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(54) A photosensitive silver halide material comprising a layer assembly

(57) A black and white silver halide photographic material is disclosed which comprises on a support in the order given:

- at least one non-light sensitive layer having a hydrophilic polymer in an total amount A between 0.1 and 0.9 g/m²,
- at least one light sensitive silver halide emulsion layer having a hydrophilic polymer in an total amount B between 1 and 2 g/m²,
- at least one non-light sensitive layer having a hydrophilic polymer in an total amount C between 0.5 and 1.6 g/m²,

wherein:

- $0 \leq A/B \leq 0.6$
and
- $0.7 \leq B/C \leq 2.25$

while the total amount of hydrophilic polymers is not more than 3 gram and the amount of silver halide less than 0,05 mole both per square meter and per side of the support.

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Description

FIELD OF THE INVENTION

- 5 **[0001]** The present invention relates to a silver halide photographic material, more specifically to a silver halide photographic material with a layer assembly specially suited for rapid processing.

BACKGROUND OF THE INVENTION

- 10 **[0002]** The need for rapid processing of photographic materials is growing and this growth is supported by the increasing trend of automation in material processing. This is especially the case for materials which need a more complicated processing procedure like silver halide photosensitive materials. These silver halide materials can win a great part in convenience and become more competitive compared with materials which can be for instance dry processed if they can be processed automatically and faster. Silver halide materials which are the central subject of the present invention
15 need a classical wet processing which strongly limits the number of possibilities wherein the processing velocity can be increased. However only few of the individual processing steps are accessible for special actions in this field.

- [0003]** A possible solution is described in US-P 3,977,879 where an oxidizing agent is incorporated in an additional light-insensitive undercoating or overcoating layer contiguous with the light-sensitive emulsion layer. The increase in processing velocity can be explained by an initial production of semiquinone radicals by a reaction between the hydroquinone developer and the oxidant which is closely present and which can accelerate the processing substantially.
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- [0004]** A critical point in the chemical reduction of silver halide in hydrophilic aqueous surroundings is that the process is diffusion-controlled. Therefore the processing velocity can only be improved by increasing the concentration gradient for reactants involved in the different processing steps. An increase of the concentration gradient can in the first place be realised by increasing the concentration of the reactants which action is limited for ecological reasons. Another possibility is decreasing the thickness of the photographic material which is only limited by the amount of binder and polymers while these are necessary to make stable dispersions of silver halide grains and if desired of ingredients which have to be coated (in an emulsion-, antistress layer, etc) on the support. Another limiting factor in decreasing the layer thickness is often the necessity for storing products in order to realize the desired photographic properties. These products can be stored in the antistress layer but when the total material thickness has to be minimized for rapid processing
25 reasons the storage of products which are not compatible with the ingredients in the emulsion layer can give practical problems (like loss of stability). Examples of these products are for instance hardeners, stabilizers, nucleating agents, etc. The incompatibility problem can be overcome by encapsulating or masking the involved products which however is disadvantageous because of the extra cost for encapsulating or chemically masking and because of the increased chemical load of the material.

- [0005]** An interesting and inexpensive solution is splitting-up one or more of the existing hydrophilic layers of the material in order to separate the products which can not be coated in the same layer. This for instance has been suggested in EP-A 0 490 302 and US-P 4,777,113 where a certain amount of colloidal silica is incorporated in an interlayer in order to decrease the pressure fog or scratch sensitivity and to adjust the friction coefficient to a certain level. In US-P 5,550,003, US-P 5,558,979 and JP-A 7-104412 more than one overcoating layer is described which is used for the storage of products for the regulation of one or more photographic parameters. Instead of applying extra overcoating layers some other patents suggest the use of undercoating layers situated between the support and the light-sensitive silver halide layer. This can for instance be found in EP-A 0 179 555 and US-P 4,711,838 where a light-sensitive material existing of at least one IR-sensitized silver halide emulsion layer is containing also a top layer and a subbing or front layer. In some patents like US-P 4,904,565 and EP-A 0 646 836 light sensitive silver halide materials have a layer assembly consisting of an undercoat layer and more than one overcoat layer. Nucleating agents are also often incorporated in an extra hydrophilic layer which can be an undercoating layer, an interlayer or an overcoating layer as described in EP-A 0 681 208. Undercoatlayers are often used for incorporating antihalation dyes (like for instance in EP-A 0 307 867, EP-A 0 307 868, US H1515H and US-P 5,230,994) or for the incorporation of dyes which decrease the cross-over in X-ray materials (like for instance in EP-A 0 401 709). However this is always carried out without paying extra attention
35 to the total layer thickness.

- [0006]** In almost all these patent proposals the additional hydrophilic layers are incorporated in silver halide materials in order to add one or more products which give the material an additional functionality. In all these patents each additional layer increases the amount of hydrophilic polymer which allways results in longer processing and drying times.

- [0007]** Therefore a solution has to be found for storing chemical products with a certain functionality (like hardening, stabilizing, matting agents, nucleating agents, etc) in a material without degrading its potentiality for rapid processing and by keeping at least the same sensitometric quality.
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- [0008]** The present invention will bring a proposal in which the described problem is solved and wherein an increase in processing velocity is realised without loss of photographic quality. This will be explained in the following description

and the appending example.

OBJECTS OF THE INVENTION.

- 5 **[0009]** It is therefore a first object of the present invention to provide a photosensitive silver halide material which is improved for rapid processing.
- [0010]** It is a further object of this invention to provide a photosensitive silver halide material comprising a silver halide emulsion which is improved concerning covering power.
- [0011]** It is even a further object of the present invention to provide a photosensitive silver halide material with
- 10 improved layer assembly which increases the functionality of the photosensitive material involved.
- [0012]** Further objects and advantages of the invention will become apparent from the description hereinafter.

SUMMARY OF THE INVENTION

- 15 **[0013]** The above mentioned objects are realised in a black and white silver halide photographic material which comprises on a support in the order given:

- at least one non-light sensitive layer having a hydrophilic polymer in an total amount A between 0.1 and 0.9 g/m²,
- at least one light sensitive silver halide emulsion layer having a hydrophilic polymer in an total amount B between
- 20 1 and 2 g/m²,
- at least one non-light sensitive layer having a hydrophilic polymer in an total amount C between 0.5 and 1.6 g/m²,

wherein:

- 25 - $0 \leq A/B \leq 0.6$
and
- $0.7 \leq B/C \leq 2.25$

- while the total amount of hydrophilic polymers is not more than 3 gram and the amount of silver halide less than 0,05
- 30 mole both per square meter and per side of the support.

[0014] Preferred embodiments of the invention are disclosed in the dependent claims.

DETAILED DESCRIPTION OF THE INVENTION

- 35 **[0015]** While the present invention will hereinafter be described in connection with preferred embodiments thereof, it will be understood that it is not intended to limit the invention to those embodiments. On the contrary, it is intended to cover all alternatives, modifications, and equivalents as may be included within the spirit and scope of the invention as defined by the appending claims.

- [0016]** The photographic material to be used in the present invention comprises a layer assembly which contains at
- 40 least at one side of a support a number of hydrophilic colloid layers which can be described as:

- light-sensitive emulsion layers,
- undercoat or front layers which are non-light sensitive and situated between the support and the light-sensitive emulsion layers, and
- 45 - overcoat or top layers which are also non-light sensitive and always further situated than the light-sensitive emulsion layers as seen from the support.

- [0017]** All these layers which are the subject of this invention are hydrophilic colloid layers which contain one or more hydrophilic polymers as binder. While the amount of these polymers has a direct influence on the thickness of the
- 50 hydrophilic layers and therefore on the thickness of the whole material it is important for the realization of this invention that the amount of polymer is restricted for each layer as follows:

- the non-light sensitive undercoat layers a total amount A of hydrophilic polymer between 0.1 and 0.9 g/m², and
- the light-sensitive emulsions which are silver halide emulsions in this invention has a total amount B of hydrophilic
- 55 polymer between 1 and 2 g/m², and
- the non-light sensitive overcoat layers a total amount C of hydrophilic polymer between 0.5 and 1.6 g/m².

[0018] While layer assemblies stated in patent proposals, as mentioned before, can also comprise layers with polymer

amounts situated between the described weight boundaries, the material can only meet the objects of this invention if the following formulae are obeyed:

- $0 \leq A/B \leq 0.6$
and
- $0.7 \leq B/C \leq 2.25$.

However the best results are realized if the amounts of hydrophilic polymer used in the different layers of the material obeys the following general formulae:

- $0 \leq A/B \leq 0.5$
and
- $0.7 \leq B/C \leq 1.4$.

[0019] It is important to note that in the context of the present invention it is necessary that the amount of hydrophilic polymer is not more than 3 gram per m^2 per side of the support while the amount of silver halide per m^2 should be less than 0.05 mole per side. However in a preferred embodiment it is recommended that the amount of silver halide is not more than 0.04 mole or more preferably not more than 0.035 mole per m^2 and per side of the support.

[0020] It is important to note that the application of this invention is also valid for materials which contain at least one light sensitive silver halide emulsion layer on each side of the support.

[0021] The hydrophilic polymer plays a central role in this invention and can be present in many different ways: alone or mixed with other hydrophilic polymers or mixed up with one or more products which can influence the typical elastomeric properties of the polymers.

[0022] Suitable hydrophilic colloids include in the first place naturally occurring substances like proteins, protein derivatives, cellulose derivatives, gelatine and derivatives and polysaccharides. This class also includes oxidized gelatine which can be formed with a oxidizing agent specially for methionine what can be realized prior to or during emulsion precipitation. Another class of hydrophilic colloids is formed by silica, derivatives and analogue products.

[0023] Hydrophilic colloids which can be used alone or in combination with one of the polymers mentioned before is the group of synthetic hydrophilic polymers like polyvinylalcohol and its derivatives, polyacrylamide, polyacrylate and many others. A special category is formed by the latex polymers which are added to achieve specific properties in the preparation stage of the photographic material or in the material itself like for instance viscosity increase, decrease of pressure sensitivity, the improve of dryability, etc. An important group of products which influence the matrix of the hydrophilic polymer fundamentally is formed by the hardeners from organic or inorganic origine which can be used alone or in combination, in free or in masked form. Typical useful hardeners are formaldehyde, free dialdehydes, epoxides and many others. All the possibilities which can be used in this invention including many references are described in Res.Disclosure, (sept. 1996), number 38957, section II.

[0024] The light sensitive emulsion of this invention is a silver halide emulsion which can be prepared in various ways by conventional methods. These always start with a nucleation phase followed by a grain growth phase. In this last phase of the emulsion preparation reactants are added to the reaction vessel in the form of solutions of silver and halide salts or in the form of preformed silverhalide nuclei or fine grains which easily dissolve in the precipitation medium.

[0025] The individual reactants can be added through surface or subsurface delivery tubes by hydrostatic pressure or by an automatic delivery system for maintaining the control of pH and/or pAg in the reaction vessel and of the rate of the reactant solutions introduced in it. The reactant solutions or dispersions can be added at a constant rate or a constantly increasing, decreasing or fluctuating rate, if desired in combination with stepwise delivery procedures. More details about the possible ways in making a silver halide emulsion which can principally be used in this invention are summarized in Res.Disclosure, (sept. 1996), number 38957, section I-C.

[0026] Beside the individual reactants necessary to form silver halide crystals additional metal salts or complexes can be added for occlusion in the crystal lattice. Such compound is replacing an appropriate amount of silver and halide ions in the silver halide lattice. These products or so-called dopants can be distinguished from the metal complexes which are added just before coating as an additive by EPR- or ENDOR-technique. These dopants can be used to modify the crystal structure or the crystal properties and can therefore be employed to influence many photographic properties like sensitivity, reciprocity failure, gradation, pressure sensitivity, fog, stability, etc.. When coordination complexes or even oligomeric coordination complexes are used the different ligands bound at the central metal ion can be occluded in the crystal lattice too and in this way influence the photographic properties of the silver halide materials as well. Dopants which are introduced in emulsions of the present invention are those which can act as a permanent or as a non-permanent electron trap.

[0027] The doping procedure itself can normally be executed at any stage during the grain growth phase of the emulsion preparation. It is important to know that the dopants can also be added in an indirect way by the addition of a dis-

persion containing very fine soluble silver halide grains or nuclei comprising the dopant. More additional information about the introduction and the use of dopants in the emulsion crystals of this invention can be found in Res.Disclosure, (sept. 1996), number 38957, section I-D.

[0028] The photographic emulsions prepared in this way contain silver halide crystals comprising chloride, bromide or iodide alone or combinations thereof. It is a preferred embodiment of this invention that the silver halide grains contain chloride if desired next to other halides. Additionally it is also possible to incorporate other silver salts like silver phosphate, silver thiocyanate, silver citrate and some other silver salts in a limited amount in the silver halide lattice. The chloride and bromide halide can be combined in all ratios to form a silverchlorobromide salt. Iodide ions however can be coprecipitated with chloride and/or bromide ions thus forming a iodohalide with an iodide amount which depends on the saturation limit of iodide in the lattice with the given halide composition; this means up to a maximum amount of about 40 mole percent in silver iodobromide and up to at most 13 mole percent in silver iodochloride both based on silver.

[0029] The composition of the halide can change in the crystal in a continuous or discontinuous way. Emulsions containing crystals composed of various sections with different halide compositions are used for several photographic applications. Such a structure with a difference in halide composition between the center and the rest of the crystal (what is called 'core-shell'-emulsion) or with more than two crystal parts differing in halide composition (called a 'band'-emulsion) may occur. The changes in halide composition can be realised by direct precipitation or in an indirect way by conversion where fine silver halide grains of a certain halide composition are dissolved in the presence of the so-called host grains forming a 'shell' or 'band' on the given grain.

[0030] The crystals formed by the methods described above have a morphology which can be tabular or non-tabular. In tabular crystals the aspect ratio (ratio of equivalent circular diameter to thickness) can vary from low (<2) over 'medium' (from 2 up to 8) to high (>8) where especially in the case of the ultra thin tabular crystals high aspect ratios can be realised. The major faces of the formed tabular grains can have a {111} or a {100}-habitus which structure is stable or should be stabilised for instance by a 'habitus modifying agent'. In the class of non-tabular grains there are a lot of possibilities which can be divided in the more regular shaped crystals or the crystals with a mixed crystal habit.

[0031] For certain applications it can be important to apply a well-defined amount of iodide on the crystal surface under controlled conditions in order to get reproducible sensitometric results after image-wise exposure and subsequent processing. This can be done by using an iodide releasing agent as described in EP-A 0 561 415 and in EP-A 0 563 708 and applied on emulsions before, during or after the chemical sensitization in addition to the method and the conditions of the present invention as described hereinbefore.

[0032] The emulsions can be coagulated and washed after precipitation in order to remove the excess soluble salts. These procedures which can be used in this invention are together with different alternative methods like dia- or ultra-filtration and ion-exchange described in Res.Disclosure, (sept. 1996), number 38957, section III.

[0033] Additional gelatin or another hydrophilic colloid, suitable as a binder material can be added at a later stage of the emulsion preparation e.g. after washing, in order to establish optimal coating conditions and/or to establish the required thickness of the coated emulsion layer. Preferably a gelatin to silver halide ratio, silver halide being expressed as the equivalent amount of silver nitrate, ranging from 0.08 to 1.0 is then obtained. Another binder may also be added instead of or in addition to gelatin. Useful vehicles, vehicle extenders, vehicle-like addenda and vehicle related addenda have been described e.g. in Res.Disclosure, (sept. 1996), number 38957, Chapter II.

[0034] The emulsions can be surface-sensitive emulsions which form latent images primarily on the surface of the silver halide grains or they can be emulsions forming their latent-image primarily in the interior of the silver halide grain. The emulsions can further be negative-working emulsions such as surface sensitive emulsions or unfogged internal latent image-forming emulsions. However direct-positive emulsions of the unfogged, latent image-forming type which are positive-working by development in the presence of a nucleating agent, and even pre-fogged direct-positive emulsions can be used in the present invention.

[0035] The silver halide emulsions can be surface-sensitized by chemical sensitization which can be done in many different ways, in presence of a chalcogen as sulfur, selenium or tellurium, in presence of a noble metal as for instance gold or in combination with a chalcogen and noble metal. The chemical sensitization can also be done by reduction sensitization if desired combined with the chalcogen/noble metal-sensitization. In reduction sensitization a reducing compound is used like thiourea dioxide, hydrazine derivatives, sulphinic acid, polyamine compounds, stannous chloride, borane compounds, reductones like ascorbic acid, etc. Reduction sensitization can also be carried out at a low pAg or a high pH or at both and if desired at elevated temperature. This kind of sensitization is referred to 'silver ripening'. More information can be found in Res.Disclosure, Vol. 307, number 307105 and in P.Glaftides "Chimie et Physique Photographique", P.Montel - Paris, 5th Ed., 1987.

The presence of certain 'modifying' agents as for instance spectral sensitizers which can optimize the chemical sensitization process are often used. A complete description of all the different possibilities with respect to this subject can be found in Res.Disclosure, (sept.1996), number 38957, section IV.

[0036] In a next step the silver halide emulsions are spectrally sensitized with dyes from different classes which

include polymethine dyes comprising cyanines, merocyanines, tri-, tetra- and polynuclear cyanines and merocyanines, oxanols, hemioxanols, styryls, merostyryls and so on. Sometimes more than one spectral sensitizer may be used in the case that a larger part of the spectrum has to be covered. Combinations of several spectral sensitizers are sometimes used to get supersensitization, which means that in a certain region of the spectrum the sensitization is greater than that from any concentration of one of the dyes alone or that which would result from the additive effect of the dyes. Generally supersensitization can be attained by using selected combinations of spectral sensitizing dyes and other addenda such as stabilizers, development accelerators or inhibitors, brighteners, coating aids, and so on. A good description of all the possibilities in spectral sensitization which are important with respect to this invention can be found in Res.Disclosure, (sept. 1996), number 38957, section V.

[0037] In the case that desensitizers should be used, as for instance in pre-fogged direct-positive or in daylight handling materials, various chemical compounds are proposed for practical use. Principally all these compounds which are used as desensitizers in silver halide materials and which are for instance summarized in EP-A 0 477 436 can be used in combination with the elements of this invention.

[0038] The photographic elements comprising the said silver halide emulsions can include various compounds which should play a certain role in the material itself or afterwards in the processing, finishing or warehousing the photographic material. These products can be stabilizers and anti-foggants (see Res.Disclosure, (sept. 1996), number 38957, section VII), brighteners (see Res.Disclosure, (sept. 1996), number 38957, section VI), light absorbers and scattering materials (see Res.Disclosure, (sept. 1996), number 38957, section VIII), coating aids (see Res.Disclosure, (sept. 1996), number 38957, section IXA), antistatic agents (see Res.Disclosure, (sept. 1996), number 38957, section IXC), matting agents (see Res.Disclosure, (sept. 1996), number 38957, section IXD) and development modifiers (see Res.Disclosure, (sept. 1996), number 38957, section XIII).

[0039] The photographic elements can be coated on a variety of supports as described in Res.Disclosure, (sept. 1996), number 38957, section XV and the references cited therein. The photographic elements can be exposed to actinic radiation, specially in the ultra-violet, visible, near-ultraviolet and near-infrared region of the spectrum, to form a latent image (see Res.Disclosure, (sept. 1996), number 38957, section XVI). This latent-image can be processed in order to form a visible image (see Res.Disclosure, (sept. 1996), number 38957, section XIX).

[0040] In this invention principally all halide combinations can be used but for rapid and convenient processing in an automatic processing machine the Cl-containing photosensitive silver halide emulsions are advantageously used. In order to prevent the disadvantages (like the formation of silver sludge) connected with automatic processing these Cl-containing materials are processed in a preferred method as described in EP-A 0 732 619. The developer described in this reference contains a combination of hydrochinon, an auxiliary developing agent, ascorbic acid or one of its isomers or derivatives, and a small amount of a thiocyanate salt. It is recommended to apply this method and to use the various ascorbic acid analogues described in EP-A 0 732 619, which is incorporated herein by reference.

[0041] The invention is described hereinafter by way of the following example.

Example.

[0042] The example described hereinafter will clearly demonstrate the practical advantages which can be realized by applying the layer assembly concept of the present invention on a photosensitive silver halide material.

[0043] For this experiment the following solutions were prepared for use during the precipitation:

- solution (1): containing 500 grams of silver nitrate in 1000 ml of demineralized water
- solution (2): containing 111.1 grams of potassium bromide, 111.3 grams of potassium chloride and 0.98 gram of potassium iodide in 827 ml of demineralized water with a pH of 3.0.
- solution (3): containing 38.4 grams of potassium chloride in 175 ml of demineralized water with a pH of 3.0.

Preparation of the emulsion.

[0044] The preparation procedure was started with adding 1.5 ml of an $3.54 \cdot 10^{-4}$ molar solution of $\text{Na}_3\text{RhCl}_6 \cdot 12\text{H}_2\text{O}$ and 1.0 ml of an $1.79 \cdot 10^{-3}$ molar solution of $\text{Na}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$ to solution (2) immediately followed by the addition of 0.5 ml of a 0.3 molar AgNO_3 -solution during 180 sec to the reaction vessel containing 46 grams of inert gelatine in 1 liter demineralized water at 50 °C. After adjusting the pH on 3.0 and the pAg on 7.04 in the reaction vessel the nucleation was started by adding 15.8 ml per min. of solution (1) and solution (2) (ca 16 ml/min) during 3 minutes so that the pAg was kept at 7.04. This nucleation phase went over continuously in the growth phase wherein the flowrate of solution (1) was increased during 27 minutes and 52 seconds from 15.8 ml/min till 40.0 ml/min while the keeping the pAg at 7.04 by adding solution (2) with increasing flowrate (till ca 40.56 ml/min). After a physical ripening periode of 5 minutes a second growth-phase was started by adding solution (1) at a constant rate of 40.0 ml/min during 4 minutes and 23 seconds while keeping the pAg constant at 7.04 with solution (3) at a rate of ca 40.6 ml/min.

The emulsion was further flocculated by adding 55 ml of a 15 weight % solution of polystyrene sulphonic acid and after ca 20 minutes sedimentation the mother liquid was removed, demineralized water added and the remaining salts were washed out by repeating this procedure. The silver halide emulsion prepared in this way contained crystals which had a mean spherical diameter of 0.20 μm .

The chemical sensitization.

[0045] After redispersing the emulsion with 54.0 grams of inert gelatine (per 500 grams of AgNO_3) and with demineralized water, a small amount of a phenolic solution was added. The emulsion was first adjusted at a pH of 5.2 and the pAg at 7.04 which was further followed by the successive addition (measured per 500 grams of silver nitrate and at 38 °C) of:

- 12 ml of a $6.32 \cdot 10^{-3}$ molar solution of $\text{Na}_2\text{S}_2\text{O}_3$,
- 36 ml of a solution containing $1.456 \cdot 10^{-3}$ mole/l of a Au-salt and 0.158 mole/l of a thiocyanate salt,
- 60 ml of a $4.76 \cdot 10^{-3}$ molar solution of sodium thiosulphonic acid, and
- 30 ml of a $7.93 \cdot 10^{-3}$ molar solution of a sulfite salt.

The temperature is then in a periode of 30 minutes raised till 50 °C followed by a 4 hours during incubation for chemical sensitization at that temperature.

The coating of the emulsion.

[0046] After the chemical ripening periode the temperature was lowered till 38 °C while the pH was adjusted at 5.0 immediately followed by the subsequent addition of an amount of triazaindolizine sufficient to stabilize the emulsions and by several wetting agents in order to coat the emulsions on a terephthalate support. The amount of silver halide was in all the coatings 6 g/m². The hardening was realized by the addition of 0.5 ml of a 2 weight % solution of divinylsulphonylmethane per gram of gelatine.

The resulting composition of the different coated materials are summarized in Table 1. The thickness is always expressed as the amount of hydrophilic polymer (in grams per m²). The values for A/B and B/C are also incorporated in the table in order to position the experimental conditions. The intention of this experiment is to demonstrate how processing and sensitometric results can be influenced by several layer assembly aspects like the decrease in overall layer thickness and the presence of a frontlayer on behalve of the antistrss layer. In the column 'Note': 'ref' means 'reference' and 'inv' means 'invention'.

Exposure and processing procedure.

[0047] The samples of these coatings were exposed during 10^{-8} sec through a stepwedge (cnst = 0.15) using the light of a laserdiode with $\lambda = 670$ nm.

The processing was carried out by using a G101c (trademark of GEVAERT), a hydrochinon-phenidon developer which was diluted with 2 parts of demineralized water on 1 part G101c, followed by a G333-fixer (trademark GEVAERT) which was diluted with 4 parts of demineralized water in one part of G333, both at a temperature of

Table 1

Composition of the layer assembly							
Ref. Nr.	A/B	B/C	Polymer amount layer A (g/m ²)	Polymer amount layer B (g/m ²)	Polymer amount layer C (g/m ²)	Total Polymer amount (g/m ²)	Note
1	0	2.1	0	2.3	1.1	3.4	ref
2	0	0.8	0	1.3	1.6	2.9	inv
3	0.23	1.0	0.3	1.3	1.3	2.9	inv
4	0.46	1.3	0.6	1.3	1.0	2.9	inv
5	0.76	2.2	1.0	1.3	0.6	2.9	inv

35 °C and each time during 15 sec. After washing and drying the density which was realized after processing as a func-

tion of the light dose was measured and used to determine the following parameters:

- the fog level D_{\min} ,
- the gradation in the shoulder of the sensitometric curve which is measured between the densities 3.0 and 3.8 above fog,
- the covering power expressed as the ratio of the density value in the maximum density D_{\max} and the coated amount of silver (expressed in grams of AgNO_3 per m^2),
- the drying time is expressed relative to the drying time of coated sample nr. 1, which was taken as 100 %.

[0048] From these results it becomes clear that decreasing the thickness of the emulsion layer gives an increase in shoulder-gradation and covering power and a significant shortening of the drying time. The formation of a 'front' layer at the cost of the thickness of the

Table 2

Sensitometric results and drying time in function of the composition of the layer assembly.				
Ref.Nr.	D_{\min}	Gradation (sh)	Covering Power	Relative Drying Time (%)
1	0.03	12.1	0.92	100
2	0.03	14.7	1.03	85
3	0.03	12.0	1.00	80
4	0.03	11.4	0.96	85
5	0.03	10.0	0.91	80

antistress layer keeps an advantage in drying time and loses a part of the gain in shoulder-gradation and covering power. In this particular experiment it can be seen that the introduction of a front layer creates the possibility for incorporating extra functionality without losing the sensitometric characteristics which was the main objective of the present invention.

[0049] Having described in detail preferred embodiments of the current invention, it will now be apparent to those skilled in the art that numerous modifications can be made therein without departing from the scope of the invention as defined in the following claims.

Claims

1. A black and white silver halide photographic material comprises on a support in the order given:

- at least one non-light sensitive layer having a hydrophilic polymer in an total amount A between 0.1 and 0.9 g/m^2 ,
- at least one light sensitive silver halide emulsion layer having a hydrophilic polymer in an total amount B between 1 and 2 g/m^2 ,
- at least one non-light sensitive layer having a hydrophilic polymer in an total amount C between 0.5 and 1.6 g/m^2 ,

wherein:

- $0 \leq A/B \leq 0.6$
- and
- $0.7 \leq B/C \leq 2.25$

while the total amount of hydrophilic polymers is not more than 3 gram and the total amount of silver halide less than 0,05 mole both per square meter and per side of the support.

2. A black and white silver halide photographic material according to claim 1, wherein:

- $0 \leq A/B \leq 0.5$
and
- $0.7 \leq B/C \leq 1.4$.

- 5 3. A black and white silver halide photographic material according to claim 1 or 2, wherein the hydrophilic polymer is a natural or modified gelatine.
4. A black and white silver halide photographic material according to any of the claims 1 to 3, wherein the hydrophilic polymer is a mixture of polymers.
- 10 5. A black and white silver halide photographic material according to claim 4, wherein the mixture of polymers contains next to the natural or modified gelatine other polymers which can be hydrophilic or hydrophobic.

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European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 20 3261

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X	US H1515 H (HATTORI YASUSHI ET AL) 2 January 1996 * Example 1; Table 1, materials 1,2,4-6 * * Example 2; Table 2, materials 10,11 * ---	1-5	
X	EP 0 307 868 A (KONISHIROKU PHOTO IND) 22 March 1989 * Example 1, table 1, samples 1-3,5,6 * ---	1-5	
X	EP 0 307 867 A (KONISHIROKU PHOTO IND) 22 March 1989 * page 3, line 24 - line 32 * * page 12, line 33 - line 42 * * page 29, line 45 * * page 33, line 33 - line 39 * * table 2, sample 42 * ---	1-5	
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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 24 February 1999	Examiner 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 P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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