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

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**EP-A- 0 209 010**  
**WORLD PATENTS INDEX LATEST Week 8826,**  
**Derwent Publications Ltd., London, GB;**  
**AN88-179022 & JP-A-63 116 149**

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**Description****FIELD OF THE INVENTION**

5       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**

10       Photosensitive silver halide materials are commonly used in photolithographic industry to obtain half-tone, dot or line, high contrast images. An example of high contrast photographic element having white reflective support is a phototypesetting material intended to produce black type character image on a white background. An example of high contrast photographic element having a transparent support is lith film, so called because it is used as contact transparency for exposing lithographic printing plates. The illusion that some areas of a  
15       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 density over the photographic film. This is an adverse effect for practical applications, and is  
20       known as pressure or kink sensitivity. According to this effect a part of a light-sensitive silver halide photographic material becomes 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 occur during handling of the photographic material (i.e., by folding, twisting and/or warping) or during roller transport processing. Pressure desensitization has been  
25       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  
30       Emulsion, Focal Press, London, 1974, pp. 133-134. Research Disclosure is published by Kenneth Mason Publications, Ltd., Emsworth, Hampshire PO10 7DD, England. However, such addenda often affect photographic characteristics without having a substantial effect on pressure sensitivity.

JP-A-63 116,149 discloses the use of organo-polysiloxanes in the outer layer of photographic materials comprising a core/shell silver halide emulsion layer to prevent formation of pressure fog.

35       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, US 4,914,002, claims a silver halide photographic material with excellent pressure properties, which contains a combination of hydrazine derivatives, cyanine derivatives having no absorption maximum in the visible  
40       light region and dihydroxybenzene derivatives.

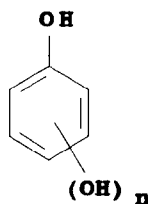
However, the use of polyhydroxybenzene to reduce pressure sensitivity is limited in that the high quantity of said compound can deteriorate anti-blocking properties, in particular, it can increase the tendency toward tackiness of the emulsion.

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

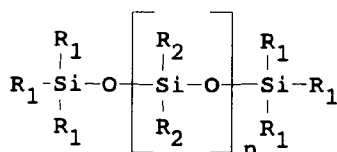
**SUMMARY OF THE INVENTION**

50       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, comprising a polyhydroxybenzene having the following formula:

55

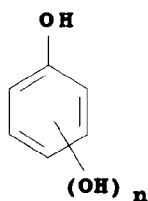


wherein n is 1,2 or 3,  
characterized in that the outermost hydrophilic layer comprises a polydialkylsiloxane.  
Preferably, said polydialkylsiloxane corresponds to the following formula:

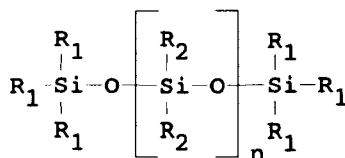


wherein  $R_1$  is an alkyl group having 1 to 3 carbon atoms,  $R_2$  is an alkyl group having 1 to 3 carbon atoms or an alkoxy group having 1 to 2 carbon atoms and n is a positive integer of from 0 to 2000.

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



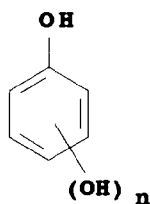
wherein n is 1,2 or 3,  
and in that the outermost hydrophilic layer of said photographic material comprises a polydialkylsiloxane preferably having the following formula:



wherein  $R_1$  is an alkyl group having 1 to 3 carbon atoms,  $R_2$  is an alkyl group having 1 to 3 carbon atoms or an alkoxy group having 1 to 2 carbon atoms and n is a positive integer of from 0 to 2000.

## DETAILED DESCRIPTION OF THE INVENTION

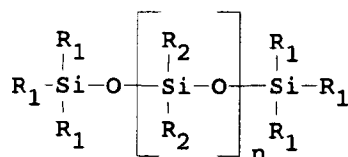
The present invention relates to a light-sensitive silver halide photographic material to obtain black-and-white half-tone, dot or line, images comprising a support and coated thereon one or more hydrophilic layers, at least one of said hydrophilic layers including a high chloride content silver halide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



5

wherein  $n$  is 1,2 or 3,  
 10 characterized in that the outermost hydrophilic layer comprises a polydialkylsiloxane preferably having the following formula:

15



20 wherein  $R_1$  is an alkyl group having 1 to 3 carbon atoms,  $R_2$  is an alkyl group having 1 to 3 carbon atoms or an alkoxy group having 1 to 2 carbon atoms and  $n$  is a positive integer of from 0 to 2000.

The polyhydroxybenzenes according to formula (I) above can be dihydroxybenzene derivatives, trihydroxybenzene derivatives, or tetrahydroxybenzene derivatives. Useful examples of dihydroxybenzene are 1,2-dihydroxybenzene, i.e., pyrocatechol, 1,3-dihydroxybenzene, i.e., resorcinol, 1,4-dihydroxybenzene, i.e., hydroquinone. Useful examples of trihydroxybenzene 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 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 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 per mole of silver, preferably of from 0.03 to 0.07 moles per mole of silver.

The polydialkylsiloxanes according to the formula (II) 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 silicone polymer is preferred but dispersions containing 1 to 50% by weight of the polymer are suitable.

Useful polydialkylsiloxanes include commercially available silicone oils such as the trialkyl and trialkoxy endblocked dialkylpolysiloxanes, e.g., dimethylpolysiloxane, diethylpolysiloxane, trimethoxy endblocked dimethylpolysiloxane and triethoxy endblocked dimethylpolysiloxane. The polydialkylsiloxanes have molecular weights of from 100 to 150,000, preferably of from 10,000 to 20,000 and a viscosity at 25°C of from 2 to 100,000 centistokes, preferably of from 200 to 800 centistokes.

The preparation and properties of such polydialkylsiloxanes are well known and described, for instance, in Reuben Gutoff's article entitled "Silicone Fluid Manufacture", published in "Industrial and Engineering Chemistry", Vol 49, pp 1807-1811.

The polydialkylsiloxanes 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.

Suitable dispersing agents are generally of non-ionic type 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 silicone oil.

Instead of being added as a dispersion, the polydialkylsiloxanes can be added in a suitable organic solvent, e.g., amyl acetate, benzene, carbon tetrachloride, ethyl ether, perchloroethylene, petroleum ether, or xylene. The organic solvent, of course, must not adversely affect the physical or photographic properties of the photographic film.

5 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.

10 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.

15 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 25 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 $\mu$ m, preferably lower than about 0.4 $\mu$ m, more preferably lower than 0.2 $\mu$ 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 at 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.

30 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 chloropalladite, etc.; each of such sensitizers being employed either alone or in a suitable combination.

40 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.

50 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 lubricants 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.

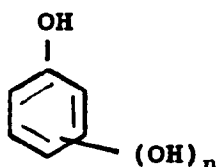
Examples of supports include films of a poly-alpha-olefin (such as polyethylene, polystyrene, etc.), a poly-

ester (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.; and lubricants such as wax, higher fatty acid glycerides, higher alcohol esters of higher fatty acids, 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".

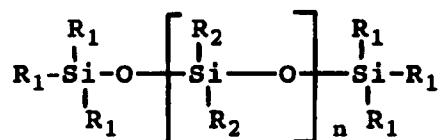
The photographic material of the present invention can include a hydrazine derivative to obtain high contrast images. Any known hydrazine derivatives can be used, such as, for example, hydrazine derivatives described in Research Disclosure 235, November 1983, Item 23510, "Development Nucleation by Hydrazine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

and in that the outermost hydrophilic layer of said photographic material comprises a polydialkylsiloxane preferably having the following formula:



wherein  $R_1$  is an alkyl group having 1 to 3 carbon atoms,  $R_2$  is an alkyl group having 1 to 3 carbon atoms or an alkoxy group having 1 to 2 carbon atoms and n is a positive integer of from 0 to 2000.

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  $\mu\text{m}$  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 - 1<sup>st</sup> 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 - 2<sup>nd</sup> 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 - 3<sup>rd</sup> Washing and Concentration:

Step 4 was repeated.

**Step 7 - Growth:**

Fifty minutes after beginning, step 5 was repeated.

5 **Step 8 - 4<sup>th</sup> Washing and Concentration:**

Step 4 was repeated.

10 **Step 9 - Growth:**

Sixty five minutes after beginning, step 5 was repeated.

**Step 10 - 5<sup>th</sup> Washing and Concentration:**

15 After complete additions of solutions (B) and (C), the emulsion was cooled to 40°C and washed by ultra-filtration 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.

20 The resulting emulsion was gold and sulfur sensitized, optically sensitized at 630 nm, divided into six parts and each part added with a polyhydroxybenzene (additive), as reported in Table 1, and coated onto a polyethylene terephthalate support at a silver coverage of 4.08 m<sup>2</sup>. A coating composition of aqueous gelatin, comprising silicone as reported in Table 1, was coated onto the emulsion layer as the gelatin protective layer at a gelatin coverage of 0.70 g/m<sup>2</sup>.

25 **TABLE 1**

| Coating | Addi tive    |        | Silicone (*)<br>g/m <sup>2</sup> |
|---------|--------------|--------|----------------------------------|
|         | Type         | M/M Ag |                                  |
| A       | -            | -      | -                                |
| B       | -            | -      | 0.05                             |
| 35 C    | Hydroquinone | 0.05   | -                                |
| D       | Hydroquinone | 0.05   | 0.05                             |
| E       | Pyrocatechol | 0.05   | 0.05                             |
| 40 F    | Resorcinol   | 0.05   | 0.05                             |

(\*) Polydimethylsiloxane SS 96/100 manufactured by Daw Corning Co.

45 The coatings A-F were subjected to the pressure sensitivity test consisting in applying a special tungsten carbide stylus with variable weight loading on 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:

| Class | Grams on stylus | Rating       |
|-------|-----------------|--------------|
| A     | 200-170         | Excellent    |
| A-B   | 170-140         | Good         |
| B     | 140-110         | Borderline   |
| B-C   | 110-85          | Unacceptable |
| C     | 85-50           | "            |
| C-D   | 50-30           | "            |
| D     | < 30            | "            |

The results are summarized in the following table 2:

TABLE 2

| Coating | Pressure | Sensitivity         | Test  |
|---------|----------|---------------------|-------|
|         | Grams    | Sensitivity         | Class |
| A       | < 25     | Strong marking      | D     |
| B       | 90       | Little marking      | B-C   |
| C       | 70       | Little marking      | C     |
| D       | 190      | No marking          | A     |
| E       | 120      | Very little marking | B     |
| F       | 95       | Little marking      | B-C   |

## EXAMPLE 2

A cubic monodispersed silver chlorobromide emulsion was prepared as described in the previous example 1, chemically and spectrally sensitized, added with hydroquinone as reported in Table 3 and coated according to Example 1. A gelatin protective layer comprising silicone was coated onto the emulsion layer as reported in Example 1.

TABLE 3

| Coating | Additive     |        | Silicone<br>g/m <sup>2</sup> |
|---------|--------------|--------|------------------------------|
|         | Type         | M/M Ag |                              |
| A       | -            | -      | -                            |
| B       | -            | -      | 0.05                         |
| C       | Hydroquinone | 0.05   | -                            |
| D       | Hydroquinone | 0.05   | 0.05                         |

The coatings A-D 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 |
| A       | < 25     | Strong marking | D     |
| B       | 100      | Little marking | B-C   |
| C       | 50       | Marking        | C-D   |
| D       | 190      | No marking     | A     |

## EXAMPLE 3

A cubic monodispersed silver chlorobromide emulsion was prepared as described in the previous example 1, chemically and spectrally sensitized, and coated using same antikinking agents disclosed in literature, such as polymers of US Patent No. 4,485,170, non-ionic surfactants of JP 62/264,042, and salts of palladium, iridium and tellurium of JP 62/229,129. We have obtained five photographic film according the following table 5:

TABLE 5

| Coating | Additive                                                  | g/M Ag |
|---------|-----------------------------------------------------------|--------|
| A       | Ethylacrylate/Methylmethacrylate 70/30 Copolymer<br>Latex | 130    |
| B       | Superamide™ L9C + Maprofix™ 563                           | 80     |
| C       | TiNO <sub>3</sub>                                         | 0.266  |
| D       | K <sub>3</sub> IrCl <sub>6</sub>                          | 0.522  |
| E       | K <sub>2</sub> PdCl <sub>4</sub>                          | 0.326  |

Superamide™ L9C and Maprofix™ 563 are trade name of the Onyx Chemical Company. Superamide is the condensation product of diethanolamine and methyl laurate. Maprofix™ 563 is sodium lauryl sulfate.

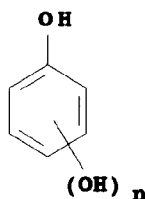
The coatings A-E were subjected to the pressure sensitivity test as described in the previous example 1. The results are summarized in the following table 6.

TABLE 6

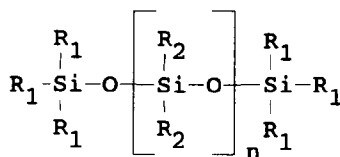
| Coating | Pressure | Sensitivity    | Test  |
|---------|----------|----------------|-------|
|         | Grams    | Sensitivity    | Class |
| A       | < 25     | Strong Marking | D     |
| B       | < 25     | Strong Marking | D     |
| C       | < 25     | Strong Marking | D     |
| D       | < 25     | Strong Marking | D     |
| E       | < 25     | Strong Marking | D     |

### 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, said silver halide emulsion comprising a polyhydroxybenzene having the following formula:



wherein n is 1,2 or 3,  
characterized in that the outermost hydrophilic layer comprises a polydialkylsiloxane having the following formula:

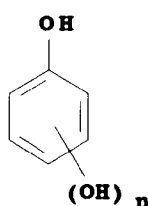


wherein R<sub>1</sub> is an alkyl group having 1 to 3 carbon atoms, R<sub>2</sub> is an alkyl group having 1 to 3 carbon atoms or an alkoxy group having 1 to 2 carbon atoms and n is a positive integer of from 0 to 2000.

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 is added to said silver halide emulsion in an amount ranging from 0.01 to 0.1 moles per

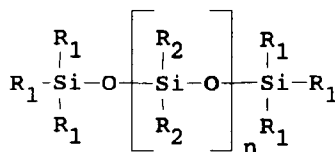
mole of silver.

6. A light-sensitive silver halide photographic material according to claim 1 characterized in that said polydialkylsiloxane is added to said hydrophilic layer as an aqueous dispersion containing 1 to 50% by weight of said silicone derivative.
7. A light-sensitive silver halide photographic material according to claim 1 characterized in that said polydialkylsiloxane is added in an amount of from 0.01 to 0.1 g/m<sup>2</sup>.
8. 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,

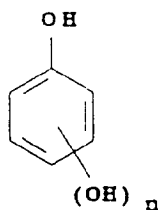
and in that the outermost hydrophilic layer of said photographic material comprises a polydialkylsiloxane having the following formula:



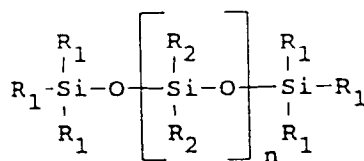
wherein R<sub>1</sub> is an alkyl group having 1 to 3 carbon atoms, R<sub>2</sub> is an alkyl group having 1 to 3 carbon atoms or an alkoxy group having 1 to 2 carbon atoms and n is a positive integer of from 0 to 2000.

## Patentansprüche

1. Lichtempfindliches photographisches Silberhalogenidmaterial zur Herstellung von schwarz-weißen Punkt- oder Linien-Halbtonbildern (Rasterbilder), umfassend einen mit einer oder mehreren hydrophilen Schichten beschichteten Träger, wobei mindestens eine der hydrophilen Schichten eine Silberhalogenidemulsion mit hohem Chloridgehalt einschließt, wobei die Silberhalogenidemulsion ein Polyhydroxybenzol der folgenden Formel

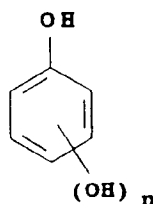


umfaßt, wobei n die Zahl 1, 2 oder 3 bedeutet, dadurch gekennzeichnet, daß die äußerste hydrophile Schicht ein Polydialkylsiloxan der folgenden Formel

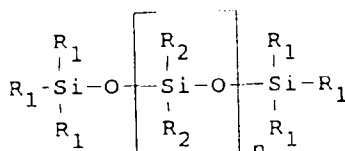


umfaßt, wobei  $\text{R}_1$  einen Alkylrest mit 1 bis 3 Kohlenstoffatomen bedeutet,  $\text{R}_2$  einen Alkylrest mit 1 bis 3 Kohlenstoffatomen oder einen Alkoxyrest mit 1 bis 2 Kohlenstoffatomen bedeutet und  $n$  eine positive ganze Zahl von 0 bis 2000 bedeutet.

2. Lichtempfindliches photographisches Silberhalogenidmaterial nach Anspruch 1, dadurch gekennzeichnet, daß die Silberhalogenidemulsion mit hohem Chloridgehalt mindestens 50 Mol-% Silberchlorid umfaßt.
3. Lichtempfindliches photographisches Silberhalogenidmaterial nach Anspruch 1, dadurch gekennzeichnet, daß die Silberhalogenidemulsion mit hohem Chloridgehalt mindestens 80 Mol-% Silberchlorid umfaßt.
4. Lichtempfindliches photographisches Silberhalogenidmaterial nach Anspruch 1, dadurch gekennzeichnet, daß die Silberhalogenidemulsion mit hohem Chloridgehalt mindestens 5 Mol-% Silberbromid umfaßt.
5. Lichtempfindliches photographisches Silberhalogenidmaterial nach Anspruch 1, dadurch gekennzeichnet, daß das Polyhydroxybenzol in einer Menge im Bereich von 0,01 bis 0,1 Mol pro Mol Silber zur Silberhalogenidemulsion zugegeben wird.
6. Lichtempfindliches photographisches Silberhalogenidmaterial nach Anspruch 1, dadurch gekennzeichnet, daß das Polydialkylsiloxan als 1 bis 50 Gew.-% des Siliconderivates enthaltende wäßrige Dispersion zur hydrophilen Schicht zugegeben wird.
7. Lichtempfindliches photographisches Silberhalogenidmaterial nach Anspruch 1, dadurch gekennzeichnet, daß das Polydialkylsiloxan in einer Menge von 0,01 bis 0,1 g/m<sup>2</sup> zugegeben wird.
8. Verfahren zur Herstellung eines Punkt- oder Linien-Halbtonebildes, wobei ein photographisches Silberhalogenidmaterial, umfassend einen mit einer oder mehreren hydrophilen Schichten beschichteten Träger, wobei mindestens eine der hydrophilen Schichten eine Silberhalogenidemulsion mit hohem Chloridgehalt einschließt, zur Erzeugung des Bildes bildweise belichtet und einem photographischen Verfahren, umfassend eine alkalische Entwicklerlösung, unterworfen wird, dadurch gekennzeichnet, daß die Silberhalogenidemulsion mit hohem Chloridgehalt des photographischen Materials ein Polyhydroxybenzolderivat der Formel



umfaßt, wobei  $n$  die Zahl 1, 2 oder 3 bedeutet, und daß die äußerste hydrophile Schicht des photographischen Materials ein Polydialkylsiloxan der folgenden Formel



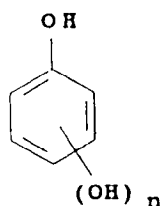
umfaßt, wobei  $R_1$  einen Alkylrest mit 1 bis 3 Kohlenstoffatomen bedeutet,  $R_2$  einen Alkylrest mit 1 bis 3 Kohlenstoffatomen oder einen Alkoxyrest mit 1 bis 2 Kohlenstoffatomen bedeutet und  $n$  eine positive ganze Zahl von 0 bis 2000 bedeutet.

5

## Revendications

1. Matériau photographique à l'halogénure d'argent sensible à la lumière pour obtenir des images en demi-teintes, en points de trame ou en traits noir et blanc comprenant un support sur lequel sont déposées une ou plusieurs couches hydrophiles, au moins une desdites couches hydrophiles incluant une émulsion d'halogénure d'argent à forte teneur en chlorure, ladite émulsion d'halogénure d'argent comprenant un polyhydroxybenzène de formule:

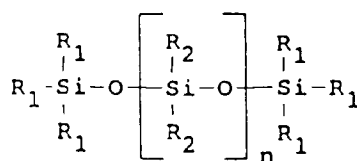
15



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dans laquelle  $n$  vaut 1, 2 ou 3, caractérisée en ce que la couche hydrophile la plus externe comprend un polydialkylsiloxane de formule:

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dans laquelle  $R_1$  est un groupe alkyle ayant de 1 à 3 atomes de carbone,  $R_2$  est un groupe alkyle ayant de 1 à 3 atomes de carbone ou un groupe alcoxy ayant de 1 à 2 atomes de carbone et  $n$  est un nombre entier positif compris entre 0 et 2000.

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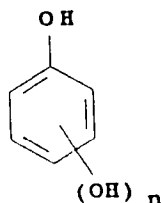
2. Matériau photographique à l'halogénure d'argent sensible à la lumière selon la revendication 1, caractérisé en ce que ladite émulsion d'halogénure d'argent à forte teneur en chlorure comprend au moins 50% molaire de chlorure d'argent.
3. Matériau photographique à l'halogénure d'argent sensible à la lumière selon la revendication 1, caractérisé en ce que ladite émulsion d'halogénure d'argent à forte teneur en chlorure comprend au moins 80% molaire de chlorure d'argent.
4. Matériau photographique à l'halogénure d'argent sensible à la lumière selon la revendication 1, caractérisé en ce que ladite émulsion d'halogénure d'argent à forte teneur en chlorure comprend au moins 5% molaire de bromure d'argent.
5. Matériau photographique à l'halogénure d'argent sensible à la lumière selon la revendication 1, caractérisé en ce qu'on ajoute ledit polyhydroxybenzène à ladite émulsion d'halogénure d'argent en une quantité allant de 0,01 à 0,1 mole par mole d'argent.
6. Matériau photographique à l'halogénure d'argent sensible à la lumière selon la revendication 1, caractérisé en ce qu'on ajoute ledit polydialkylsiloxane à ladite couche hydrophile sous la forme d'une dispersion aqueuse contenant de 1 à 50% en poids dudit dérivé de silicone.
7. Matériau photographique à l'halogénure d'argent sensible à la lumière selon la revendication 1, caractérisé en ce qu'on ajoute ledit polydialkylsiloxane en une quantité comprise entre 0,01 et 0,1 g/m<sup>2</sup>.
8. Procédé d'obtention d'une image en demi-teintes, points de trame ou traits, dans lequel on expose image

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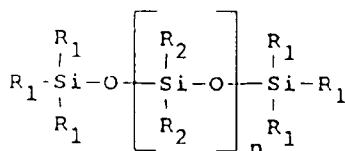
par image un matériau photographique à l'halogénure d'argent, comprenant un support sur lequel sont déposées une ou plusieurs couches hydrophiles, au moins une desdites couches hydrophiles incluant une émulsion d'halogénure d'argent à forte teneur en chlorure, pour former ladite image, et en ce que le sou-

5 met à un procédé photographique comprenant une solution de développement alcaline, caractérisé en ce que l'émulsion d'halogénure d'argent à forte teneur en chlorure dudit matériau photographique comprend un polyhydroxybenzène de formule:



dans laquelle n vaut 1, 2 ou 3,

et en ce que la couche hydrophile la plus externe dudit matériau photographique comprend un polydialkylsiloxane de formule:



dans laquelle  $\text{R}_1$  est un groupe alkyle ayant de 1 à 3 atomes de carbone,  $\text{R}_2$  est un groupe alkyle ayant de 1 à 3 atomes de carbone ou un groupe alcoxy ayant de 1 à 2 atomes de carbone et n est un nombre entier positif compris entre 0 et 2000.