layer. In other words, any layer will do provided the development nucleator(s) is not prevented from diffusing to the internal latent image-type silver halide emulsion layer.

The development nucleator(s) used according to the present invention preferably is (are) incorporated into the layer(s) in an amount as mentioned above that yields satisfactory maximum density values of e.g.

at least 1.50 when the internal latent image-type emulsion is developed with a surface-developer. When the development nucleator(s) is(are) incorporated into a hydrophilic colloid layer that stands in water-permeable relationship with the internal latent image-type silver halide emulsion layer, it is adequate to incorporate the development nucleator(s) in the above amounts while taking into account the amount of silver contained in the associated internal latent image-type emulsion layer.

An internal latent image-type silver halide emulsion is an emulsion, the maximum density of which obtained when developing it with an "internal type" developer exceeds the maximum density that is achievable when developing it with a "surface-type" developer. The internal latent image-type emulsions that are suited for use in accordance with the present invention yield a maximum density that, when these emulsions have been coated on a transparent support and are exposed to light for a fixed time of from 1/100 to 1 s and then developed for 3 min at 20 °C with the internal-type Developer A as described hereinafter, is higher by at least 5 times than the maximum density obtained when the silver halide emulsion exposed as described above is developed for 4 min at 20 °C with the surface-type Developer B as described hereinafter.

Internal-type Developer A	
hydroquinone	15 g
monomethyl-p-aminophenol sulphate	15 g
anhydrous sodium sulphite	50 g
potassium bromide	10 g
sodium hydroxide	25 g
crystalline sodium thiosulphate	20 g
Water to make	1 l

Surface-type Developer B	
p-hydroxyphenylglycine	10 g
crystalline sodium carbonate	100 g
water to make	1 l

Internal latent image-type silver halide emulsions that can be used in accordance with the present invention have been described in e.g. US-P 2,592,250, 3,206,313, 3,271,157, 3,447,927, 3,511,662, 3,737,313, 3,761,276, GB-A 1,027,146, and JA Patent Publication No. 34,213/77. However, the silver halide emulsions used in the present invention are not limited to the silver halide emulsions described in these documents.

Internal latent image-type silver halide emulsions that are suited for use in the method of the present invention generally are emulsions that have not been prefogged or only slightly so and have not been ripened chemically or only slightly so, e.g. as described in US-P 3,761,276 and 3,850,637.

The photographic emulsions can be prepared according to different methods as described e.g. by P. Glafkides in "Chimie et Physique Photographique", Paul Montel, Paris (1967), by G.F. Duffin in "Photographic Emulsion Chemistry", The Focal Press, London (1966), and by V.L. Zelikman et al in "Making and Coating Photographic Emulsion", The Focal Press, London (1966).

The photographic silver halide emulsions used in the method of the present invention can be prepared by mixing the halide and silver solutions in partially or fully controlled conditions of temperature, concentrations, sequence of addition, and rates of addition. The silver halide can be precipitated according to the single-jet method, the double-jet method, or the conversion method. The conversion method has proved to be particularly suitable. According to this method a more soluble silver halide is converted into a less soluble silver halide. For instance a silver chloride emulsion is converted in the presence of water-soluble bromide and possibly iodide, the amounts of which are selected with regard to the finally required composition, into a silver chlorobromoiodide or a silver bromoiodide emulsion. This conversion is preferably carried out very slowly in several consecutive steps i.e. by converting a part of the more soluble silver halide at a time. Another technique by which emulsions with an increased internal latent image sensitivity can be prepared has been described in GB-A 1,011,062.

The silver halide particles of the photographic emulsions used in the method of the present invention may have a regular crystalline form such as a cubic or octahedral form or they may have a transition form.

They may also have an irregular crystalline form such as a spherical form or a tabular form, or may otherwise have a composite crystal form comprising a mixture of said regular and irregular crystalline forms.

The silver halide grains may have a multilayered grain structure. According to a simple embodiment the grains may comprise a core and a shell, which may have different halide compositions and/or may have undergone different modifications such as the addition of dopes. Besides having a differently composed core and shell the silver halide grains may also comprise different phases inbetween so that electron trapping systems can be obtained through the presence of phase boundaries in the so-called "core-shell" emulsion type.

Two or more types of silver halide emulsions that have been prepared differently can be mixed for forming a photographic emulsion for use in the method of the present invention.

The average size of the silver halide grains may range from 0.1 to 2.0 μm, preferably from 0.3 to 0.8 μm.

The size distribution of the silver halide particles of the photographic emulsions used in the method of the present invention can be homodisperse or heterodisperse. A homodisperse size distribution is obtained when 95% of the grains have a size that does not deviate more than 30% from the average grain size.

In addition to silver halide the emulsions may also comprise organic silver salts such as e.g. silver benzotriazolate and silver behenate.

The silver halide crystals can be doped with Rh^{3+}, Ir^{4+}, Cd^{2+}, Zn^{2+}, Pb^{2+}.

The photographic emulsions may comprise substances that will provide iodide and/or bromide ions (in excess of any such ions provided by the light-sensitive emulsion itself) during the development of the exposed emulsions. Such compounds and the method using them have been described in GB-A 1,195,837.

The emulsion can be left unwashed or it can be desalted in the usual ways e.g. by dialysis, by flocculation and re-dispersing, or by ultrafiltration.

Commonly, the light-sensitive silver halide emulsion used in the method of the present invention has not been sensitized chemically. However, it may have been chemically sensitized or prefogged. Chemical sensitization can be performed as described i.a. in the above-mentioned "Chimie et Physique Photographique" by P. Glafkides, in the above-mentioned "Photographic Emulsion Chemistry" by G.F. Duffin, in the above-mentioned "Making and Coating Photographic Emulsion" by V.L. Zelikman et al, and in "Die Grundlagen der Photographischen Prozesse mit Silberhalogeniden" edited by H. Frieser and published by Akademische Verlagsgesellschaft (1968). As described in said literature chemical sensitization can be carried out by effecting the ripening in the presence of small amounts of compounds containing sulphur e.g. thiosulphate, thiocyanate, thioureas, sulphites, mercapto compounds, and rhodamines. The emulsions can be sensitized also by means of gold-sulphur ripeners or by means of reductors e.g. tin compounds as described in GB-A 789,823, amines, hydrazine derivatives, formamidine-sulphinic acids, and silane compounds. Chemical sensitization can also be performed with small amounts of Ir, Rh, Ru, Pb, Cd, Hg, Tl, Pd, Pt, or Au. One of these chemical sensitization methods or a combination thereof can be used. Chemical sensitization of core-shell type direct positive emulsions can be obtained through the chemical ripening of the AgX-core, followed by a shell-type silver halide precipitation. After completing the precipitation of the shell, the surface of the silver halide grains can be chemically sensitized in accordance with the procedures mentioned before.

The spectral photosensitivity of the silver halide can be adjusted by proper sensitization to any desired spectral range comprised between 300 and 900 nm e.g. to blue light, to green light, to red light, to infrared light, by means of the usual mono- or polymethine dyes such as acidic or basic cyanines, hemicyanines, oxonols, hemioxonols, styryl dyes or others, also tri- or polynuclear methine dyes e.g. rhodacyanines or neocyanines. Such spectral sensitizers have been described by e.g. F.M. Hamer in "The Cyanine Dyes and Related Compounds" (1964) Interscience Publishers, John Wiley & Sons, New York. The spectral photosensitivity of the silver halide can also be adjusted for exposure by laser light e.g. helium-neon laser light, argon laser light, and solid state laser light. Dyes that can be used for adjusting the photosensitivity to laser light have been described in i.a. JA-A 62284344, 62284345, 62141561, 62103649, 62139555, 62105147, 62105148, 62075638, 62062353, 62062354, 62062355, 62157027, 62157028, 62113148, 61203446, 62003250, 60061752, 55070834, 51115821, 51115822, 51106422, 51106423, 51106425; DE-A 3,826,700; US-A 4,501,811, 4,725,532, 4,784,933; GB-A 1,467,638; and EP-A 100,654 and in documents cited therein. The silver halide can also be sensitized with dyes providing a spectral sensitivity mainly in the range of 400 to 540 nm and not extending the sensitivity substantially beyond 540 nm so that the resulting photosensitive element can be handled in safelight conditions prior to the image-wise exposure. Suitable dyes that can be used for that purpose have been described in e.g. US-P 4,686,170.

Other useful sensitizing dyes that can be employed in accordance with the present invention have been described in e.g. US-P 2,503,776, 2,526,632, 3,522,052, 3,556,800, 3,567,458, 3,615,613, 3,615,632, 3,615,635, 3,615,638, 3,615,643, 3,617,293, 3,619,197, 3,625,698, 3,628,964, 3,632,349, 3,666,480, 3,667,960, 3,672,897, 3,677,765, 3,679,428, 3,703,377, 3,705,809, 3,713,828, 3,713,828, 3,745,014, 3,769,025, 3,769,026, 3,770,440, 3,770,449, GB-A 1,404,511, and BE-A 691,807.

A particular effect of gradation enhancement can be obtained by using at least one merocyanine dye; if desired, in combination with at least one rhodacyanine dye. For this effect these dyes need not necessarily absorb in the wavelength range of the exposure light.

The sensitizing dyes employed in the present invention are used in a concentration almost equivalent to that used in ordinary negative silver halide emulsions. In particular, it is advantageous that the sensitizing dyes be employed in a dye concentration to a degree that does not substantially cause desensitization in the region of intrinsic sensitivity of the silver halide emulsion. It is preferred that the sensitizing dyes be employed in a concentration of from about 1.0×10^{-5} to about 5×10^{-4} mol per mol of silver halide, and particularly in a concentration of from about 4×10^{-5} to 2×10^{-4} mol per mol of silver halide.

Other dyes, which per se do not have any spectral sensitization activity, or certain other compounds, which do not substantially absorb visible radiation, can have a supersensitization effect when they are incorporated together with said spectral sensitizing agents into the emulsion. Suitable supersensitizers are i.a. heterocyclic mercapto compounds containing at least one electronegative substituent as described e.g. in US-P 3,457,078, nitrogen-containing heterocyclic ring-substituted aminostilbene compounds as described e.g. in US-P 2,933,390 and 3,635,721, aromatic organic acid/formaldehyde condensation products as described e.g. in US-P 3,743,510, cadmium salts, and azaindene compounds.

It may be advantageous to develop the image-wise exposed element in the additional presence of at least one substituted phenol derivative as described in the above cited EP Application N° 91201725.8, which corresponds to the US Serial N° . Preferably, the substituted phenol derivative is 5-sulfosalicylic acid. The phenol derivative may be added to the developer in amounts of from 0.02 to 1.00 mole/l, preferably from 0.02 to 0.5 mole/l.

In the processing method of the present invention any of the known methods can be employed. Specifically, the processing method of the present invention basically includes a development step and a fixing step. A stopping step and a rinsing step can be included as well, if desired. The processing temperature is usually selected within the range of from 18°C to 50°C. However, temperatures lower than 18°C and temperatures higher than 50°C can be employed, if desired. The processing time may vary within broad ranges provided the mechanical strength of the elements to be processed is not adversely influenced and no decomposition takes place. As is generally known sensitometric results obtained can strongly depend on the temperature of the developer. A more important independence of the sensitometry from development conditions can be demonstrated in the presence of density-stabilizing amounts of organic non-aromatic onium salt. So it has been found that in the range of developer temperatures between 32 and 39°C no significant changes in photographic results are obtained. The fact that in this range the temperature of the developer is not critical can be considered as a real advantage for the customer. Another unexpected advantage is the accessibility of the new developing system to rapid processing times: shorter development times, e.g. 30 s instead of 45 s, are now available.

The pH of the developer usually has a value ranging from 10.5 to 14, preferably from 11.5 to 12.5.

The hydroquinone-type developer used for developing an exposed photographic element in accordance with the present invention need not comprise an alkanolamine, but may incorporate a primary, secondary, or tertiary alkanolamine e.g. triisopropanolamine.

In the developer used in the processing method of the present invention, a hydroquinone alone or a combination of a hydroquinone with a secondary developing agent of the class of 1-phenyl-3-pyrazolidinone compounds and p-N-methyl-aminophenol can be used as developing agent. Specific examples of hydroquinones include hydroquinone, methylhydroquinone, t-butyl-hydroquinone, chlorohydroquinone, and bromohydroquinone. The amount of the hydroquinone used is not limited,but the previously mentioned stabilizing effect on the sensitometry after developer exhaustion is also observed when the developer is containing less than 25 g of hydroquinone.

Particularly useful 1-phenyl-3-pyrazolidinone developing agents that can be used in combination with a hydroquinone are 1-phenyl-3-pyrazolidinone, 1-phenyl-4-methyl-3-pyrazolidinone, 1-phenyl-4-ethyl-5-methyl-3-pyrazolidinone, and 1-phenyl-4,4-dimethyl-3-pyrazolidinone.

N-methyl-p-aminophenol and 2,4-diaminophenol can be used in combination with a hydroquinone as a developing agent.

When the secondary developing agent used in the processing method of the present invention is one of the class of the 1-phenyl-3- pyrazolidinone compounds it is preferably present in an amount of 2 to 20 g per litre. When the secondary developing agent is p-N-methyl-aminophenol it is preferably present in an amount of 1 to 40 g per litre.

The developer comprises a preservative such as a sulphite e.g. sodium sulphite in an amount ranging from 45 g to 160 g per litre.

The developer comprises such alkali-providing substances like hydroxides of sodium and potassium, alkali metal salts of phosphoric acid and/or silicic acid e.g. trisodium phosphate, orthosilicates, metasilicates, hydrodisilicates of sodium or potassium, and sodium carbonate. The alkali-providing substances can be substituted in part or wholly by alkanolamines.

The developer may comprise a buffering agent such as a carbonate e.g. sodium carbonate, potassium carbonate, trisodium phosphate, and sodium metaborate.

For the purpose of decreasing the formation of fog (Dmin) the developer may further contain an inorganic anti-fogging agent such as a bromide e.g. potassium bromide and/or an organic anti-fogging agent such as a benzimidazole e.g. 5-nitro-benzimidazole, a benzotriazole like benzotriazole itself and 5-methyl-benzotriazole.

The developer may contain other ingredients such as i.a. toning agents, development accelerators, oxidation preservatives, surface-active agents, defoaming agents, water-softeners, anti-sludge agents, hardeners including latent hardeners, and viscosity-adjusting agents.

Regeneration of the developer according to known methods is, of course, possible.

The development may be stopped - though this is often not necessary - with an aqueous solution having a low pH. An aqueous solution having a pH not higher than 3.5 comprising e.g. acetic acid and sulphuric acid, and containing a buffering agent is preferred.

Buffered stop bath compositions comprising a mixture of sodium dihydrogen orthophosphate and disodium hydrogen orthophosphate are preferred.

Conventional fixing solutions may be used. Examples of useful fixing agents include organic sulphur compounds known as fixing agents, as well as a thiosulphate, a thiocyanate, etc. The fixing solution may contain a water-soluble aluminium salt as a hardening agent.

The photographic light-sensitive silver halide element for use in the method of the present invention comprises an internal latent image-type silver halide emulsion layer, which preferably is a gelatin silver halide emulsion layer. However, instead of gelatin or in admixture with gelatin a variety of other hydrophilic colloids can be used as the binder for the silver halide.

Other suitable hydrophilic colloids that can be used as the binder for the silver halide are synthetic, semi-synthetic, or natural polymers. Synthetic substitutes for gelatin are e.g. polyvinyl alcohol, poly-N-vinyl pyrrolidone, polyvinyl imidazole, polyvinyl pyrazole, polyacrylamide, polyacrylic acid, and derivatives thereof, in particular copolymers thereof. Other synthetic substitutes for gelatin are latices such as a latex of poly(ethyl acrylate). Natural substitutes for gelatin are e.g. other proteins such as zein, albumin and casein, cellulose derivatives, saccharides, starch, and alginates. In general, the semi-synthetic substitutes for gelatin are modified natural products e.g. gelatin derivatives obtained by conversion of gelatin with alkylating or acylating agents or by grafting of polymerizable monomers on gelatin, and cellulose derivatives such as hydroxyalkyl cellulose, carboxymethyl cellulose, phthaloyl cellulose, and cellulose sulphates. The presence of such other binders often has a favourable photographic effect on the formation of the direct-positive image. For instance, the addition of polyvinyl pyrrolidone and of said latex of poly(ethyl acrylate) often increases the maximum density of the direct-positive image.

Suitable additives for improving the dimensional stability of the photographic element can also be incorporated together with the hydrophilic colloid. Suitable examples of this type of compounds include i.a. dispersions of a water-soluble or hardly soluble synthetic polymer e.g. polymers of alkyl (meth)acrylates, alkoxy(meth)acrylates, glycidyl (meth)acrylates, (meth)acrylamides, vinyl esters, acrylonitriles, olefins, and styrenes, or copolymers of the above with acrylic acids, methacrylic acids, α-β-unsaturated dicarboxylic acids, hydroxyalkyl (meth)acrylates, sulphoalkyl (meth)acrylates, and styrene sulphonic acids.

The binder should dispose of an acceptably high number of functional groups, which by reaction with an appropriate hardening agent can provide a sufficiently resistant layer. Such functional groups are especially the amino groups, but also carboxylic groups, hydroxy groups, and active methylene groups.

The gelatin can be lime-treated or acid-treated gelatin. The preparation of such gelatin types has been described in e.g. "The Science and Technology of Gelatin", edited by A.G. Ward and A. Courts, Academic Press 1977, page 295 and next pages. The gelatin can also be an enzyme-treated gelatin as described in Bull. Soc. Sci. Phot. Japan, N° 16, page 30 (1966).

Various compounds can be added to the photographic emulsion to prevent the reduction in sensitivity or fog formation during preparation, storage, or processing of the photographic light-sensitive element. A great many compounds are known for these purposes, and they include homopolar or salt-like compounds of mercury with aromatic or heterocyclic rings such as mercaptotriazoles, simple mercury salts, sulphonium mercury double salts and other mercury compounds. Other suitable stabilizers are azaindenes, preferably tetra- or penta-azaindenes, especially those substituted with hydroxy or amino groups e.g. 4-hydroxy-6-methyl-1,3,3a,7-tetra-azaindene.Compounds of this kind have been described by Birr in Z. Wiss. Photogr. Photophys. Photochem. 47, 2-27 (1952). Other suitable stabilizers are i.a. heterocyclic mercapto compounds e.g. 1-phenyl-5-mercaptotetrazole, 3-methyl-benzothiazole, quaternary benzothiazole derivatives, benzotriazole. Specific examples of stabilizers have been mentioned by K. Mees in The Theory of the Photographic Process, 3rd ed. 1966 by reference to the papers that first reported such compounds, and in addition, have been described in i.a. US-P 1,758,576, 2,110,178, 2,131,038, 2,173,628, 2,304,962, 2,324,123, 2,394,198, 2,444,605, 2,444,606, 2,444,607, 2,444,608, 2,476,536, 2,566,245, 2,694,716, 2,697,040, 2,697,099, 2,708,162, 2,728,663, 2,728,664, 2,728,665, 2,824,001, 2,843,491, 2,886,437, 3,052,544, 3,137,577, 3,220,839, 3,226,231, 3,236,652, 3,251,691, 3,252,799, 3,287,135, 3,326,681, 3,420,668, and 3,622,339, GB-A 893,428, 403,789, 1,173,609, and 1,200,188.

The silver halide emulsions may comprise other ingredients e.g. development accelerators, wetting agents, and hardeners. The binder of the silver halide emulsion layer and/or of other hydrophilic colloid layers can, especially when the binder used is gelatin, be hardened with appropriate hardening agents such as those of the epoxide type, those of the ethylenimine type, those of the vinylsulfone type e.g. 1,3-vinylsulphonyl-2-propanol, chromium salts e.g. chromium acetate and chromium alum, aldehydes e.g. formaldehyde, glyoxal, and glutaraldehyde, N-methylol compounds e.g. dimethylolurea and methyloldimethylhydantoin, dioxan derivatives e.g. 2,3-dihydroxy-dioxan, active vinyl compounds e.g. 1,3-,5-triacryloylhexahydro-s-triazine, active halogen compounds e.g. 2,4-dichloro-6-hydroxy-s-triazine, and mucohalogenic acids e.g. mucochloric acid and mucophenoxychloric acid. These hardeners can be used alone or in combination. The binders can also be hardened with fast-reacting hardeners such as carbamoylpyridinium salts and the phosphorus compounds described in EP Application N° 89201865.6, which corresponds to the US Serial N° .

Compounds that release iodine ions e.g. potassium iodide can be incorporated into the photographic silver halide emulsion. Additionally, the developer used in the method of the present invention may also contain iodine ions.

The photographic light-sensitive element used in the method of the present invention may contain a water-soluble dye in a hydrophilic colloid layer as a filter dye or for other various purposes such as for the prevention of irradiation or anti-halation. Such dyes include oxonol dyes, hemioxonol dyes, styryl dyes, merocyanine dyes, cyanine dyes, and azo dyes. Of these, oxonol dyes, hemioxonol dyes, and merocyanine dyes are useful.

When a hydrophilic colloid layer of the photographic light-sensitive element used in the method of the present invention contains a dye or an UV-absorbing agent, these compounds may be mordanted by means of a cationic polymer e.g. polymers described in GB-A 1,468,460 and 685,475, US-P 2,675,316, 2,839,401, 2,882,156, 3,048,487, 3,184,309, 3,445,231, and 3,986,875, DE-A 1,914,362.

The photographic light-sensitive element for use in the method of the present invention may comprise various kinds of surface-active agents in the photographic emulsion layer or in at least one other hydrophilic colloid layer. Surface-active agents can be used for various purposes e.g. as coating aids, as compounds preventing electric charges, as compounds improving slidability, as compounds facilitating dispersive emulsification, as compounds preventing or reducing adhesion, and as compounds improving the photographic characteristics e.g higher contrast, sensitization, and development acceleration.

Development acceleration can be accomplished with the aid of various compounds, preferably polyalkylene derivatives having a molecular weight of at least 400 such as those described in e.g. US-P 3,038,805, 4,038,075, and 4,292,400.

The photographic light-sensitive element for use in the method of the present invention may further comprise in the silver halide emulsion layer various other additives such as e.g. UV-absorbers, matting agents or spacing agents, lubricants, and plasticizers.

Suitable UV-absorbers are i.a. aryl-substituted benzotriazole compounds as described in US-P 3,533,794, 4-thiazolidone compounds as described in US-P 3,314,794 and 3,352,681, benzophenone compounds as described in JP-A 2784/71, cinnamic ester compounds as described in US-P 3,705,805 and 3,707,375, butadiene compounds as described in US-P 4,045,229, and benzoxazole compounds as described in US-P 3,700,455.

Suitable spacing agents are e.g. finely divided silica particles and polymer beads as described US-P 4,614,708.

In general, the average particle size of spacing agents is comprised between 0.2 and 10 µm. Spacing agents can be soluble or insoluble in alkali. Alkali-insoluble spacing agents usually remain permanently in the photographic element, whereas alkali-soluble spacing agents usually are removed therefrom in an alkaline processing bath. Suitable spacing agents can be made i.a. of polymethyl methacrylate, of copolymers of acrylic acid and methyl methacrylate, and of hydroxypropylmethyl cellulose hexahydrophthalate. Other suitable spacing agents have been desribed in US-P 4,614,708.

A matting agent and/or a lubricant may be added to an emulsion layer and/or a protective layer of the direct-positive photographic light-sensitive element used in the method of the present invention. Suitable matting agents are e.g. water-dispersible vinyl polymers such as poly(methyl methacrylate) having an appropriate particle size of from 0.2 to 6 µm and inorganic compounds e.g. silver halide and strontium barium sulphate. The lubricant is used to improve the slidability of the photographic element. Suitable examples of lubricants are e.g. liquid paraffin, waxes such as esters of higher fatty acids, polyfluorinated hydrocarbons or derivatives thereof, silicones such as polyalkylpolysiloxanes, polyarylpolysiloxanes, polyalkylarylpolysiloxanes and alkyleneoxide addition derivatives thereof.

A variety of photographic supports can be employed for the photographic light-sensitive element used in the method of the present invention. The silver halide emulsion can be coated onto one side or both sides of the support. The support may be transparent or non-transparent. Suitable supports are e.g. a baryta-coated paper, a resin-coated paper e.g. a polyolefin-coated paper, a synthetic paper, a cellulose triacetate film, a polyethylene terephthalate film or another plastic base or glass plate.

In a first step for making a direct-positive image the photographic light-sensitive silver halide element is exposed image-wise. This exposure can either be a high-intensity exposure such as a flash exposure or a normal intensity exposure such as a daylight exposure, a low-intensity exposure such as an exposure by means of a printer, or an exposure of even lower intensity. The light source used for the exposure should match the wavelength sensitivity of the light-sensitive element. Natural light (sunlight), the light emitted by an incandescent lamp, a halogen lamp, a mercury vapour lamp, a fluorescent tube, an electronic flash lamp, or by a metal-burning flash bulb can be used. Gas, dye or semiconductor lasers emitting light in the wavelength ranges from ultraviolet to infrared as well as a plasma light source are also suitable light sources for exposing the photographic light-sensitive silver halide element for use in the method of the present invention. A line-shaped light source or a planar light source as well as a microshatter arrangement with a fluorescing area (CRT, etc.), the fluorescence of which is produced by fluorescing substances stimulated by means of electron rays, or even a liquid-crystal display (LCD) or a lanthanum-doped lead-titanium zirconate can be used as well as light sources for exposing the photographic light-sensitive silver halide element for use in the method of the present invention. If necessary, the spectral distribution of the exposure light can be controlled by means of a colour filter.

The photographic light-sensitive silver halide element used in the method of the present invention may serve different purposes. Application fields, in which direct-positive images can be made in accordance with the present invention, are i.a. graphic arts recording processes, silver salt diffusion transfer reversal processes, duplicating processes for cinematographic black-and-white negatives, infrared laser recording processes, X-ray recording processes, cathode-ray recording processes, fototype-setting processes, etc., particularly microfilm recording processes.

The present invention will be explained in greater detail by reference to the following examples. The present invention should, however, not be construed as being limited thereto.

EXAMPLE 1

An internal latent image-type direct-positive gelatin silver halide emulsion was prepared by conversion of a silver chloride emulsion in the presence of water-soluble bromide and iodide to form grains having a core of silver chloride (4 mol%) and a shell of silverbromoiodide (95/1 mol%). The average grain diameter was 0.4 µm.

A 3% solution (in methanol) of the development nucleator 1-formyl-2-phenyl-hydrazine was made and added to the silver halide emulsion so that the hydrazine compound was present in an amount of 0.075 mol per mol of silver halide.

The resulting emulsion was coated on a polyester support at a ratio of 0.035 mol of silver halide per m^2 and dried.

Four samples 1A to 1D of the light-sensitive element in the form of micro-cards were exposed identically for 10^{-5} s to white light emitted by a U460 flashlight sold by EG&G ING, 45 William street, Wellesley, Ma.02181, USA and each of the samples was then developed for 45 s with exhausted hydroquinone-type developer at a temperature of 35 °C. The exhaustion was simulated by the presence in the developer of but 10 g of hydroquinone and the presence of 5 g of sodium bromide. The "exhausted" developer contained the following ingredients :

demineralized water	600 ml
hydroquinone	10 g
p-N-methyl-aminophenol	1.8 g
5-sulfosalicylic acid	100 g
triisopropanolamine	27
sodium sulphite	76 g
sodium bromide	5 g
ethylenediamine tetraacetic acid	1.25 g
5-methyl-benzotriazole	0.36 g
tetra-n-butylammonium bromide (TBAB)	amount as specified in Table 1
demineralized water to make	1 l
sodium hydroxide to a pH value of 12.1	

The "exhausted" developers used for developing the 4 samples differed only from one another in that different amounts of TBAB as specified in Table 1 were present therein. The Dmin and Dmax values were measured and are also listed in Table 1.

TABLE 1

development in exhausted developer			
Development of	in the presence of TBAB (in g/l)	Dmin	Dmax
Sample 1A	none	0.05	1.61
Sample 1B	1	0.04	2.12
Sample 1C	2	0.04	2.56
Sample 1D	3	0.04	2.25

It appears from the results listed in Table 1 that the presence of TBAB in an exhausted hydroquinone-type developer leads to a significantly enhanced Dmax value.

EXAMPLE 2

Three samples identical to samples 1A, 1C, and 1D described in Example 1 and called 2A, 2C, and 2D respectively herein were exposed and each of the samples was developed for 45 s with a hydroquinone-type developer at a temperature of 35 ° C as described in Example 1, but with the only difference that the developer was fresh. The freshness of the developer was obtained by the presence therein of 24 g of hydroquinone instead of 10 g (as used in the exhausted developer described in Example 1) and by the absence of sodium bromide (as compared with the presence of 5 g of sodium bromide in the exhausted developer of Example 1).

The fresh developers used for developing the 3 samples differed only from one another in that different amounts of TBAB (see Table 2) were present therein. Dmin and Dmax were measured and are listed in Table 2.

TABLE 2

development in fresh developer			
Development of	in the presence of TBAB (in g/l)	Dmin	Dmax
Sample 2A	none	0.09	1.97
Sample 2C	2	0.11	2.21
Sample 2D	3	0.11	2.24

It appears from the results listed in Table 2 that the presence of TBAB in a fresh hydroquinone-type developer also leads to a significantly enhanced Dmax value.

Claims

1. Method of making direct-positive images, said method comprising the steps of:
   - image-wise exposing a photographic light-sensitive silver halide element comprising a support and at least one internal latent image-type silver halide emulsion layer, and
   - developing said exposed silver halide element with a hydroquinone surface-type developer comprising 10 to 50 g of hydroquinone per litre in the presence of at least one development nucleator and in the presence of density-stabilizing amounts of organic non-aromatic onium salt.

2. A method according to claim 1, wherein hydroquinone is present in said developer in an amount of 20 to 40 g per litre.

3. A method according to claim 1 or 2, wherein said organic non-aromatic onium salt is a tetraalkylated ammonium salt.

4. A method according to any of the foregoing claims, wherein said organic non-aromatic onium salt is tetra-n-butylammonium bromide.

5. A method according to any of the foregoing claims, wherein said development nucleator belongs to the class of the hydrazines and derivatives thereof.

6. A method according to any of the foregoing claims, wherein said development nucleator is a phenyl hydrazine.

7. A method according to any of the foregoing claims, wherein said development nucleator is present in said emulsion layer or in a hydrophilic colloid layer in water-permeable relationship therewith.

8. A method according to any of the foregoing claims, wherein the develop ment nucleator is present in said silver halide emulsion layer in a concentration of 10^{-4} mol to 10^{-1} mol per mol of silver halide.

9. A method according to any of the foregoing claims, wherein the pH of said developer has a value ranging from 11.5 to 12.5.

10. Developing solution having a pH ranging from 10.5 to 14 and comprising per litre :
    - 10 to 50 g of hydroquinone and
    - 0.2 to 5 g of organic non-aromatic onium salt.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 92 20 4047

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US-A-4 481 285 (Y TAKAGI ET AL) * column 1, line 30 - line 37 * * column 2, line 35 - column 3, line 2 * * column 7, line 40 - line 46 * ---	1-9	G03C1/485 G03C5/305 G03C1/295
X	US-A-3 637 387 (G L VANREUSEL ET AL) * column 1, line 11 - line 12 * * column 3, line 50 - column 5, line 10 * * column 6, line 1 - line 24 * ---	1,3,5, 7-8	
X	US-I-T884013 (N W KALENDA) * the whole document * ---	1,5-9	
A	US-A-2 563 785 (C E IVES) * column 1, line 10 * * column 3, line 27 - column 5, line 23 * ---	1,5-9	
X	US-A-3 972 719 (G L VANREUSEL ET AL) * column 6, line 8 - line 27; claims 1,7-9 * ---	10	**TECHNICAL FIELDS SEARCHED (Int. Cl.5)**
A	GB-A-566 314 (ELLIOT AND SONS LIMITED) * page 1, line 69 - line 105 * ---	10	G03C
A	RESEARCH DISCLOSURE no. 297, January 1989, HAVANT GB pages 45 - 50 KOK PIET ET AL -----	10	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	23 SEPTEMBER 1993	BOLGER W.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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L : document cited for other reasons

& : member of the same patent family, corresponding document