

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 890 874 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
13.01.1999 Bulletin 1999/02

(51) Int. Cl.⁶: **G03C 1/043**, G03C 1/89,
G03C 1/76, G03C 1/005

(21) Application number: **98202001.8**

(22) Date of filing: **12.06.1998**

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **10.07.1997 EP 97202115**

(71) Applicant: **AGFA-GEVAERT N.V.**
2640 Mortsel (BE)

(72) Inventor: **Pattyn, Walter**
2640 Mortsel (BE)

(54) **Silver halide photographic compositions preserved against formation of yellow fog**

(57) A light-sensitive silver halide photographic material is provided comprising a support, one or more water-permeable light-sensitive silver halide layer(s) on one or both sides of the said support and a protective antistress layer, wherein each layer of said material comprises a non-ionic polyoxyalkylene compound in an amount of from 0 to less than 5 mg/m², wherein said protective antistress layer and/or said light-sensitive layer(s) comprise(s) an ionic polyoxyalkylene compound and wherein said material has a lateral surface resistance, determined as prescribed in DIN 53482, of less than 1 x 10¹⁰ Ohm/square.

EP 0 890 874 A1

Description**1. FIELD OF THE INVENTION.**

5 The present invention relates to silver halide photographic compositions and more particularly to radiographic materials comprising additives improving stability against yellow fog formation.

2. BACKGROUND OF THE INVENTION.

10 Yellow fog formation in light-sensitive silver halide photographic materials is known in the art as a problem which is in most general cases related with the presence of fine silver nuclei. These nuclei generated by reduction before, during or after processing of silver salts present in the emulsion layer and/or more outermost layers of the said materials occur therein as particles. In the particular case wherein silver halide light-sensitive photographic materials are susceptible to yellowing after storage, the cause thereof has nearly always been sought in the occurrence of adsorption phenomena
 15 of finely divided silver particles formed by reduction in more or less exhausted developers at the surface of the processed material where the physical development of silver ions takes place. The yellowing phenomenon is most likely due to the deposition of finely divided silver in a non-light-sensitive colloid layer coated in water-permeable relationship with the light-sensitive emulsion layer.

In order to prevent yellowing of such silver halide light-sensitive photographic materials, especially when a developer comprises silver halide solvents, the dissolved silver salts are reduced on silver nuclei by physical development.
 20 The presence of e.g. chloride ions in exhausted developers after development of silver halide photographic materials comprising emulsions rich in silver chloride has led to specific measures in that dedicated chemical additives are incorporated into the non-light-sensitive water-permeable colloid layer as has e.g. been disclosed in US-A's 3,362,826; 3,364,028; 3,365,294 and 3,600,178.

25 Photographic light-sensitive silver halide materials for radiography are often coated with high amounts of silver per sq.m. in order to reach the required speed. When use is made of less soluble but more sensitive emulsions rich in silver bromide or bromiodide and/or of processing in automatic processors provided with replenishing means, in order to avoid problems of exhaustion (and build-up in excess of silver salt dissolving ions) of developer and fixer the problem is not encountered. Even during the last decade wherein rapid processing with lower amounts of replenishing solutions
 30 has become, and is still, a topic of prior interest, no stringent problems with respect to the occurrence of yellow stain or yellow fog have specifically been mentioned in the (patent) literature. Nowadays the trend nevertheless exists to give preference to the use of silver halide emulsions having crystals rich in chloride.

In some particular cases the problem of "yellowing" may however occur. When unexposed radiographic film materials are preserved in quite severe atmospheric circumstances of heat and humidity as in tropical geographic regions,
 35 combination with the use of non-automatic tray development (also called dish or scale development, performed by still a huge number of customers living in tropical regions) leads to the "yellowing" problem. It is clear that in that particular case no automatic replenishment occurs and that development is often carried out in exhausted developers.

If, in addition, an interleaving paper is used between consecutive films piled up in a package in order to avoid sticking and surface damaging of the said films in contact with each other in the severe preservation conditions described
 40 hereinbefore and/or if said films are hardened to a lower extent in order to avoid loss in speed, the problem of "yellowing" or "yellow stain" appears to become even more stringent. Said undesirable stain then often appears in form of depicting fibrous structures of the interleaving paper or spacing paper on the radiographic film material, thereby disturbing a suitable unambiguous medical diagnosis.

45
3. OBJECTS OF THE INVENTION.

A first object of the present invention is to provide silver halide light-sensitive photographic materials free from yellowing or yellow staining after processing.

50 More particularly it is an object of the present invention to avoid depiction of fibrous structures from interleaving papers present between the said film materials piled up in packages as yellowing or yellow staining.

Moreover it is an object of the present invention to avoid the said yellowing or yellow staining mentioned above even after preservation of unexposed materials in circumstances of high temperature and high relative humidity.

55
4. SUMMARY OF THE INVENTION.

In order to reach the objects of the present invention a light-sensitive silver halide photographic material has been provided comprising a support, one or more water-permeable light-sensitive silver halide layer(s) on one or both sides

of the said support and a protective antistress layer, wherein each layer of said material comprises a non-ionic polyoxyalkylene compound in an amount of from 0 to less than 5 mg/m², wherein said protective antistress layer and/or said light-sensitive layer(s) comprise(s) an ionic polyoxyalkylene compound and wherein said material has a lateral surface resistance, determined as prescribed in DIN 53482, of less than 1 x 10¹⁰ Ohm/square.

When moreover an afterlayer is present the said layer is free from any polyoxyalkylene compound.

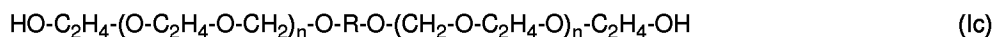
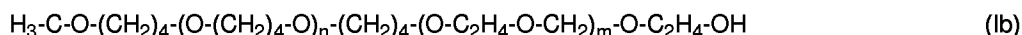
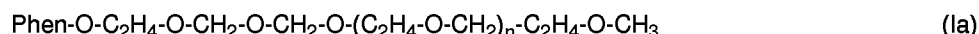
5. DETAILED DESCRIPTION OF THE INVENTION.

It is an essential feature of the present invention to get a measured lateral surface resistance of less than 1 x 10¹⁰ Ohm/square determined as prescribed in DIN 53482 for the light-sensitive silver halide photographic material having a layer arrangement comprising a support and coated on one (single-side coated) or both sides (double-side coated or duplitzed) one or more water-permeable hydrophilic light-sensitive silver halide layer(s), a protective layer and, optionally, an afterlayer.

It is normally common to use non-ionic polyalkylene surfactant(s) having antistatic characteristics in the protective antistress layer of a photographic material as an antistatic agent as has e.g. been described in EP-A 0 644 456 and the corresponding US-A 5,561,032. In the material of the present invention each hydrophilic layer of the said material comprises a non-ionic polyoxyalkylene compound in an amount of from 0 to less than 5 mg/m² and more preferred from 0 to less than 3 mg/m². It is indeed an essential feature of the present invention that all layers of the photographic material are "substantially free" of said non-ionic polyoxyalkylene compounds, wherein the presence of minor amounts as presented herein is still acceptable, but wherein complete absence of said non-ionic compounds is preferred.

Examples of such non-ionic polyoxyalkylenes which should be present in minor amounts and the presence of which should even be avoided in each of the hydrophilic water-permeable layers of the single- or double-side coated radiographic material of the present invention are e.g. polyethylene glycol, polyethylene glycol/polypropylene glycol condensation products, polyethylene glycol alkyl ethers or polyethylene glycol alkylaryl ethers, polyethylene glycol esters, polyethylene glycol sorbitan esters, polyalkylene glycol alkylamines or alkylamides, silicone-polyethylene oxide adducts, glycidol derivatives, fatty acid esters of polyhydric alcohols and alkyl esters of saccharides.

More particularly following compounds should be avoided:



wherein n and m are integers having a value of at least 4 and, more preferably, between 8 and 30, R represents a long chain (substituted or unsubstituted) alkyl or alkylaryl group having at least 10 C-atoms as e.g. oleyl and Phen represents substituted or unsubstituted phenyl.

Also excluded are non-ionic polyoxyalkylene compounds having fluorinated alkyl chains, like e.g. the N-polyoxyethylene ethyl perfluoro caprylic acid amide compound having caprylic acid amide as a terminal group, corresponding to the formula (II), which should particularly be avoided:



A survey of non-ionic polyalkylene compounds has been given in Chapter IX of the Research Disclosures 36544, September 1994, and 38957, September 1996.

It is however not always possible to completely avoid the presence of non-ionic polyoxyalkylene compounds in one or more layers of the photographic material of the present invention. Indeed coating solutions may contain non-ionic polyoxyalkylene compounds as preferred surfactants, or may contain said compounds as impurities present in minor amounts.

Instead of the non-ionic polyoxyalkylene compounds discussed hereinbefore it is preferred to use ionic polyoxyalkylene compounds in one or more layers of the photographic material of the present invention in order to reach the objects of the present invention as set forth hereinbefore.

An especially preferred ionic polyoxyalkylene compound is



As ionic surfactant(s) having antistatic characteristics any of the generally known polyoxyalkylene compounds having an ionizable group, like e.g. a carboxylic acid or sulphonic acid group, may be used in the protective antistress layer.

The compound given in formula (III), wherein Phen represents "phenyl" is e.g. very representative therefore and may be further substituted or unsubstituted. References related therewith have also been given in the survey of Research Disclosures 36544, September 1994 and 38957, September 1996, Chapter IX.

In one embodiment of the present invention one or more ionic polyoxyalkylene compound(s) is (are) present in the protective antistress layer and/or in one or more light-sensitive silver halide emulsion layer(s), wherein maximum amounts of less than 30 mg/m², more preferably from 10 to 25 mg/m² and even more preferably from 10 to 20 mg/m² are present.

As a hydrophilic colloid binder present in the hydrophilic layers of the photographic material according to the present invention proteinaceous colloids, e.g. gelatin, polysaccharides, e.g. (potatoe) starch, and synthetic substitutes as e.g. polyvinyl alcohol, poly-N-vinyl pyrrolidone, polyvinyl imidazole, polyvinyl pyrazole, polyacrylamide, polyacrylic acid, and derivatives thereof can be used. Another preferred alternative is colloidal silica sol. Furthermore the use of mixtures of said hydrophilic colloids is not excluded. Among these binders the most preferred is gelatin. Conventional lime-treated or acid treated gelatin can be used. 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). In order to minimize the amount of binder, gelatin can however be replaced in part or integrally by synthetic polymers as cited hereinbefore or by natural or semi-synthetic polymers. Natural substitutes for gelatin are e.g. other proteins such as zein, albumin and casein, cellulose, saccharides, starch, and alginates. Semi-synthetic substitutes for gelatin are modified natural products as 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.

If an afterlayer is present on top of the outermost protective layer for whatever a reason the silver halide photographic material of the present invention should preferably be completely free from any hydrophobic or hydrophilic polyoxyalkylene compound.

Ionic cross-linked copolymers, known from e.g. US-A's 4,301,240 and 5,561,032 may be present in the protective antistress coating of the material according to the present invention. A preferred latex used therein is a latex of a cross-linked polymer, being a copolymer of an acrylic and/or methacrylic acid ester including 90-99 mole % of acrylate and/or methacrylate units and 1 to 10 mole % of tetraallyloxyethane units as polyfunctional cross-linking monomer, wherein in said copolymer at least 75 % of the ester groups have been transformed into alkali metal carboxylate groups, thus exhibiting ionic characteristics. An especially preferred latex of a cross-linked ionic polymer is poly([c.l.]tetra-allyloxyethane-comethyl acrylate/acrylic acid) with a 3/18/79 molar ratio. Following polymers or copolymeric combinations of monomers have been found to be very useful as ionic or nonionic polymers, whether or not in combination with cross-linked copolymers cited hereinbefore: polyvinylpyrrolidone, polyacrylamide, polyacrylic acid, polyamethylacrylate, polyethylacrylate, polymethylmethacrylate, polyethylmethacrylate as well as styrene-maleic acid or a styrene-maleic acid anhydride type copolymer. Cross-linked copolymers are applied in an amount of at least 10% by weight versus the amount of hydrophilic colloid present in the antistress layer.

In addition the said latex-type copolymers may be present in an outermost gelatin free afterlayer coating (if any) applied over the said antistress layer.

As has been described in US-A 5,561,032 the presence of at least one ionic or non-ionic polymer or copolymer latex in the protective antistress coating, and, optionally, in the afterlayer coated thereover, provides the preservation of good antistatic properties of the material and the absence of water spot defects for the dry film after processing as well as the appearance of an improved surface glare. Furthermore even for thin coated layers for applications in rapid processing conditions the same advantages can be recognized and the appearance of sludge in the processing is significantly reduced in hardener free as well as in hardener containing processing solutions.

The protective antistress layer and the afterlayer (if present) may further comprise spacing agents and coating aids such as wetting agents as e.g. perfluorinated surfactants. Spacing agents which may also be present in the protective antistress layer generally have an average particle size which 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 described in US-A 4,614,708.

A preferred protective antistress layer is made from gelatin hardened up to a degree corresponding with a water absorption of less than 2.5 grams of water per m² at 38°C. The gelatin coverage in the protective layer is preferably not higher than about 1.20 g per m² and is more preferably in the range of 1.20 to 0.60 g per m².

In a preferred embodiment gelatin in the antistress layer is partially replaced by colloidal silica as it gives rise to a further improvement of physical properties. Preferably colloidal silica having an average particle size not larger than 10 nm and with a surface area of at least 300 m² per gram is used, the colloidal silica being present at a coverage of at

least 50 mg per m². Further the coverage of said colloidal silica in the antistress layer is preferably in the range of 50 mg to 500 mg per m². Particularly good results which are fully in accordance with the present invention are obtained by using an antistatic layer consisting for at least 50 % by weight of colloidal silica versus the preferred ionic polymer latex described hereinbefore. Especially preferred colloidal silica particles have a surface area of 500 m² per gram and an average grain size smaller than 7 nm. Such type of silica is sold under the name KIESELSOL 500 (KIESELSOL is a registered trade name of Bayer AG, Leverkusen, Germany).

In admixture with the hardened gelatin the antistress layer may further contain friction-lowering substance(s) such as dispersed wax particles (carnaubawax or montanwax) or polyethylene particles, fluorinated polymer particles, silicon polymer particles, etc., in order to further reduce the sticking tendency of the layer especially in an atmosphere of high relative humidity.

The gelatin binder can be forehardened 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-vinyl-sulphonyl-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-triacryloyl-hexahydro-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 binder can also be hardened with fast-reacting hardeners such as carbamoylpyridinium salts as disclosed in US-A 4,063,952 and onium compounds as disclosed in EP-A 0 408 143.

In another embodiment of the present invention the presence in the protective layer of the light-sensitive silver halide photographic material according to the present invention of a mercapto compound and/or a polyhydroxybenzene compound is highly preferred in order to exclude any risk for yellowing.

Those products, if present, are added to the coating composition of the protective antistress layer in an amount of from 0.01 to 10 mg/m², more preferably from 0.04 to 4 mg/m², and/or in an amount of from 2.5 to 250 mg/m² and more preferably from 1 to 100 mg/m² respectively.

Preferred mercapto-compounds are unsubstituted or substituted mercaptotetrazole compounds as e.g. 1-phenyl-5-mercaptotetrazole, wherein, if substituted, a substituent making the said compound(s) soluble in alkaline medium, like e.g. a carboxylic or a sulphonic group, however not being limited thereto, is highly preferred.

Preferred polyhydroxybenzene compounds are unsubstituted or substituted dihydroxybenzene compounds, wherein dihydroxybenzene disulphonate is a particularly preferred compound.

A common support of a photographic silver halide emulsion material is a hydrophobic resin support or hydrophobic resin coated paper support. Hydrophobic resin supports are well known to those skilled in the art and are made e.g. of polyester, polystyrene, polyvinyl chloride, polycarbonate, preference being given to polyethylene terephthalate or polyethylene naphthalate.

The hydrophobic resin support is commonly provided with one or more hydrophobic subbing layers known to those skilled in the art for adhering thereto a hydrophilic colloid layer. Suitable subbing layers for polyethylene terephthalate supports are known e.g. from US-A's 3,397,988, 3,649,336, 4,123,278 and 4,478,907.

The light-sensitive silver halide photographic materials according to the present invention have a lateral surface resistance of less than 1×10^{10} Ohm/square, and more preferably of not more than 1×10^9 Ohm/square, when measured by the method as prescribed in DIN 53482 in order to fully reach the objects of the present invention. In order to obtain such a low lateral surface resistance measured as described in DIN 53482 besides good adhesion properties between the support and the hydrophilic light-sensitive layer(s) of the material according to the present invention, the presence of a subbing layer in contact with the said support and a hydrophilic colloidal layer coated thereupon is highly preferred, wherein in a preferred embodiment said hydrophobic subbing layer comprises vinylidene chloride and wherein in a further preferred embodiment of the present invention the said subbing layer comprises a polythiophene compound as a particularly suitable antistatic agent having electronic conductive properties. More particularly for materials according to the present invention a polyethylene dioxythiophene compound should be present in the subbing layer coated onto the support as disclosed e.g. in US-A's 5,312,681 and 5,391,472.

According to the present invention the material thus has a subbing layer on one or both sides and adhered to the support, wherein said subbing layer further comprises vinylidene chloride and a polyethylene dioxythiophene compound.

In a further preferred embodiment a hydrophilic colloidal layer coated upon the subbing layer of the material according to the present invention is a gelatinous layer having gelatin in a preferred amount of from 0.1 to 0.3 g/m², which corresponds with a rather thin intermediate layer between subbing layer and light-sensitive silver halide emulsion layer.

Said intermediate layer may comprise one or more antihalation dyes. Antihalation dyes are non-spectrally sensitising dyes which are widely used in photographic elements in order to absorb reflected and scattered light. Examples of the said dyes have been described e.g. in US-A's 3,560,214; 4,857,446; 5,344,749; 5,478,708; 5,502,205.

The filter dye(s) can be coated in layers of photographic elements in the form as has been described in EP-A's 0 401 709; 0 384 633; 0 323 729; 0 274 723; 0 276 566; 0 351 593; in US-A's 4,900,653; 4,904,565; 4,949,654;

4,940,654; 4,948,717; 4,988,611 and 4,803,150; and in Research Disclosure 19551 (July 1980), wherein these examples are not limitative.

Light-sensitive silver halide photographic materials according to the present invention are coated with at least one light-sensitive silver halide emulsion layer.

Silver halide emulsions present in said emulsion layer may comprise silver halide emulsion crystals having whatever a crystal habit (e.g. cubic, octahedral, tabular or irregular, in the presence or in the absence of rounded edges, further eventually provided with protrusions, whether or not in form of epitaxial deposits) and a silver halide composition (e.g. silver bromide, silver bromiodide, silver bromochloride, silver bromochloriodide, silver chloride, silver chlorobromide, silver chlorobromiodide, silver chloriodide).

Preferably emulsions comprising crystals having a tabular crystal habit with {100} or {111} major faces are preferred, wherein said crystals have an average crystal thickness of less than 0.3 μm and an average aspect ratio of more than 2, more preferably a thickness of less than 0.2 μm and an average aspect ratio of more than 5, and even more preferably more than 8, and wherein tabular crystals account for at least 50 % of the total projective surface of the said crystals. More preferably silver bromiodide crystals having an iodide concentration of 1 mole % or less are present wherein said crystals have a variation coefficient of less than 25% and more preferably from 10 to 20%.

Mixtures of emulsions may be present in one or more emulsion layers as well as crystals differing in crystal habit and/or composition as has been described e.g. in EP-A 0 770 909.

Preferred total amounts of silver halide expressed as equivalent amounts of silver nitrate per square meter and per side are in the range from 3 to 5 g and more preferably from 3.5 to 4.5 g.

Coating of a gelatin free afterlayer, if present, as well as coating of the protective antistress layer and light-sensitive emulsion layer or layers may proceed by any coating technique known in the art, e.g. by doctor blade coating, air knife coating, curtain coating, slide hopper coating or meniscus coating, which are coating techniques known from the production of photographic silver emulsion layer materials. Curtain coating and slide hopper coating techniques have e.g. been applied in EP-A 0 752 617. Spray coating technique, known from US-A 4,218,533, may be applied, e.g. when an afterlayer is coated.

Any thickening agent may be used in order to regulate the viscosity of the solution used for any of the said coating techniques provided that they do not particularly effect the photographic characteristics of the silver halide light-sensitive photographic material. Preferred thickening agents include aqueous polymers such as polystyrene sulphonic acid, sulphuric acid esters, polysaccharides, polymers having a sulphonic acid group, a carboxylic acid group or a phosphoric acid group, polyacrylamide, polymethacrylic acid or its salt, copolymers from acrylamide and methacrylic acid and salts derived thereof, copolymers from 2-acrylamido-2-methyl-propanesulphonic acid, polyvinyl alcohol, alginate, xanthane, carraghenan, etc..

Polymeric thickeners well-known from the literature resulting in thickening of the coating solution may be used independently or in combination. Patents concerning thickening agents are US-A 3,167,410, Belgian Patent No. 558.143, JP-A Nos. 53-18687 and 58-36768 and DE 3,836,945. As a particularly interesting thickening agent use can be made of synthetic clay as has been described e.g. in EP-A 0 813 105.

In a preferred embodiment according to the present invention said light-sensitive silver halide photographic material is a radiographic material, either single-side coated or double-side coated.

It is clear that besides advantages with respect to the absence of yellow fog and formation of static charges in the particular circumstances described in the background of the present invention materials according to the present invention also offer advantages in contact of a silver halide emulsion layer side with the rear side of the recording material, friction with substances such as rubber and hydrophobic polymeric binder, e.g. the binder constituent of phosphor screens used as X-ray intensifying screens, etc.. Building up of static charges and subsequent dust attraction and/or sparking, e.g. during loading of films in cassettes, e.g. X-ray cassettes, or in cameras, or during the taking or projection of a sequence of pictures as occurs in automatic cameras or film projectors is thus prevented.

The following examples illustrate the present invention without however limiting it thereto.

6. EXAMPLES.

6.1.1. Support coated with subbing layer, covered with a gelatinous layer.

A blue tinted, longitudinally stretched polyethylene terephthalate film support having a thickness of approximately 0.61 μm was subbed on both sides (for the comparative subbing layer called "SUBCOMP") with a coating solution at a coverage of 130 m^2 per liter. For the subbing layer "SUBCOMP" the composition was as follows per m^2 and per side:

- 0.17 g of latex copolymer vinylidene chloride (88 wt%), methylacrylate (10 wt%) and itaconic acid (2 wt%),
- 0.06 g of latex copolymer of methylmethacrylate (47.5 wt%), 1,3-butadiene (47.5 wt%) and itaconic acid (2 wt%),
- 0.001 g polymethylmethacrylate-particles with an average diameter of 3.5 μm as a matting agent,

- 0.003 g AKYPO OP 80 (from CHEMY) and 0.001 g HOSTAPAL BV (HOECHST AG) as coating aids, (AKYPO OP 80 for sale as a 100 % pure polymeric compound is a polyoxyethylene compound having a carboxylic acid group and a Phenyl-C(CH₃)₂-CH₂-C(CH₃)₃ group as terminal groups; HOSTAPAL BV is available as a 50 % aqueous solution of a polyethylene compound having a sulphonic acid group (in sodium salt form) as one terminal group and a 2,4, 6-tri-[CH(CH₃)(C₂H₅)]-Phenyl group as the other terminal group.

These layers were dried in a hot air stream whereafter the coated support was stretched transversally to 3.5 times its original width, at a temperature of about 110°C.

The final thickness of the film was 175 µm. The film was then heat-set while being kept under tension at a temperature of 220°C for about 10 seconds.

After heat setting the film was cooled.

The subbing procedure (called "SUBTHIO") for the inventive material was analogous and resulted in the following layer composition per m² and per side:

- 0.48 g of copolymer vinylidene chloride (88 wt%), methylacrylate (10 wt%) and itaconic acid (2 wt%),
- 0.06 g of copolymer of methylmethacrylate (47.5 wt%), 1,3-butadiene (47.5 wt%) and itaconic acid (2 wt%),
- 0.1 g of silica particles (Kieselsol 100F from Bayer AG, Leverkusen, Germany) as a matting agent,
- 10.4 mg of poly-3,4-ethylenedioxythiophene-polystyrene sulphonic acid
- 0.1 g of sorbitol.

The composition of the gelatinous layer (expressed in amounts per sq. meter) covering the subbing layer was as follows:

- 0.20 g of gelatin (Rousselot type R10985),
- 0.18 g of silica particles (Kieselsol 300F, from Bayer AG),
- 13 mg of ULTRAVON W (CIBA-GEIGY), 7 mg of ARKOPAL N060 (HOECHST AG) and 67 mg of trimethylolpropane as coating aids,
- 1 mg of polymethylmethacrylate (average particle diameter : 2.5 µm) as a matting agent.

ULTRAVON W is mixture of sulphonic acid sodium salt substituted benzimidazole compounds wherein the 2-position between the two N-atoms is substituted by a C₁₇H₃₅-group and wherein the said product is partly substituted at one N-atom with a benzyl-group, which is further partially substituted with a sulphonic acid sodium salt group;

ARKOPAL N060 is a polyethyleneglycol, having as one terminal group a phenyl-group having a C₉H₁₉-substituent.

6.1.2. Preparation of the coating solution of emulsion layer (EM)

1.2.1. Emulsion preparation.

A tabular silver bromiodide emulsion, containing 1 mole % of AgI and 99 mole % of AgBr, was precipitated using the double jet technique as described in US-A 5,595,864.

The excess KNO₃ was removed by the flocculation and washing technique after precipitation. The thus obtained tabular grain emulsion, containing 75 grams of gelatin pro mole of AgNO₃, had the following characteristics:

- mean diameter of the circle with the same projective surface of the tabular grain: 1.12± 0.23 µm (0.23 = standard variation s).
- mean thickness of the tabular grains : 0.23 µm.
- aspect-ratio : 5.5.
- percentage of total projective surface covered by the tabular grains: 98%.

1.2.2. Chemical sensitization.

This emulsion was chemically sensitized in the presence of anhydro-5,5'-dichloro-3,3'-bis(n.sulfobutyl)-9-ethyl-oxacarbocyanine hydroxide, chloro auric acid, sodium thiosulphate and potassium thio-cyanate in order to get an optimized fog-sensitivity relationship.

1.2.3. Additional ingredients of the emulsion solution.

Per mole of AgNO_3 (an amount of 4.1 g/m^2 and per side was coated) the following ingredients were added to the emulsion at 40°C :

- 0.29 g of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene;
- 9.1 g of sorbitol;
- 14.5 g of polyethylacrylate (MW=1000000);
- 3.05 g of 1,3- dihydroxybenzene;
- 31 g of dextrane (MW=10000);
- 0.42 g of $\text{C}_8\text{H}_{17}\text{-Phen-(O-C}_2\text{H}_4)_8\text{-CH}_2\text{-COONa}$
- 10 g of gelatin and
- demineralized water in an amount necessary to get the desired wet coating thickness.

1.3.1. Composition of the protective antistress layer (AS) (compounds, expressed in grams per square meter per side) :

gelatin	1.10
polymethylmethacrylate (average particle diameter : $6 \mu\text{m}$)	0.023
1-p-carboxyphenyl-4,4'-dimethyl-3-pyrazolidine-1-one	0.054
$\text{C}_7\text{H}_{15}\text{-CO-NH-(CH}_2\text{-CH}_2\text{-O-)}_{17}\text{-H}$	0.0188
$\text{C}_8\text{H}_{17}\text{-Phen-(O-C}_2\text{H}_4)_8\text{-CH}_2\text{-COONa}$	0.004
formaldehyde	0.1

The X-ray photographic material was provided with an afterlayer as a gelatin free outermost layer on top of the protective antistress layer covering the silver halide emulsion layer, described hereinbefore.

1.3.2. Composition of the outermost layer ("afterlayer" (AL)):

A non-ionic polyoxyethylene (POE) compound represented by the formula $\text{R-O-(CH}_2\text{CH}_2\text{O)}_n\text{-H}$ with $n=10$ and R=oleyl was added to an aqueous solution ready for coating. Said product was present in an amount of 5.0 g/l and was coated in an amount of 40.0 mg/m^2 . As a non-ionic ammoniumperfluoro compound the compound represented by the formula $\text{F}_{15}\text{C}_7\text{COONH}_4$ was present therein in an amount of 3 mg/m^2 .

Use was made of the slide hopper coating technique for simultaneous application of the emulsion layer (EM), the protective antistress layer (AS) and the antistatic afterlayer coating (AL). The resulting material corresponding with comparative coating No. 13 in Table 1 hereinafter, was preserved for 3 days (35°C and $80\% \text{ RH}$).

Remark that $\text{C}_8\text{H}_{17}\text{-Phen-(O-C}_2\text{H}_4)_8\text{-CH}_2\text{-COONa}$ was present as ionic polyoxyalkylene compound in the emulsion layer as well as in the protective antistress layer. In its absence coating failures were observed and irreproducible values of relative surface resistances.

Other materials were differing from the comparative material No. 13 in that the polyoxyethylene compound represented by the formula $\text{R-O-(CH}_2\text{CH}_2\text{O)}_n\text{-H}$ with $n=10$ and R=oleyl was incorporated in the protective antistress layer (AS) for Material No. 14 and in the emulsion layer (EM) for Material No. 15 instead of incorporation in the afterlayer (AL).

For the Materials Nos. 1 to 12, no afterlayer was coated, and the polyoxyethylene compound, called compound A in Table 1, represented by the formula $\text{R-O-(CH}_2\text{CH}_2\text{O)}_n\text{-H}$ with $n=10$ and R=oleyl , was incorporated in the protective antistress layer.

The Materials Nos. 7-12 were differing from the Materials Nos. 1-6 in that as a polyoxyethylene compound, the compound A was present in the protective antistress layer, whereas for Materials Nos. 1-6 the compound B, N-polyoxyethylene ethyl perfluoro caprylic acid amide corresponding to the formula $\text{C}_7\text{F}_{15}\text{CONH-(C}_2\text{H}_4\text{)-OC}_2\text{H}_4\text{)}_{17}\text{-OH}$ was used.

Amounts in mg/m^2 and per side of the respective polyoxyethylene compounds A or B are given in Table 1.

Further differences should be noted with respect to the composition of the subbing layer from the Materials Nos. 4-6 and 10-12 (called "SUBTHIO" in Table 1, indicating the presence of polythiophene compound in the subbing layer containing vinylidene chloride as indicated above) on both sides of the support and Materials Nos. 1-3, 7-9 and 13-15 (called "SUBCOMP" in Table 1, referring to the comparative character of the subbing layer, SUBCOMP (comparative

subbing layer) without polythiophene compound).

As an objective evaluation of the antistatic properties the lateral surface resistance in Ohm/square was measured before processing, as prescribed in DIN 53482, at a relative humidity RH of 30 %.

In order to controll the presence of "yellow fog" or "yellow stain" on the processed film the following test was performed.

The whole package containing 10 piled-up film sheets (14" x 17") separated by paper interleaves was put between cardboard. This package was further inserted in a light-tight plastic bag. In a conditioning room ("clima chamber") having a temperature of 60°C and a relative humidity of 11 % this plastic bag was preserved during 7 days in order to simulate real circumstances the customers are working in. A plate of polyvinyl chloride having a weight of 2.8 kg and covering the whole bag surface was placed upon said plastic bag.

For the processing of the preserved film sheets following developer and fixer solution were used.

Per liter of developer solution:

-hydroquinone	8 g
-phenidone	0.6 g
-sodium sulphite	40 g
-potassium bromide	40 g
-sodium hexametaphosphate	1 g
-sodium carbonate	50 g

Per liter of fixer solution:

-tri-sodium sequestrene	1 g
-sodium thiosulphate	130 g
-sodium sulphite	10 g
-sodium carbonate	6 g
-sodium bicarbonate	14 g

In a developer tank and a fixer tank both having a volume of 45 liter, 6.5 liter of the developer solution and of the fixer solution the composition of which have been given hereinbefore were poured out respectively. Inbetween the developer and the fixer tank and after the fixer tank rinsing tanks, filled with tap-water, were positioned. In order to exhaust the developer and fixer solutions 150 m² of film material (1200 sheets of film having format of 14" x 17 ") were processed over a period of 4 days in order to imitate practical processing of the film sheets, preserved in the "clima chamber" in really existing marginal conditions, thereby causing the problems set forth in the background of the present invention.

During 3 minutes at 29°C the preserved film sheets were developed in the exhausted developer solution, further rinsed in the tap-water tank for 5 seconds, fixed in the fixer solution for 4 minutes and rinsed in the second tap-water tank for 5 minutes.

The presence after processing of "yellow fog" or "yellow stain" depicting the fibrous structure of the paper interleaves (delivered by INTERMILL'S, Belgium) was indicated with a '+'-sign in Table 1, whereas its absence was indicated with a '-'-sign.

Moreover the presence of spark exposures detected after the processing cycle described hereinbefore was qualitatively evaluated by means of figures going from "0" (good, free from sparks) to "5" (very bad), wherein "bad" corresponds to a figure of "3". Therefore in the "clima chamber" (room with the well-determined preservation conditions described hereinbefore) 10 unexposed sheets having a format of 14" x 17" were transported through a "Hitashi Model TU 130 V" cassetteless table for medical radiology.

Table 1.

MATL. No.	Subbing Layer	POE*-comp	Amt.of POE* comp./side	SR($\times 10^{-9}$ Ohm/sq.)	Yellow fog	Sparks
1(comp)	SUBCOMP	B	20	10000	+	3
2(comp)	SUBCOMP	B	10	50000	+	4
3(comp)	SUBCOMP	B	2	500000	-	5
4(comp)	SUBTHIO	B	20	1	+	1
5(comp)	SUBTHIO	B	10	1	+	1
6(inv)	SUBTHIO	B	2	1	-	0
7(comp)	SUBCOMP	A	50	5000	+	2
8(comp)	SUBCOMP	A	25	10000	+	3
9(comp)	SUBCOMP	A	2.5	500000	-	5
10(cmp)	SUBTHIO	A	50	1	+	0
11(cmp)	SUBTHIO	A	25	1	+	0
12(inv)	SUBTHIO	A	2.5	1	-	0
13(cmp)	SUBCOMP	A(AL)	50	5000	+	2
14(cmp)	SUBCOMP	A(AS)	50	10000	+	3
15(cmp)	SUBCOMP	A(EM)	50	50000	+	5

* non-ionic polyoxyethylene compound.

As can be concluded from Table 1 the objects of the present invention i.e. to provide a material, piled up between paper interleaves in an atmosphere of high temperature and high relative humidity, having sufficient antistatic properties (lateral surface resistance of less than 1×10^{10} Ohm/square), showing no spark exposure nor yellow fog formation after processing in an exhausted developer (due e.g. to the absence of replenishment) is only realized if in the protective antistress layer and/or the emulsion layer a non-ionic polyoxyalkylene compound is reduced to a minimum amount (from 0 to less than 5 mg/m^2) and if a lateral surface resistance of less than 1×10^{10} Ohm/square is measured before processing, as prescribed in DIN 53482.

In the presence of compound B as a polyoxyalkylene compound having caprylic acid amide as a terminal group an acceptable sensitivity for the formation of sparks is observed, but the risk to get sparks is still present and is only taken away completely (as well as yellow fog formation) if the said compound B is present in an amount within the range as claimed and if a lateral surface resistance as claimed is measured as prescribed in DIN 53482.

If moreover an ionic polyoxyalkylene compound is present as becomes clear from the composition of the coating solutions of the emulsion layer (1.2.3) and of the antistress layer composition (1.3.1) hereinbefore the risk of getting sparks and yellow fog formation is further reduced to a minimum.

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 appending claims.

Claims

1. Light-sensitive silver halide photographic material comprising a support, one or more water-permeable light-sensitive silver halide layer(s) on one or both sides of the said support and an outermost protective antistress layer, wherein each layer of said material comprises a non-ionic polyoxyalkylene compound in an amount of from 0 to less than 5 mg/m^2 , wherein said protective antistress layer and/or said light-sensitive layer(s) comprise(s) an ionic polyoxyalkylene compound and wherein said material has a lateral surface resistance, determined as prescribed in DIN 53482, of less than 1×10^{10} Ohm/square.

2. Material according to claim 1, wherein said ionic polyoxyalkylene compound is present in an amount of from 10 to

25 mg/m².

3. Material according to claim 1 or 2, wherein said protective antistress layer further comprises a mercapto compound and/or a polyhydroxybenzene compound.

4. Material according to claim 3, wherein said mercapto compound is a mercaptotetrazole compound.

5. Material according to claim 3, wherein said polyhydroxybenzene compound is a dihydroxybenzene disulphonate compound.

6. Material according to any of claims 1 to 5, wherein said material has a subbing layer on one or both sides and adhered to the said support, wherein said subbing layer comprises vinylidene chloride and a polyethylene dioxythiophene compound.

7. Material according to claim 6, wherein between said subbing layer and a light-sensitive layer more close to the said support, the said material further comprises a hydrophilic colloidal layer.

8. Material according to claim 7, wherein said hydrophilic colloidal layer is a gelatinous layer having gelatin in an amount of from 0.1 to 0.3 g/m².

9. Material according to any of claims 1 to 8, wherein at least one light-sensitive silver halide layer comprises an emulsion having tabular silver halide crystals with an average crystal thickness of less than 0.3 µm and an average aspect ratio of more than 2, and wherein tabular crystals account for at least 50 % of the total projective surface of the said crystals.

10. Material according to any of claims 1 to 8, wherein at least one light-sensitive silver halide layer comprises an emulsion having tabular silver halide crystals with an average crystal thickness of less than 0.2 µm and an average aspect ratio of more than 5, and wherein tabular crystals account for at least 50 % of the total projective surface of the said crystals.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 20 2001

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.6)
A	GB 2 299 680 A (KODAK LIMITED) 9 October 1996 * page 2, line 8 - line 10 * * page 2, line 27 - page 8, line 10 * * page 9, line 1 - line 4 * * page 9, line 10 - line 16 * * page 10, line 32 - line 6 * * page 12, line 29 - page 13, line 2 * * page 13, line 29 - page 14, line 7 * * page 21, line 9 - line 14 * * table 7 * * claims 1,5 * ---	1-10	G03C1/043 G03C1/89 G03C1/76 G03C1/005
A	EP 0 650 088 A (KODAK LIMITED; EASTMAN KODAK COMPANY) 26 April 1995 * page 2, line 27 - line 31 * * page 3, line 5 - page 5, line 55 * * page 6, line 28 - line 33 * * page 7, line 4 - line 9 * * page 7, line 50 - page 8, line 2 * * examples * * claims 1,5,8,9,11 * ---	1-10	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
D,A	EP 0 644 456 A (AGFA-GEVAERT NAAMLOZE VENNOOTSCHAP) 22 March 1995 * page 2, line 55 - page 3, line 3 * * page 4, line 43 - page 5, line 1 * * page 5, line 55 - page 6, line 7 * * examples * * claims 1,4,5,13 * -----	1-10	G03C
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 1 October 1998	Examiner Binder, R
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 (Prelim)