

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 581 006 A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **93109607.7**

(51) Int. Cl.⁵: **G03C 1/76, G03C 1/34**

(22) Date of filing: **16.06.93**

(30) Priority: **02.07.92 IT MI921619**

(43) Date of publication of application:
02.02.94 Bulletin 94/05

(84) Designated Contracting States:
DE FR GB IT

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(54) **Silver halide photographic material having improved resistance to pressure desensitization.**

(57) Light-sensitive silver halide photographic material to obtain black-and-white half-tone, dot or line, images comprising a support and coated thereon one or more hydrophilic layers, at least one of said hydrophilic layers including a high chloride content silver halide emulsion, wherein said silver halide emulsion comprises a polyhydroxybenzene and wherein the outermost hydrophilic layer comprises wax-like polyolefine particles having an average size ranging from 0.5 to 3 μm .

The photographic material shows a better resistance to pressure desensitization.

EP 0 581 006 A1

FIELD OF THE INVENTION

The present invention relates to a photosensitive silver halide material for obtaining black-and-white half-tone, dot, or line, images having improved resistance to pressure desensitization.

BACKGROUND OF THE ART

Photosensitive silver halide materials are commonly used in the photolithographic industry to obtain half-tone, dot, or line, high contrast images. An example of high contrast photographic element having a white reflective support is a phototypesetting material intended to produce black, type character images on a white background. An example of a high contrast photographic element having a transparent support is lith film, so called because it is used as a contact transparency for exposing lithographic printing plates. The illusion that some areas of a printed image are of intermediate density is created by the viewer's inability to resolve tiny dots or lines of maximum density and background areas of minimum density that separate them. Such images are referred to as half-tone images.

It is known in the art of silver halide photography that unevenly applied pressure can result in localized differences in the image density of the photographic film. This is an adverse effect for practical applications, and is known as pressure or kink sensitivity. This effect causes a part of a light-sensitive silver halide photographic material to become spuriously black or white by sensitization or by desensitization. In some instances the density produced by the silver halide grains is increased, but more commonly the silver halide grains are desensitized. Pressure sensitization or desensitization occurs during handling of the photographic material (i.e., by folding, twisting and/or warping) or during roller transport processing. Pressure desensitization has been most often observed in large format photographic elements, which are more susceptible to kinking.

Pressure sensitivity of the silver halide photographic material can be reduced by the incorporation of various addenda, such as, for example, the addenda described in *Research Disclosure*, Vol 176, December 1978, Item 17643, Section VI, K; *Research Disclosure*, Vol 184, August 1979, Item 18431, Section II, H; *Research Disclosure*, Vol 308, December 1989, Item 308,119, Section VI, K-L; and E.J.Birr, Stabilization of Silver Halide Emulsion, Focal Press, London, 1974, pp. 133-134. *Research Disclosure* is published by Kenneth Mason Publications, Ltd., Emsworth, Hampshire PO10 7DD, England. However, some of these addenda often affect photographic characteristics without having a substantial effect on pressure sensitivity.

The incorporation of substituted or unsubstituted polyhydroxybenzenes in silver halide photographic material to reduce pressure sensitivity is disclosed in EP 209,010, claiming a negative working photographic material of high contrast and reduced pressure sensitivity, which comprises polyhydroxybenzenes and arylhydrazides, and in US 4,914,002, claiming a silver halide photographic material with excellent pressure properties, which contains a combination of hydrazines, cyanines and dihydroxybenzenes having no absorption maximum in the visible light region.

However, the use of polyhydroxybenzene to reduce pressure sensitivity is limited in that the necessarily high quantity of said compound can deteriorate anti-blocking properties, in particular, it can increase the tendency toward tackiness of the emulsion.

Accordingly, there is still the need for a silver halide photographic material which reduces all the above mentioned problems.

It is known in the art to protect photographic materials against mechanical damage by coating them with a thin protective gelatin surface layer. It is also known to include into protective layers a lubricant, such as a water-insoluble wax, to reduce the formation of scratch markings. The water-insoluble waxes for that purpose can be any of the water-insoluble wax-like materials of the known six classes of waxes, i.e., vegetable waxes, petroleum waxes, insect waxes, animal waxes, mineral waxes, and synthetic waxes. Waxes are also used in other than protective layers for various purposes.

GB 1,519,864 describes a photographic material having an antistatic backing comprising a polymeric electrolyte as antistatic agent and dispersed polyolefin particles measuring less than 0.5 μm as sliding agents.

US 2,726,955 describes a photographic material comprising a silver halide emulsion layer containing solid particles of a wax containing an anti-plumming agent.

US 3,676,142 describes a photographic element comprising a continuous phase containing a hydrophilic colloid and a dispersed phase comprising a color coupler dispersed in water-insoluble wax particles.

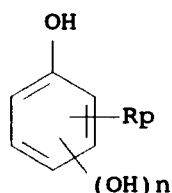
US 4,766,059 describes a photographic element comprising a silver halide emulsion layer and a protective hydrophilic colloid layer comprising finely divided spherical beads having an average size

ranging from 0.5 to 20 μm , said beads comprising a hydrophobic polymeric material and a water-insoluble wax distributed throughout said polymeric material. This combination reduces the sticking tendency and the formation of scratch markings in stacked photographic elements.

Research Disclosure 16743, March 1978, describes a light sensitive silver halide photographic material, coated on polyolefin laminated paper or synthetic paper, comprising oil drops of an organic water-insoluble compound in a silver halide emulsion layer. The size of the oil drops is 1.5 to 10 times the average particle diameter of the silver halide. The organic high-boiling compound has a melting point of about 50°C or below. Examples of such compounds include paraffin. Pressure fog inhibition may be achieved when such oil drops are included in the light-sensitive silver halide emulsion layer, whereas there is no benefit when such oil drops are added to non-light-sensitive layer (eg., a protective layer).

SUMMARY OF THE INVENTION

The present invention relates to a light-sensitive silver halide photographic material to obtain black-and-white half-tone, dot, or line, images comprising a support and coated thereon one or more hydrophilic layers, at least one of said hydrophilic layers including a high chloride content silver halide emulsion, characterized in that said silver halide emulsion comprises a polyhydroxybenzene having the following formula:



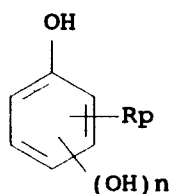
wherein n is 1, 2, or 3,

R is hydrogen, halogen, alkyl, alkoxy, amino, amido, sulfonamido, carboxy and the like, and

p is 0, 1 or 2,

and in that the outermost hydrophilic layer, coated on the same side of the support as the silver halide emulsion layer, comprises wax-like polyolefin particles having an average size ranging from 0.5 to 3 μm .

In a further aspect the present invention relates to a method for obtaining a half-tone, dot or line, image, wherein a silver halide photographic material, comprising a support and coated thereon one or more hydrophilic layers, at least one of said hydrophilic layers including a high chloride content silver halide emulsion, is image-wise exposed for forming said image, and subjected to a photographic process comprising an alkaline developing solution, characterized in that the high-chloride content silver halide emulsion of said photographic material comprises a polyhydroxybenzene derivative of formula



wherein n is 1, 2 or 3,

R is hydrogen, halogen, alkyl, alkoxy, amino, amido, sulfonamido, carboxy and the like, and

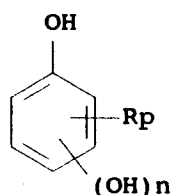
p is 0, 1 or 2,

and in that the outermost hydrophilic layer, coated on the same side of the support as the silver halide emulsion layer, comprises wax-like polyolefin particles having an average size ranging from 0.5 to 3 μm .

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a light-sensitive silver halide photographic material for black-and-white half-tone, dot, or line images comprising a support and coated thereon one or more hydrophilic layers, at

least one of said hydrophilic layers including a high chloride content silver halide emulsion, characterized in that said silver halide emulsion comprises a polyhydroxybenzene having the following formula:



wherein n is 1, 2 or 3,

R is hydrogen, halogen, alkyl, alkoxy, amino, amido, sulfonamido, carboxy and the like, and

p is 0, 1 or 2,

and in that the outermost hydrophilic layer, coated on the same side of the support as the silver halide emulsion layer, comprises wax-like polyolefin particles having an average size ranging from 0.5 to 3 μm .

The polyhydroxybenzenes according formula (I) above can be dihydroxybenzene compounds, trihydroxybenzene compounds, or tetrahydroxybenzene compounds. Useful examples of dihydroxybenzene compounds are 1,2-dihydroxybenzene, i.e., pyrocatechol, 1,3-dihydroxybenzene, i.e., resorcinol, 1,4-dihydroxybenzene, i.e., hydroquinone. Useful examples of trihydroxybenzene compounds are 1,2,3-trihydroxybenzene, i.e., pyrogallol, 1,3,5-trihydroxybenzene, i.e., phloroglucinol, 1,2,4-trihydroxybenzene, i.e., hydroxyhydroquinone. Useful examples of tetrahydroxybenzene compounds are 1,2,3,4-tetrahydroxybenzene, 1,2,4,5-tetrahydroxybenzene, 1,3,4,5-tetrahydroxybenzene.

Said polyhydroxybenzenes can be unsubstituted or substituted with, for example, halogen, alkyl, alkoxy, amino, amido, sulfonamido, carboxy, and the like. Unsubstituted polyhydroxybenzenes are preferred.

The polyhydroxybenzenes (PHB) are added to the photographic emulsion comprising light sensitive silver halide grains and a carrying medium or binder in an amount of from 0.01 to 0.1 moles PHB per mole of silver, preferably of from 0.03 to 0.07 moles per mole of silver.

Waxes may be either natural or synthetic, and of petroleum, mineral, vegetable or animal origin. Waxes are generally water-insoluble, glossy, lustrous, and relatively firm solids at room temperature and are fusible when warmed. Waxes used in the present invention are synthetic polyolefin waxes, such as polyethylene, polypropylene, polytrifluoroethylene and copolymers thereof. They are produced by the polymerization of alkene monomers and, when they have molecular weights in the range of 2000 to 6000, preferably in the range of 2000 to 4000, they have the properties of high-molecular-weight hydrocarbon waxes. The preparation and properties of polyolefin waxes are well known and described for example in *The Chemistry and Technology of Waxes*, by Alvin H. Warth, 2nd Edition, page 443 and foll., Reinhold Publishing Co., and in *Encyclopedia of Polymer Science and Technology*, Vol. 14, page 768 and foll., Interscience Publishers. Polyolefins of the wax-like type appear on the market in the form of fine micronised powders, which do not tend to agglomeration, in spite of their fine particle size, and can be dispersed, without the necessity of high shear conditions nor of melting, by means of low-speed mixers in aqueous compositions. Polyolefins of the wax-like type also appear on the market in the form of dispersions of micronised particles in aqueous or water-miscible solvent compositions, which can be easily incorporated into aqueous gelatin compositions by low speed stirring. The use of polyolefin dispersions according to the present invention allows manufacturers to dispense with chlorinated hydrocarbons used as solvents for dispersing waxes other than polyolefin waxes. The polyolefin dispersions used in the present invention contain particles having an average size of from about 0.5 μm to about 3 μm . These polyolefin dispersions, formed by dispersing a polyolefin which is already in solid form, contain substantially larger particles than dispersions which are obtained directly by the polymerization of olefins in the aqueous phase and in the presence of catalysts and dispersing agents. Dispersions of polyethylene, polypropylene, polytrifluoroethylene and of the corresponding copolymers have been found to be particularly suitable in the present invention.

The polyolefins above are generally added to the carrying medium or binder which forms the outermost layer of the film as an aqueous dispersion in the presence of a suitable dispersing agent, preferably a non-ionic dispersing agent. An aqueous dispersion containing 35% by weight of the polyolefin is preferred, but dispersions containing 1 to 50% by weight of the polymer are suitable.

Suitable dispersing agents are generally non-ionic such as alkyl phenyl polyethylene glycol ethers, e.g., nonyl phenyl polyethylene glycol ether, and undecyl phenyl polyethylene glycol ether; alkyl and aralkyl polyether alcohols, e.g., iso-octyl phenyl polyethoxyethanol, nonyl phenyl polyethoxyethanol, and tetradecyl phenyl polyethoxyethanol. Other suitable dispersing agents include saponin and the oxyalkylene ethers of

hexitol ring dehydration products, e.g., the polyoxyethylene sorbitan monolaurates, monostearates and monooleates which contain 2 to 20 oxyethylene groups divided in three chains; salts of alkyl-substituted aryloxy alkylene ether sulfonates, e.g., sodium p-t-octylphenoxyethoxyethyl sulfonate; sodium dodecyl, tetradecyl and octadecyl sulfates and the dioctyl ester of sodium sulfosuccinic acid. Certain soaps, e.g., morpholine oleate and sodium stearate, can also be used. The dispersing agents are used in amount of from 1 to 50%, preferably of from 2 to 20% by weight of the polyolefin.

The polyolefins can be used in any concentration which is effective for the intended purpose. A suitable concentration is of from 0.01 to 0.1, preferably of from 0.02 to 0.08 grams per square meter of the photographic material.

As a vehicle or binder for the hydrophilic layer of the photographic material of the present invention, any hydrophilic binder known in the art can be used. Suitable binders include natural polymers, synthetic resins, polymers and copolymers, and other film forming media. The binders may range from thermoplastic to highly cross-linked, and may be coated from aqueous or organic solvents or emulsions.

Gelatin is the preferred hydrophilic colloid for use in the present invention. However, other water-soluble colloidal substances or mixtures thereof can also be used. Exemplary hydrophilic colloidal substances include gelatine derivatives, such as phthalated gelatin and acetylated gelatine, cellulose derivatives, such as carboxymethyl cellulose, starch, casein, zein, synthetic hydrophilic colloids such as polyvinyl alcohol, polyvinyl pyrrolidone, copolymers of acrylic acid esters, acrylonitrile and acrylamides, etc.

The amount of hydrophilic binder used in practice depends on the dispersing solvent amount and the coating thickness required. Since an excessive amount of binder can reduce maximum density and contrast, for the purpose of the present invention, the binder is advantageously used in an amount lower than 250 grams per mole of silver halide, preferably in an amount of from 20 to 200 grams per mole of silver halide.

The silver halide emulsions used in the present invention are preferably monodispersed, but emulsions having a wide grain size distribution can also be used. The term "monodispersed" refers to an emulsion having a coefficient of variation lower than 45%, preferably lower than 35%, more preferably lower than 20%. The emulsions suitable in the present invention are of the type normally employed to obtain halftone, dot, and line images and are usually called lith emulsions. Lith emulsions contain preferably at least 50 mole % of silver chloride, more preferably at least 80% of silver chloride and at least about 5% mole of silver bromide. If desired, the silver halide grains can contain a small amount of silver iodide, in an amount that is usually less than about 5 mole %, preferably less than 1 mole %. Other references to lith materials can be found in Research Disclosure 235, November 1983, Item 23510, **"Development Nucleation by Hydrazine and Hydrazine derivatives"**. The silver halide grain average size is lower than about 0.7 μ m, preferably lower than about 0.4 μ m, more preferably lower than 0.2 μ m. The term "grain size" refers to the diameter of a circle having the area of the same value as the average area projected by the silver halide crystals seen in the electron microscope. The silver halide grains may be those having a regular crystal form, such as a cube or an octahedron, or those having an irregular crystal form, such as a sphere or tablet, etc., or may be those having a composite crystal form. They may be composed of a mixture of grains having different crystal forms.

The silver halide emulsion may be chemically sensitized with a sulfur sensitizer, such as allylthiocarbamide, thiourea, cysteine, etc.; an active or inert selenium sensitizer; a reducing sensitizer such as stannous salt, a polyamine, etc.; a noble metal sensitizer, such as gold sensitizer, more specifically potassium aurithiocyanate, potassium chloraurate, potassium chloroplatinate, etc.; or a sensitizer of a water soluble salt such as, for instance, of ruthenium, rhodium, iridium, palladium and the like, more specifically, ammonium chloropalladate, sodium chloropalladate, etc.; each of such sensitizers being employed either alone or in a suitable combination.

Further, the silver halide emulsion may be spectrally sensitized by making it, in addition to its blue light sensitivity, sensitive to, e.g., green light (ortho-sensitive) or sensitive to green and red light (pan-sensitive). For that purpose the usual monomethine or polymethine dyes such as acid and basic cyanines, hemicyanines, streptocyanines, merocyanines, oxonoles, hemioxonoles, styryl dyes or others, as well as trinuclear or higher nuclear methine dyes, e.g., rhodacyanines or neocyanines can be used. Sensitizers of this kind have been described, for example, in F.M. Hamer, **"The Cyanine Dyes and Related Compounds"**, 1964 Interscience Publishers, John Wiley and Sons, New York, and in Research Disclosure 308, December 1989, Item 308119, **"Photographic Silver Halide Emulsions, Preparation, Addenda, Processing and System"**, Section IV.

Both chemical and spectral sensitization are not necessarily required and, if practiced, must not affect the high contrast value.

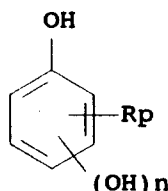
The silver halide emulsions can be prepared using a single-jet method, a double-jet method, or a combination of these methods or can be matured using, for instance, an ammonia method, a neutralization method, an acid method, etc. At the end of grain precipitation, water soluble salts are removed from the emulsion with procedures known in the art, such as ultrafiltration. The emulsions can contain optical brighteners, antifogging agents and stabilizers, filtering and antihalo dyes, hardeners, coating aids, plasticizers, and other auxiliary substances, as those described, for instance, in Research Disclosure 17643, V, VI, VIII, X, XI and XII, December 1978. The above described emulsions can be coated onto several support bases by adopting various methods, as described in Research Disclosure 17643, XV and XVII, December 1978.

Examples of supports include films of a poly- α -olefin (such as polyethylene, polystyrene, etc.), a polyester (such as polyethyleneterephthalate, etc.), cellulose esters (such as cellulose triacetate, etc.), paper, synthetic paper or resin-coated paper and the like.

The above emulsions may also contain various additives conveniently used depending upon their purpose. These additives include, for example, stabilizers or antifoggants such as azaindenes, triazoles, tetrazoles, imidazolium salts, polyhydroxy compounds and others; film hardeners such as of the aldehyde, aziridine, isoxazole, vinylsulfone, acryloyl, triazine type, etc.; developing promoters such as benzyl alcohol, polyoxyethylene type compounds, etc.; image stabilizers such as compounds of the chromane, cumaran, bisphenol type, etc. Also, coating aids, modifiers of the permeability in the processing liquids, defoaming agents, antistatic agents and matting agents may be used. References for the kind and for the use of these additives can be found in Research Disclosure 308, December 1989, Item 308119, **"Photographic Silver Halide Emulsions, Preparation, Addenda, Processing and System"**.

The photographic material of the present invention can include a hydrazine derivative to obtain high contrast images. Any known hydrazine derivatives can be used, such as, for example, hydrazine derivatives described in Research Disclosure 235, November 1983, Item 23510, **"Development Nucleation by Hydrazine and Hydrazine derivatives"**.

In a further aspect the present invention relates to a method for obtaining a half-tone, dot or line, image, wherein a silver halide photographic material, comprising a support and coated thereon one or more hydrophilic layers, at least one of said hydrophilic layers including a high chloride content silver halide emulsion, is image-wise exposed for forming said image, and subjected to a photographic process comprising an alkaline developing solution, characterized in that the high-chloride content silver halide emulsion of said photographic material comprises a polyhydroxybenzene of formula



wherein n is 1, 2 or 3,

R is hydrogen, halogen, alkyl, alkoxy, amino, amido, sulfonamido, carboxy and the like, and p is 0, 1 or 2,

and in that the outermost hydrophilic layer, coated on the same side of the support as the silver halide emulsion layer, comprises wax-like polyolefin particles having an average size ranging from 0.5 to 3 μm .

The present invention does not put any particular restriction on the developing process of the photosensitive material. In general any developing process can be adopted (comprising the developing, fixing and etching steps) which is used to process conventional photographic materials to be used in the lithographic field. Such developing process can be performed manually or by using automatic processors, at a processing temperature generally ranging from 18 to 50 °C, but also outside said range, if desired.

The developing solution can contain any known developing agent. Examples of developing agents (which can be used alone or in mixture) comprise the dihydroxybenzenes (e.g., hydroquinone), aminophenols (e.g., N-methyl-p-aminophenol), 3-pyrazolidones (e.g., 1-phenyl-3-pyrazolidone), ascorbic acid, and the like. Moreover, such developing solutions can contain preservatives, alkali agents, buffering agents, antifoggants, water softening agents, hardeners, and the like. A suitable developing solution which can be used with the photographic material of the present invention is the so-called lith developing solution, which comprises a dihydroxybenzene developing agent, an alkali agent, a small quantity of free sulfite and a buffering agent for the sulfite ions (such as formaline and sodium bisulfite adducts and acetone and

sodium bisulfite adducts) to monitor the free sulfite concentration, etc.

The fixing solution can have any conventional composition. Examples of fixing agents which can be used comprise thiosulfates, thiocyanates and sulfur organic compounds, known as fixing agents. The fixing solution can further contain water-soluble aluminium salts as hardeners. The etching solution can have any conventional composition as well, and, for instance, the compositions described by C.E.K. Mees in "*The Theory of the Photographic Process*", McMillan, 1954, pp. 737-744 and precisely an etching solution can be used which comprises, as a reducing agent, a permanganate, a ferric salt, a persulfate, a cupric acid, a ceric acid, a hexacyanoferrate-(III) or a dichromate, alone or in combination and, possibly, an inorganic acid such as sulfuric acid, and an alcohol; or an etching solution can be used which comprises a reducing agent such as a hexacyanoferrate-(III), ethylenediaminetetracetatoferrate-(III) or the like and a silver halide solvent such as thiosulfate, thiocyanate, thiourea or a derivative thereof and, possibly, an inorganic acid such as sulfuric acid. Representative examples of etching solutions are Farmer's solutions comprising potassium ferrocyanide and sodium thiosulfate, an etching solution comprising persulfate, an etching solution comprising a ceric salt, etc.

The present invention is now illustrated with more details by making reference to the following examples.

EXAMPLE 1

A cubic monodispersed 0.32 μm silver chlorobromide (40 mole percent bromide) was prepared as follows. A solution (A) consisting of 4.700 l water, 0.9 g adenine and 84 g of gelatin was initially introduced into a reaction vessel. The components used for the silver halide grain formation were a solution (B) of 5.379 l water and 2380 g silver nitrate and a solution (C) of 5.281 l water, 688 g KCl, 733 g KBr and 0.002 g $\text{Na}_3\text{RhCl}_6 \cdot 18\text{H}_2\text{O}$.

Step 1 - Nucleation:

Solutions (B) and (C) were introduced into the reaction vessel through two separate inlets simultaneously with a vigorous stirring for a period of 9 minutes with a flow rate of 51.0 ml/min while the pAg of the content into the vessel was maintained at 8.3 and the volume of the content in the vessel was increased from 4764 ml to 5682 ml and the temperature was maintained at 56 °C.

Step 2 - 1st Washing and Concentration:

Nine minutes after beginning the precipitation, the addition of solutions (B) and (C) was stopped and the content of the reaction vessel was cycled for 3 minutes through an ultrafiltration module (fitted with a polysulfone semipermeable membrane, type PTHK000C5, commercially available from Millipore Co., USA, having a NMWL [Nominal Molecular Weight Limit] of 100,000) to reduce the content volume in the reaction vessel from 5682 ml to 2082 ml. The potassium nitrate aqueous solution formed as a by-product during the precipitation of silver chlorobromide grains passed through the membrane was withdrawn, while the filtered silver halide dispersion was returned to the reaction vessel.

Step 3 - Growth:

Twelve minutes after beginning, the addition of solutions (B) and (C) into the reaction vessel was started again for a period of 25 minutes with a flow rate of 72.0 ml/min and the volume of content in the reaction vessel was increased from 2082 to 5682 ml.

Step 4 - 2nd Washing and Concentration:

Step 2 was repeated to reduce the content in the reaction vessel from 5682 to 3288 ml.

Step 5 - Growth:

Forty minutes after beginning, the addition of solutions (B) and (C) to the reaction vessel started again for a period of 7 minutes with a flow rate of 171 ml/min and the volume of content in the reaction vessel was increased from 3288 to 5682 ml.

Step 6 - 3rd Washing and Concentration:

Step 4 was repeated.

Step 7 - Growth:

Fifty minutes after beginning, step 5 was repeated.

Step 8 - 4th Washing and Concentration:

Step 4 was repeated.

Step 9 - Growth:

Sixty five minutes after beginning, step 5 was repeated.

Step 10 - 5th Washing and Concentration:

After complete additions of solutions (B) and (C), the emulsion was cooled to 40 °C and washed by ultrafiltration until the conductivity was 9,000 micro S.

Gelatin (1050 g) was added to the content in the reaction vessel while stirring at 45 °C until the gelatin was dissolved.

The resulting emulsion was gold and sulfur sensitized, optically sensitized at 630 nm, divided into fourteen parts, and each part added with hydroquinone as reported in Table 1 and coated onto a polyethylene terephthalate support at a silver coverage of 4.0 g/m². A coating composition of aqueous gelatin, comprising the polyolefin waxes as reported in Table 1, was coated onto the emulsion layer as a gelatin protective layer at a gelatin coverage of 0.70 g/m².

TABLE 1

Coating	Hydroquinone M/M Ag	Polyolefin wax	g/m ²
A	-	-	-
B	0.05	-	-
C	-	Lancoglidd CE	0.05
D	0.05	Lancoglidd CE	0.05
E	-	Lancoglidd ET	0.05
F	0.05	Lancoglidd ET	0.05
G	-	Lancoglidd TFW	0.05
H	0.05	Lancoglidd TFW	0.05
I	-	Lancoglidd PME	0.05
L	0.05	Lancoglidd PME	0.05
M	-	Lancoglidd PMW	0.05
N	0.05	Lancoglidd PMW	0.05
O	-	Lancoglidd PPW	0.05
P	0.05	Lancoglidd PPW	0.05

Lancoglidd™ CE is a dispersion in ethanol of polyethylene having average particle size of 1.3 μm; trade name of Langer & CO, Ritterhude-Ihlpohl, Germany.

Lancoglidd™ ET is a dispersion in ethanol of polyethylene having average particle size of 1.2 μm; trade name of Langer & CO, Ritterhude-Ihlpohl, Germany.

Lancoglidd™ TFW is a dispersion in water of polyethylene/polytrifluoroethylene copolymer having average particle size of 2.5 μm; trade name of Langer & CO., Ritterhude-Ihlpohl, Germany.

Lancoglidd™ PME is a dispersion in ethanol of polyethylene/polytrifluoroethylene copolymer having average particle size of 1.5 μm; trade name of Langer & CO, Ritterhude-Ihlpohl, Germany.

Lancoglidd™ PMW is a dispersion in water of polyethylene/polytrifluoroethylene copolymer having average particle size of 1.5 μm; trade name of Langer & CO, Ritterhude-Ihlpohl, Germany.

Lancoglidd™ PPW is a dispersion in water of poly-propylene having average particle size of 1.5 μ m; trade name of Langer & CO, Ritterhude-Ihlpohl, Germany.

The above polyolefin dispersions were added under stirring to the coating composition of aqueous gelatin used to form the protective gelatin layer before coating.

5 The coatings A-O were subjected to the pressure sensitivity test in which a special diamond stylus with variable weight loading is moved along the surface of unprocessed film. The coatings were then processed in 3M RDC V lith developer and evaluated by measuring the minimum weight necessary to make a visible line. The samples were evaluated according the following classification:

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Class	Grams on stylus	Rating
A	>70	Excellent
B	66 - 70	Good
C	55 - 65	Borderline
D	<55	Unacceptable

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The results are summarized in the following Table 2:

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TABLE 2

Coating	Pressure Sensitivity Test		
	Grams	Marking	Class
A	35	Strong marking	D
B	53	Marking	C
C	61	Marking	C
D	71	No marking	A
E	65	Marking	C
F	76	No marking	A
G	67	Little marking	B
H	78	No marking	A
I	65	Marking	C
L	78	No marking	A
M	65	Marking	C
N	73	No marking	A
O	62	Marking	C
P	73	No marking	A

40

EXAMPLE 2

A cubic monodispersed silver chlorobromide emulsion was prepared as described in the previous Example 1, chemically and spectrally sensitized, was divided into five parts, and each part added with hydroquinone as reported in Table 3 and coated onto a polyethylene terephthalate support at a silver coverage of 4.0 g/m². A coating composition of aqueous gelatin, comprising the polyolefin waxes as reported in Table 3, was coated onto the emulsion layer as a gelatin protective layer at a gelatin coverage of 0.70 g/m².

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TABLE 3

Coating	Hydroquinone M/M Ag	Polyolefin wax	g/m ²
Q	-	Lanco TF 1780	0.025
R	-	Lanco TF 1780	0.05
S	-	Lanco TF 1780	0.075
T	0.05	Lanco TF 1780	0.05
U	0.05	-	-

Lanco™ TF 1780 is a micronised, synthetic polyolefine wax in powder form of a polyethylene/polytrifluoroethylene copolymer having average particle size of 2.5 μm; trade name of Langer & Co., Ritterhude-Ihlpohl, Germany.

The Lanco™ TF 1780 polyolefin wax was dispersed by means of an homogenizer in a 5% aqueous solution of gelatin in the presence of Tergitol™ 4 (an anionic wetting agent, trade name of Union Carbide Co., USA) as dispersing agent and the dispersion added to the gelatin coating composition for the protective layer before coating.

The coatings Q to U were subjected to the pressure sensitivity test as described in the previous Example 1.

The results are summarized in the following Table 4.

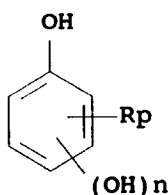
TABLE 4

Coating	Pressure Sensitivity Test		
	Grams	Sensitivity	Class
Q	41	Strong marking	D
R	45	Strong marking	D
S	43	Strong marking	D
T	72	No marking	A
U	55	Marking	C

Other commercially available wax-like materials, such as carnauba wax (a vegetable wax), bees wax (an insect wax) and ceresin (a mineral wax), to be dispersed in aqueous gelatin, have been dissolved in trichloroethylene and emulsified in an aqueous gelatin solution in the presence of Tergitol™ 4 with the help of a high speed mixer (a Silverson™ homogenizer). This means that a noxious chlorinated hydrocarbon must be used as a solvent during manufacture of the wax dispersion and that this solvent must be removed upon evaporation before adding the dispersion to the coating composition. The polyolefin wax-like compounds according to this invention allow manufacturers to dispense with said noxious solvents.

Claims

1. A light-sensitive silver halide photographic material to obtain black-and-white half-tone, dot, or line images comprising a support and coated thereon one or more hydrophilic layers, at least one of said hydrophilic layers including a high chloride content silver halide emulsion, characterized in that said silver halide emulsion comprises a polyhydroxybenzene having the following formula:



wherein n is 1, 2 or 3,

R is hydrogen, halogen, alkyl, alkoxy, amino, amido, sulfonamido, carboxy and the like, and

p is 0, 1 or 2,

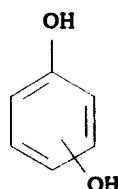
and in that the outermost hydrophilic layer, coated on the same side of the support as the silver halide emulsion layer, comprises wax-like polyolefin particles having an average size ranging from 0.5 to 3 μm .

2. A light-sensitive silver halide photographic material according to claim 1 characterized in that said high-chloride content silver halide emulsion comprises at least 50 mole % of silver chloride.

3. A light-sensitive silver halide photographic material according to claim 1 characterized in that said high-chloride content silver halide emulsion comprises at least 80 mole % of silver chloride.

4. A light-sensitive silver halide photographic material according to claim 1 characterized in that said high-chloride content silver halide emulsion comprises at least 5 mole % of silver bromide.

5. A light-sensitive silver halide photographic material according to claim 1 characterized in that said polyhydroxybenzene has the following formula:



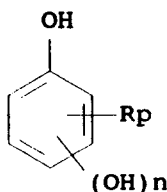
6. A light-sensitive silver halide photographic material according to claim 1 characterized in that said polyhydroxybenzene is added to said silver halide emulsion in an amount ranging from 0.01 to 0.1 moles per mole of silver.

7. A light-sensitive silver halide photographic material according to claim 1 characterized in that said polyolefin particles are added in an amount of from 0.01 to 0.1 g/m^2 .

8. A light-sensitive silver halide photographic material according to claim 1 characterized in that said polyolefins are selected within the group consisting of polyethylene, polypropylene, polytrifluoroethylene and copolymers thereof.

9. A light-sensitive silver halide photographic material according to claim 1 characterized in that said polyolefins have weight-average molecular weights in the range of 2,000 to 6,000.

10. A method for obtaining a half-tone, dot or line, image, wherein a silver halide photographic material, comprising a support and coated thereon one or more hydrophilic layers, at least one of said hydrophilic layers including a high chloride content silver halide emulsion, is image-wise exposed for forming said image, and subjected to a photographic process comprising an alkaline developing solution, characterized in that the high-chloride content silver halide emulsion of said photographic material comprises a polyhydroxybenzene of formula



wherein n is 1, 2 or 3,

R is hydrogen, halogen, alkyl, alkoxy, amino, amido, sulfonamido, carboxy and the like, and

p is 0, 1 or 2,

and in that the outermost hydrophilic layer, coated on the same side of the support as the silver halide emulsion layer, comprises wax-like polyolefin particles having an average size ranging from 0.5 to 3 μm .

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European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 93 10 9607

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)
D,A	EP-A-0 209 010 (EASTMAN KODAK COMPANY) * page 3, line 36 - page 4, line 36 * * page 5, line 22 - line 28 * * claims 1, 9 - 11 * ---	1,5,10	G03C1/76 G03C1/34
A	US-A-3 847 618 (EMIEL ALEXANDER HOFMAN) * column 1, line 4 - line 9 * * column 3, line 33 - line 38 * * column 6, line 35 - line 39 * * claims 17, 22 * ---	1-6,10	
A	US-A-2 059 829 (ERWIN J. WARD) * column 1, line 1 - line 12 * * column 1, line 24 - line 30 * * column 1, line 42 - line 55 * * claim 1 * ---	1	
A	PATENT ABSTRACTS OF JAPAN vol. 13, no. 382 (P-912)24 August 1989 & JP-A-11 33 056 (RICOH CO LTD) 25 May 1989 * abstract * ---	1,8	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
P,A	EP-A-0 518 627 (INTERNATIONAL PAPER COMPANY) * page 3, line 11 - line 20 * * page 8, line 19 - line 28 * * page 9, line 38 * -----	1-10	G03C
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 21 OCTOBER 1993	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			