

1

3,415,651

LIGHT-SENSITIVE MATERIAL WITH INCORPORATED DEVELOPER

Anita von Konig, Helmut Mader, and Edith Weyde,
Leverkusen, Germany, assignors to Agfa Aktiengesellschaft, Leverkusen, Germany, a corporation of Germany

No Drawing. Filed Apr. 20, 1965, Ser. No. 449,633
Claims priority, application Germany, May 13, 1964,
A 46,041

13 Claims. (Cl. 96—95)

ABSTRACT OF THE DISCLOSURE

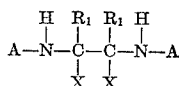
Developers suitable for incorporation in light-sensitive silver halide emulsions are ortho- or para-aminophenol derivatives or ortho- or para-naphthol derivatives having a 2-carbon chain bridged between the amine groups of two such compounds and having a phosphonic acid group or an arylsulfonyl group substituted on each carbon of the branch. These developers can be either in the emulsion layer or in a separate layer contiguous to the emulsion layer and they provide a product having improved storage stability as well as less fog and high sensitivity.

This invention relates to a light-sensitive photographic material which contains developers preferably incorporated in the photographic silver halide emulsion layers.

It is common practice to incorporate developers in photographic emulsions layers but the substances customarily used for this purpose are based on aromatic compounds substituted with hydroxy or amino groups, and do not meet all the requirements. Some of these compounds do not have a sufficient developer effect whereas others, which are sufficiently powerful developers, reduce the storage stability of the light-sensitive layers. The reason for this is the sensitivity to oxidation of the developers by atmospheric oxygen so that the light-sensitive layers are liable to develop spontaneously without exposure, uniform fogging thus being produced.

It is the object of the present invention to provide a photographic material with incorporated developers, which developer has an adequate developing effect and satisfactory stability to oxidation.

It has now been found that o- or p-aminophenol derivatives or o- or p-aminoaphthol derivatives of the following formula exhibit particular utility for this purpose



wherein

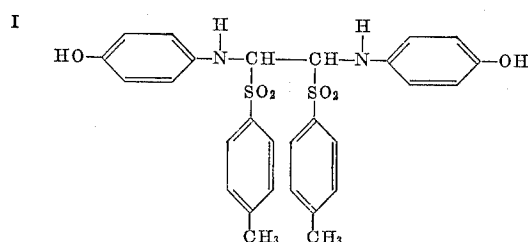
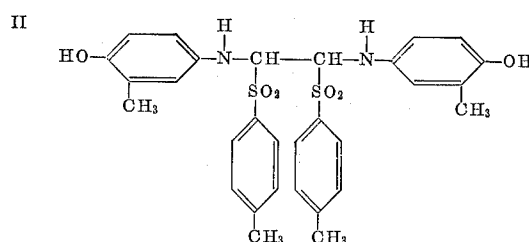
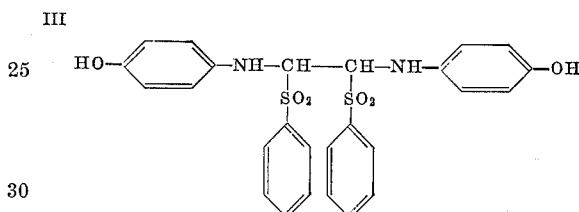
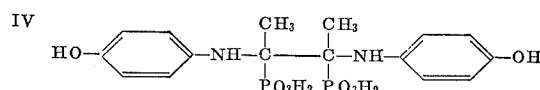
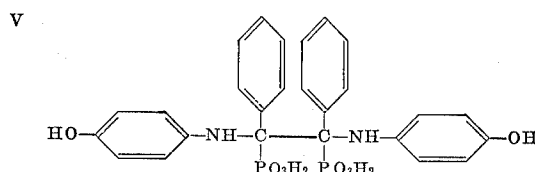
A=o- or p-hydroxyphenyl or o- or p-hydroxynaphthyl, R₁=hydrogen, short-chained alkyl radicals, preferably with 1 to 3 C-atoms, aryl, preferably phenyl or naphthyl, cycloalkyl, such as cyclohexyl or heterocyclic radicals such as furyl, thienyl or pyridyl,

X=phosphonic acid or its salts, especially with alkali metal or alkaline earth metals, or an arylsulfonyl group preferably a phenyl sulfonyl or a naphthyl sulfonyl.

The substituents A, R₁ and X may further be substituted in any desired manner. The chemical structure of the substituents is not critical. The only condition which has to be met is that the developing effect must not be impaired. Especially suitable are alkyl having 1 to 5 C-atoms, preferably 1 to 3 C-atoms, alkoxy whose alkyl groups also contain 1 to 5, preferably 1 to 3 C-atoms, halogen such as chlorine or bromine, cyano, nitro and the like.

2

The following compounds are particularly suitable:



The sulfonyl compounds may be prepared by reacting the corresponding aminophenol or aminonaphthol derivatives with glyoxal and an arylsulfinic acid. In the case of the phosphonic acid derivatives, the developer component is reacted with a dihydroxyethylene diphosphonic acid. For the preparation of the dihydroxyethylene diphosphonic acids, the process described in Houben-Weyl, Methods of Organic Chemistry, vol. 12, part 1 ("Phosphorus Compounds"), pages 363 to 365 may be used, which process consists in reacting the corresponding aldehydes or ketones with phosphorus trichloride, followed by hydrolysis.

The detailed preparation of some compounds is described below. Other compounds of the type according to the invention can be prepared by analogous methods.

Compound I: Approximately 500 ml. of water, 22.5 g. of polyglyoxal, 66 g. of 4-aminophenol and 58 g. of p-toluenesulfinic acid sodium are heated to boiling. Glacial acetic acid (about 30 ml.) is added until the components are dissolved and the mixture heated for another 2 hours. The dark solution is treated with active charcoal, filtered and thoroughly cooled. The product is isolated by suction filtration and recrystallized from water. Yield: 12 g., melting point above 200° C. with decomposition.

Compound IV: 50 g. of 2,3-dihydroxybutane-2,3-diphosphoric acid and 44 g. of 4-aminophenol are heated under reflux for 6 hours in 400 ml. of alcohol. The precipitated product is removed by suction filtration and

washed several times with ether. Yield: 14 g., melting point 179° C.

2,3-dihydroxybutanephosphonic acid is prepared from PCl_3 and diacetyl according to the process described in Houben-Weyl, vol. 12.

Since some of the compounds decompose on heating to regenerate the starting materials, purification by recrystallization is often not possible. Purification is best carried out by reprecipitation from suitable solvents or by washing with ethanol or diethyl ether. In some cases, the reaction of aminophenol derivatives with hydroxymethanephosphonic acids only produces resinous products which do not crystallize. The compounds are then isolated by conversion into the naphthalene-1,5-disulfonates.

The photographic materials according to the invention, containing a developer compound as defined hereinbefore are in principle not subject to any limitations as regards their use for photographic purposes.

The photographic processes can be divided into two main groups, one group comprising processes in which the exposed photographic element is treated with aqueous processing baths and the other methods in which the exposed photographic materials are processed at elevated temperatures without the use of processing baths.

The photographic elements according to the invention are suitable for both groups of processes. It is possible to find out by simple tests which is the optimum developer for the particular photographic process. For processing with aqueous baths it is preferred to use photographic materials the layers of which are hardened with the usual agents such as formalin. For heat copying processes, on the other hand it is preferable to use unhardened layers.

When using wet methods the exposed photographic element can be developed after exposure merely by the action of an alkaline solution. In addition, the developers may also be used in alkaline solutions.

After exposure, the layers according to the invention may be developed in alkaline thiosulfate-containing solutions such as customarily employed for the silver salt diffusion process.

Compared with the known developers such as hydroquinone, aminophenol, p-methylaminophenol and other developers, the developers according to the invention, after they have been incorporated in the emulsion layer, are distinguished not only by better stability to oxidation but also increased utilization of the sensitivity. The photographic elements of the present invention show practically no fogging, as compared with photographic materials which contain conventional developer compounds.

The light-sensitive materials according to the invention which contain developers having phosphonic acid groups are especially advantageous for use in heat copying processes. The principle of such processes is described in German Patent 888,045. According to this, the material is developed by simple heating after exposure. In this method, development at elevated temperatures can be obtained with a transfer process in which either substances from the exposed and developed parts or from the unexposed and undeveloped parts of the photographic material or whole parts of the layer are transferred to a reception material. In this connection, the so-called developer sublimation processes have gained special importance, the principle of which consists in that the unused developer in the unexposed parts are transferred by sublimation to a reception material where they react with a component of the reception material to form a dye image which is a positive, non-reversed copy of the original.

Suitable reception materials may contain—

(1) Substances which produce colored compound by reaction with the developer:

(a) A combination of a color coupler which reacts with the oxidation product of the primary aromatic amino developer to form a dye and an oxidizing agent capable

of oxidizing the developer, for instance, a combination of sodium bromate and methylphenyl pyrazolidone (see German Patent No. 895,101);

(b) Nitroso compounds, e.g., sodium o-nitrosobenzoate (see German Patent 895,101);

(c) Aromatic diazo compounds in combination with oxidizing agents, e.g., diazo-1-amino-2-naphthol-4-sulfonic acid and potassium bichromate (see German Patent No. 1,003,577);

(d) Sulfur and alkali polysulfides (see German Patent No. 1,004,043);

(e) Oxidizing agents, e.g., copper (II) chloride (see German Patent No. 895,101).

In all these cases only the developing agents are transferred to the transfer material and the image obtained consists only of the dye formed in the process.

(2) Development nuclei, e.g., colloidal silver sulfide. In this case the development is performed in the presence of moisture and silver halide is transferred to the transfer material by diffusion.

(3) A combination of 1 and 2, in this case the image consists of transferred silver and of a dye formed in the process.

The reaction components described above can be added to one or more transfer layers which are applied on one or both sides of a suitable support. According to another embodiment the support itself can be impregnated with the compounds required for the image-forming reaction.

Since oxidation products of developers of the present invention are capable of tanning or hardening film-forming proteins, especially gelatin, they can also be used for so-called tanning heat development processes. The properties of the developed layer are in this case so differentiated that either the undeveloped and therefore unhardened parts of the layer or the hardened parts of the layer can be transferred to a transfer material or parts of a transfer layer of the transfer material can be transferred to the unexposed and unhardened parts of the layer. If no special measures are taken, only the unexposed and unhardened parts of the exposed and developed silver halide emulsion layer are transferred and in most cases transfer materials are used that contain substances which react with compounds present in the transferred parts of the silver halide emulsion layer for example the silver halide or the developer, to form colored products. A positive, non-reversed relief image of the original is obtained. Such processes are described in German patent specifications 1,002,628 and 1,150,999, British patent specifications 821,506 and 984,838, Belgian Patents 638,214, 643,960 and 644,162 and in the published German Auslegeschrift 1,189,383.

In the preparation of photographic emulsion the new developer of the invention is preferably added to the washed, finished silver halide emulsion and should of course be uniformly distributed throughout the emulsion. It is convenient to add the developer compounds from solutions in appropriate solvents preferably from water. The concentration of the developer compounds in the silver halide emulsion layers can vary widely, for instance, from about 15–150 g. per mol of silver halide. The specific concentration will vary according to the type of light-sensitive material and the reproduction process and according to the effects desired. The suitable and most economical concentration for the given photographic material will be apparent to those skilled in the art upon making the tests customarily used in the art. Preferred are concentrations of 30–60 g. per mol of silver halide. Since 1 kg. of an emulsion ready for casting contains about 0.05 to 0.5 mol of silver halide, the quantity of developer in 1 kg. of casting solution corresponds.

The developers according to the invention can also be used in the form of their salts, e.g., alkali metal or alkaline earth salts, or in the form of salt-type addition compounds with acids such as naphthalene-1,5-disulfonic acid or toluene sulfonic acid.

For the preparation of the silver halide emulsion layers, any desired silver halide emulsions may be used such as silver chloride, silver bromide or silver chlorobromide emulsions, which may also contain silver iodide. These emulsions may contain 0.05 to 0.5 mol of silver halide per liter.

As layer-forming agents it is possible to use any of the binders customarily used in photographic practice that can be hardened in the heat by oxidation products of the developer and by aldehydes or ketones, e.g., gelatin and zein which may partly be replaced by other layer-forming substances, e.g., cellulose derivatives such as carboxyalkyl-cellulose, particularly carboxymethyl cellulose or methyl hydroxyethyl cellulose, polyvinyl alcohol, polyvinylacetate, polyvinyl acetal partially hydrolyzed polyvinyl acetates, alginic acid and derivatives thereof such as alkali salts or esters particularly alginic acid propylene glycol ester, galactomannanes, polyvinyl pyrrolidone or other natural and synthetic substances.

Photographic layers containing the new developer compounds may be coated on any of the usual photographic materials including for example paper, glass, cellulose ester, particular cellulose acetate or synthetic film-forming resins, such as polystyrene, polycarbonates, in particular of bis-hydroxyphenylalkanes, polyesters in particular polyethyleneterephthalates, polyamides, etc. If the photographic material is to be used for heat copying process, care should be taken that the support material is stable at the processing temperature.

The emulsions containing the new developer compounds can be chemically sensitized by any of the accepted procedures. Suitable chemical sensitizers are for example sulfur compound, reducing agents such as stannous salts, polyamines, such as diethyl triamine, and salts of the noble metals, such as gold, ruthenium, rhodium, palladium, iridium and platinum.

The emulsions can also be optically sensitized with the usual optical sensitizers such as cyanines, merocyanines, rhodacyanines, neocyanines and the like.

The emulsions can also be stabilized with the usual stabilizers such as organic mercury compounds, triazoles, such as described in the British patent specification 919,061, heterocyclic mercapto compounds, and azaindenes such as described by Birr in "Z. wiss. Phot.," vol. 47, 1952, pages 2-28.

The emulsions can be hardened with any of the usual hardeners for gelatine, such as formaldehyde and halogen-substituted aliphatic acids, such as mucobromic acid.

The photographic materials containing the developer compounds can also additionally contain matting agents, such as starch ether, dextrine, colloidal silicic acid, finely dispersed silicon oxide, aluminum oxide, titanium dioxide and the like.

If the photographic materials which contain the new developer compounds are to be used for heat copying processes it has been found particularly advantageous to employ additional substances which provide a desired amount of moisture during the heat development step. Such substances are compounds which split off water on heating or compounds which increase the residual moisture content of the layer. Compounds of the first mentioned type are urea, caprolactam, β -nitroethanols or β -cyanoethanols as described in Belgian Patent 643,960, salts containing water of crystallization such as sodium citrate or preferably sodium acetate; compounds of the second mentioned type are, for example, polyhydric alcohols such as sorbitol, glycerol or polyethylene glycols. These compounds may be added in such quantities to the casting solution for the negative layer, that the dried layer contains between 0.05 and 25 g. per square meter thereof.

An intermediate layer can be applied between the support and the hydrophilic photographic layer. The intermediate layers are intended to modify the adhesion of hydrophilic photographic layer, which is in most cases

the silver halide emulsion layer, in the desired manner in order, for example, to facilitate the transfer of the unexposed and unhardened or of the hardened parts of the said layer. Especially suitable for such intermediate layers are heat resistant substances such as ethyl cellulose, polyvinyl pyrrolidone, zein, polyvinyl acetate, alginic acid derivatives and starch ether or the intermediate layers described in the published German Auslegeschrift 1,189,383.

Any heat-resistant sheet may be used as transfer material, such as any desired impregnated or untreated paper or also textile fabrics, synthetic resins or metal foils. In the case of coated or treated transfer papers, the transfer layer may contain both additives which supply water and additives which cause the recording to be blackened in known manner, e.g., N-diethylaminoethanol, triethanolamine, tetramethylammonium hydroxide, pyridine, piperazine, reducing agents and/or sulfur-containing compounds.

The preparation of a positive or of a printing form as in the transfer process, may be carried out either simultaneously with the developing or at a later time. In addition, several copies may be prepared from one light-sensitive layer either immediately after the first transfer or at a later date. The hardened silver halide emulsion layer may be fixed in a fixing bath or stabilized by stabilizers. The negative images obtained by heat development are fairly insensitive to light and therefore the process is suitable for purposes which require a quick access to the recorded signal.

The image-forming process is generally accomplished by first exposing the light-sensitive negative material to an object to be reproduced. Thereafter, the exposed material is brought into contact with the light-insensitive transfer material.

The combination of both materials is subjected to heat development by heating to a temperature of between 80 and 200° C. preferably 100 to 170° C. for a period of time of between 1/2 second and 3 minutes.

In some cases it is advantageous to develop the negative alone by application of heat, contact the developed emulsion layer with the transfer material and subject the combination again to a heat treatment.

EXAMPLE 1

Light-sensitive material

To 1 liter of a silver chloride emulsion are added 20 mg. of 1-phenyl-5-mercaptotetrazole (1% in ethanol), 150 g. of sodium acetate (cryst.) 5.5 g. of cyclohexanone bisulfite, 30 g. of starch, 20 g. of colloidal silicic acid and 20 g. of Compound I.

The pH of the emulsion is adjusted to 4.9 with sulfuric acid. The emulsion is applied in known manner to a baryted paper and dried.

Reception material A

A solution of 8 g. of galactomannane, 1.1 g. of carboxymethyl starch, 200 g. of potassium bromate, 0.8 g. of copper sulfate, 4 ml. of polyethyleneglycol having an average molecular weight of 200, 0.8 g. of a 50% solution of a wetting agent which consists of a combination of paraffin sulfonic acid sodium and an alkyl-aryl polyglycol ether, 45 ml. of a 15% hydrosol of silicic acid (having a surface of 200 sq. m. per gram) in 1 liter of water is adjusted to pH 3.5 with sulfuric acid and applied in known manner to a paper and dried.

Processing.—The exposed light-sensitive layer and reception layer are brought into contact with each other and are subjected for 2 to 30 seconds to a temperature of 110 to 200° C., preferably 120 to 150° C., using a heat development apparatus without a moistening device or by means of a high gloss press or drying drum. In this process, the reception material may be exposed to a higher temperature than the light-sensitive material. A black-brown image is obtained.

Reception material B

A paper is dipped in a solution of 100 g. of sodium bromate, 1 g. of ammonium vanadate, 20 ml. of a polyethylene glycol having an average molecular weight of 300 and 0.2 g. of a 50% solution of a wetting agent which consists of a combination of paraffin sulfonic acid sodium and an alkyl-aryl-polyglycol ether and 80 ml. of a 15% hydrosol of silicic acid (having a surface of 200 sq. m. per gram) in 1.5 l. of water, and dried. Processing is carried out as described above. A black-brown image is obtained.

EXAMPLE 2

Light-sensitive material

To 1 liter of a silver chloride emulsion are added 0.1 g. of benztriazole (5% in ethanol), 125 g. of sodium acetate, 5 g. of cyclopentanone bisulfite, 20 g. of Compound IV, 100 ml. of a 15% hydrosol of silicic acid (having a surface of 200 sq. m. per gram). The pH is adjusted to 5.0 with citric acid. The emulsion is applied in known manner to a baryta-coated paper and dried.

Reception material C

A solution of 20 g. of alginic acid propylene glycol ester, 4 g. of gelatine, 5 g. of polyvinyl acetate, 0.6 g. of colloidal silver sulfide, 0.08 g. of 3-mercapto-4,5-dimethyltriazole-(1,2,4), 2 ml. of a polyethylene glycol having an average molecular weight of about 400 and 2 ml. of a 5% aqueous solution of saponin in 1 liter of water are applied to a paper and dried.

The exposed light-sensitive layer and the reception layer are brought into contact and are passed through a heat development apparatus with moistening device for 10 seconds at a roller temperature of 125° C. After a further 15 seconds contact time, the layers are separated from each other. A black-brown image is obtained.

After processing as described in Example 1, a black-brown dye image is obtained with the reception materials A and B described in Example 1.

EXAMPLE 3

A paper is coated with a solution of 4.2 g. of sodium alginate, 80 g. of maltose and 20 g. of Compound IV or V in 1 l. of water.

This material is further coated with the following silver halide emulsion:

1 kg. of silver chloride emulsion containing 2.2 mols of AgCl per kg. of gelatine,
25 mg. of 1-phenyl-5-mercaptotetrazole, dissolved in ethanol,
140 g. of sodium acetate (cryst.),
5 g. of colloidal silicic acid,
10 g. of Compound IV or V,
4 g. of cyclohexanone bisulfite, and
5 ml. of saponin (30% aqueous solution).

Processing is carried out as described in Example 1 or the exposed light-sensitive layer is developed and then brought into contact with the reception material A or B of Example 1. After separation of the papers, a dark brown or brown image is obtained.

EXAMPLE 4

Light-sensitive material

To 1 kg. of any silver bromide gelatine emulsion are added 200 mg. of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene dissolved in ethanol, 140 g. of sodium acetate (cryst.), 2 g. of cyclohexanone bisulfite, 15 g. of Compound III and 5 ml. of saponin (30% aqueous solution).

The pH is adjusted to 5.8. The emulsion is applied in known manner to a sheet-like support and dried.

Processing.—The rear surface of the exposed light-sensitive material is brought into contact for 0.5 to 60 sec-

onds with a metal or synthetic resin surface heated to 90 to 200° C. or with a liquid heat transfer agent. The development apparatus used may be heatable presses, drying drums, rollers or the apparatus described in Belgian Patent 628,174 or the exposed light-sensitive material may be exposed to infrared radiation for about 10 to 180 seconds.

The developed material which is tanned at the exposed areas has little sensitivity to light. It can be stabilised by fixation and washing in water or by bathing it in an alcoholic solution of 2,5-dimercaptothiadiazole-(1,3,4) or 1-phenyl-5-mercaptotetrazole.

EXAMPLE 5

Light-sensitive material

A paper is coated with a solution of 100 g. of polyurea sulfonic acid sodium prepared by polyaddition of 4,4'-diaminodiphenylethane-2,2'-disulfonic acid sodium with toluylene diisocyanate, 125 g. of cane sugar and 2.5 liters of water.

To 1 kg. of silver chloride emulsion containing 2.2 mols of AgCl per kg. of gelatine is added:

200 mg. of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene dissolved in ethanol,
50 mg. of benztriazole (dissolved in ethanol),
140 g. of sodium acetate (cryst.),
5 g. of cyclopentanone bisulfite,
20 g. of Compound II or III,
3 g. of colloidal silicic acid, and
5 ml. of saponin (30% aqueous solution).

The pH is adjusted to 4.9 with citric acid and the resulting emulsion is applied in known manner to the intermediate layer and dried.

Processing.—The exposed material is developed as described in Example 4. The developed light-sensitive material which is tanned on the exposed areas is brought into contact with a reception material to produce a non-reversed print copy, the materials being exposed to a temperature of 100 to 200° C., preferably 140 to 180° C., whereby the unexposed and untanned parts of the emulsion layer are torn out and transferred to the reception material and blackened there. The two papers are immediately separated after heating, a black positive relief image of the original being obtained on the reception material. In the transfer process, the light-sensitive material or the reception material or the rear surface of both papers, depending on the apparatus used, can be slightly moistened with water or steam, whereby the flat positioning of the papers is improved. Suitable transfer materials are described in German patent specification 1,166,620. For example, these can be prepared according to the following method:

Transfer material

An untreated paper is coated with the following solution and dried:

70 g. of polyvinyl alcohol,
10 g. of thiosemicarbazide,
8 g. of benzenesulfonic acid hydrazide,
10 g. of an ester wax for instance a wax which is sold under the name Wax KSE by Farbwerke Hoechst AG,
1 l. of water.

EXAMPLE 6

Light-sensitive material

A paper is coated with a dispersion of 1.8 g. of galactomannane, 17.5 g. of polyvinyl acetate, 15 g. of cane sugar, 20 g. of Compound I or III, 2 g. of cyclohexanone bisulfite, 5 ml. of saponin (30% aqueous solution) and 1 litre of water.

This material is coated with the following mixture:

- 1 kg. of silver chloride emulsion containing 2.2 mols of AgCl per kg. of gelatine.
 200 mg. of 4-hydroxy-6-methyl-1,3,3a-7-tetraazaindene,
 and
 20 mg. of N-phenyl-N'-(5)-benztriazolyl-urea, dissolved in ethanol,
 150 g. of sodium acetate (cryst.),
 5 g. of colloidal silicic acid,
 5 ml. of saponin (30% aqueous solution).

The product is processed as described in Example 5.

EXAMPLE 7

A paper is coated with a dispersion of 10 g. of alginic acid propylene glycol ester, 200 g. of polyvinyl acetate, 20 g. of cane sugar, 20 g. of Compound II, 8 ml. of saponin (5% aqueous solution) and 1.5 l. of water.

This material is coated with the silver halide emulsion mixture described in Example 6.

Processing.—The exposed light-sensitive material is developed in contact with a rice paper normally used for screen printing, using one of the apparatus mentioned in Example 4. After development, the rice paper is slightly moistened with water or alternatively the whole paper is bathed in water. The moist rice paper can then be separated from the light-sensitive material. The exposed and tanned parts of the emulsion layer are torn out and transferred onto the rice paper while the unexposed untanned parts of the emulsion layer remain adhered on the intermediate layer. On the rice paper, the tanned gelatine parts form a relief image which is impermeable to printing dye, a printing form suitable for screen printing being thus obtained.

EXAMPLE 8

Reception material

70 g. of sodium polyacrylate and 2 g. of colloidal silicic acid are dissolved in 1 l. of water. This solution is applied to a sheet-like support and dried.

Processing.—The light-sensitive material described in Example 7 is exposed to a negative original to be reproduced. The exposed light-sensitive material is developed in contact with the above reception material. After separation of the two materials, a positive copy of the negative original is obtained since the exposed and tanned portions of the emulsion layer are transferred to the reception material.

EXAMPLE 9

Light-sensitive material

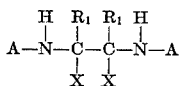
A paper is coated with a dispersion of 4.2 g. of sodium alginate, 80 g. of lactose and 1 liter of water.

This material is further coated with the silver halide emulsion layer described in Example 5, processing and results being as described in Example 7 or 8.

Instead of the silver chloride emulsion given in the examples, a silver chlorobromide emulsion such as is customary for photographic enlargement papers may be used.

We claim:

1. A light-sensitive material having at least one supported light-sensitive silver halide emulsion layer in intimate contact with an effective amount of a developer compound of the formula



wherein:

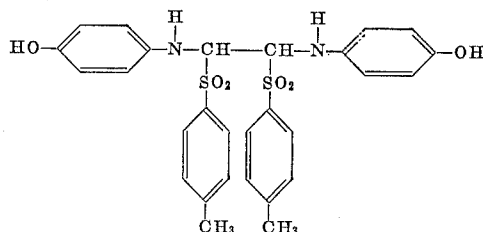
A represents a member of the group consisting of o-hydroxyphenyl, p-hydroxyphenyl, o-hydroxynaphthyl, p-hydroxynaphthyl;

R₁ stands for a substituent of the group consisting of hydrogen, short-chained alkyl, aryl, cycloalkyl, furyl, thienyl and pyridyl; and

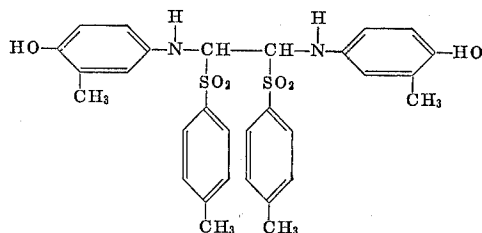
X represents a phosphonic acid group, a neutralized phosphonic acid group, a sulfo group, sulfophenyl and a sulfonaphthyl.

2. A light-sensitive material as defined in claim 1, which contains the developer compound in the amount of between 15–150 g. per mol of silver halide.

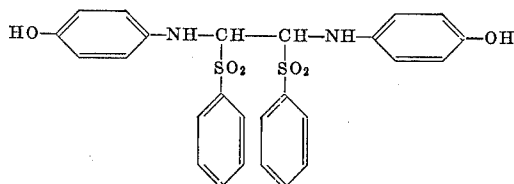
3. A photosensitive material according to claim 1 characterized in that it contains a developer of the formula



4. A photosensitive material according to claim 1 characterized in that it contains a developer of the formula



5. A photosensitive material according to claim 1 characterized in that it contains a developer of the formula



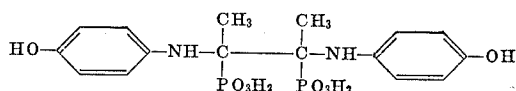
6. The light-sensitive material according to claim 1 wherein A, R₁ and X are further substituted with alkyl having up to 5 carbon atoms, alkoxy having up to 5 carbon atoms, halogen, cyano or nitro.

7. In a process for producing photographic images wherein at least one light-sensitive silver halide emulsion is exposed and the exposed emulsion is contacted with a developer in the presence of an aqueous alkaline processing bath, the improvement of using as the developer, the developer compound according to claim 1.

8. The process of claim 7 wherein the developer compound is incorporated within the light-sensitive silver halide emulsion prior to exposure.

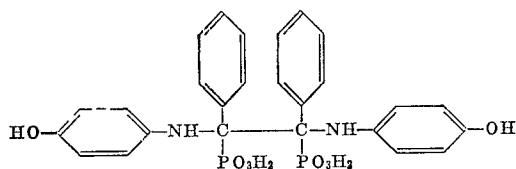
9. In a process of producing photographic images wherein at least one light-sensitive silver halide emulsion containing a developer is exposed and the exposed emulsion is developed by applying elevated temperature to the emulsion, the improvement comprising using as the developer, the developer compound according to claim 1.

10. A photosensitive material according to claim 1 characterized in that it contains a developer of the formula



11

11. A photosensitive material according to claim 1 characterized in that it contains a developer of the formula



12. The light-sensitive material of claim 1 in which the developer compound is in the emulsion layer.

13. The light-sensitive material of claim 1 in which

12

the developer compound is in a layer different from but contiguous to the emulsion layer.

References Cited

5

UNITED STATES PATENTS

2,618,657 11/1952 Vaughn et al. ----- 96-66

NORMAN G. TORCHIN, *Primary Examiner*.

10

G. COHN, *Assistant Examiner*.

U.S. Cl. X.R.

96-66, 95