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3,574,621

PROCESS FOR THE DEVELOPMENT OF PHOTOGRAPHIC SILVER IMAGES IN ACID MEDIUM 1,4-DIAZINE

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Int. Cl. G03c *5/30*
U.S. Cl. 96—66 **10 Claims**

ABSTRACT OF THE DISCLOSURE

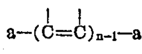
This invention is based on the completely surprising observation that a large class of organic compounds is excellently suitable for the development of photographic silver images in an acid medium. The subject of this invention is accordingly a process for the development of photographic silver images from silver salts in which the silver is liberated from the silver salts in an acid medium in the presence of reduction products of 1,4-diazine compounds which have at most been reduced to the dihydro stage.

Numerous substances are known which are capable of reducing silver salts to silver metal in suitable media, especially silver halide which has been exposed to light, the unexposed silver halide being reduced so slowly that photographic silver images can be developed in this way in known manner.

Thus metal ions for example Fe^{2+}, Ti^{3+} or V^{2+} are capable of reducing silver ions to silver. Such developers have however not attained any practical significance, since the normal potentials of these systems (for example $Fe^{2+} \rightarrow Fe^{3+}$) are too positive and therefore the reduction comes to a stop even at low concentrations of oxidized metal ions (for example Fe^{3+}). Whilst the redox potential can be lowered by adding suitable complex-forming agents, the action of the metal ion developers is generally weak, that is to say their sensitivity utilisation is low, and they are more of historical and theoretical significance.

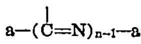
Furthermore a large number of purly organic developers are known which, apart from very few exceptions, correspond to one of the formulae

(I)



$$a-(\overset{|}{C}=\overset{|}{C})_{n-1}-a'$$

(II)



$$a-(\overset{|}{C}=N)_{n-1}-a'$$

wherein *n* denotes an integer and *a* and *a'* each denotes a hydroxyl groups or a primary to tertiary amino group. More details about the developer substances may be found in the book by Mees, "The Theory of the Photographic Process," 3rd edition, 1966, pages 278 to 311.

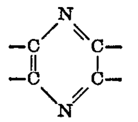
Amongst the large number of known developers corresponding to Formula I or II, only a few are used in practice.

All these developers only exert a sufficient effect for practical purposes at pH-values above 7, and at pH-values below 7 they are either completely inactive or their development speed is very low.

This invention is based on the completely surprising observation that a large class of organic compounds is excellently suitable for the development of photographic silver images in an acid medium. The subject of this invention is accordingly a process for the development of photographic silver images from silver salts in which the silver is liberated from the silver salts in an acid medium in the presence of reduction products of 1,4-diazine compounds which have at most been reduced to the dihydro stage.

It is to be quite generally understood that diazine compounds are those which contain at least one ring of formula

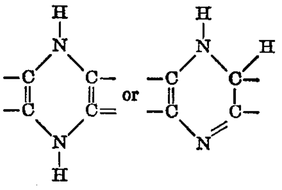
(III)



but which apart from this may be substituted at the ring carbon atoms as desired, especially also by further condensed ring systems.

For the reduction process these compounds to be used as reducing agents must themselves be in a reduced state relative to the diazine. This state may be in equilibrium anywhere between the diazine and the dihydro stage

(IV)



and in a borderline case it is also possible, at least at the beginning of the development process, for practically the whole quantity of reducing agent to be present as dihydro compound. Furthermore the reduction products of the diazines may occur as protonisation products. Accordingly, the mono-valent or divalent reduction products of the 1,4-diazine compound are suitable for the development in accordance with the present process. The divalent reaction stages or dihydro compounds (IV) are mostly protonised in an acid medium, whilst the monovalent reaction stage represents a radical which in general is present in the protonised form up to high pH-values.

Representing the diazine by A, the reduction proceeds as follows:

(a) $$A+e+H^{+} \rightarrow AH \text{ (radical)}$$

(b) $$AH+e+H^{+} \rightarrow AH_2 \text{ (dihydro form)}$$

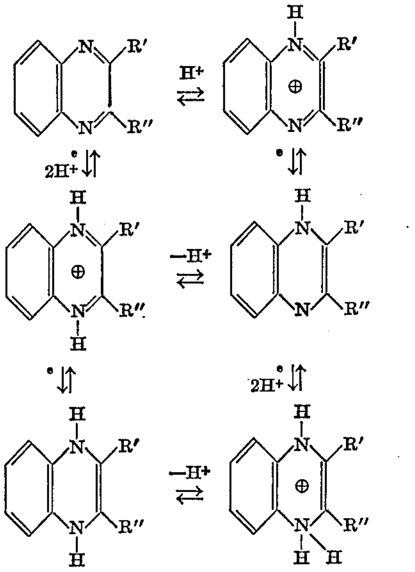
The protonisation equilbria may be represented as follows:

(c) $$A+H^{+} \rightleftarrows [AH]^{+}$$

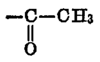
(d) $$AH+H^{+} \rightleftarrows [AH_2]^{+}$$

(e) $$AH_2+H^{+} \rightleftarrows [AH_2]^{+}$$

An example of the redox and protonisation equilibria is given below;



R': Substituent, for example —CH_3.R'': Substituent, for example



$$-\underset{\underset{O}{\|}}{C}-CH_3$$

Details of such redox and protonisation processes are extensively explained in the book by W. M. Clark, "Oxidation-Reduction Potentials of Organic Systems," 1960, Williams & Wilkins, Baltimore.

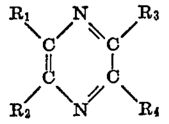
In general it is advantageous to add the reducing agents for the reduction of the silver salts to the reduction medium in the form of the dihydro compounds, since the dihydro compounds can easily be manufactured from the corresponding diazines, for example by catalytic reduction, by reduction with suitable reducing agents for example Cr^{2+}— compounds or sodium dithionite, by electrolytic reduction or with the aid of electron exchangers. In part, the dihydrodiazine compounds are directly obtainable by ring closure.

The radical stage forms from the dihydro stage and the corresponding diazine at a certain equilibrium concentration, with the maximum concentration of radical depending on the difference of the two redox potentials $E°_{AH}—E°_{AH_2}$. The radical can be easily detected by electron spin resonance spectra. Thus the present process may be carried out for example between the diazine and monohydro stage or between the monohydro and dihydro stage.

As has been mentioned, reduction products of any desired compounds which contain the ring of Formula III at least once can be used in the present process, for example the monovalent or divalent reduction products of pyrazines, quinoxalines and phenazines, and/or their protonisation products.

Thus for example reduction products of basic diazines of formula

(V)

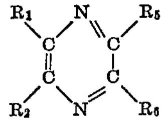


(quinoxalines)

may be used, wherein R_1 and R_2 together form a 6-membered aromatic-carbocyclic ring and R_3 and R_4 each denotes a hydrogen atom, an alkyl group having preferably at most 3 carbon atoms (especially a methyl group), a phenyl residue or a heterocyclic residue, R_3 and R_4 may be different or preferably identical with one another.

Further materials are reduction products of basic diazines of formula

(VI)

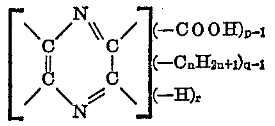


(quinoxalines)

wherein R_1 and R_2 together form a 6-membered aromatic-carbocyclic ring, R_5 denotes a hydrogen atom or preferably an alkyl group, especially a methyl group, or a phenyl residue and R_6 denotes an acetyl group (—OC—CH_3) or a benzoyl group (—OC—C_6H_5).

A further group of diazines corresponds to the formula

(VII)

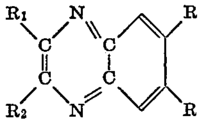


(pyrazines)

wherein *n*, *p* and *q* denote integers, each having a value of at most 3, and $r=6-p-q$. At the same time *n* is preferably equal to 1 and $p+q$ are preferably at most equal to 4.

Finally there may still be mentioned the basic diazines of formula

(VIII)



(phenazines)

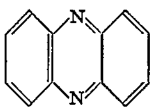
wherein R_1 and R_2 together form a 6-membered aromatic-carbocyclic ring, R_7 and R_8 each denotes a hydrogen atom or R_7 denotes an H_2N— group and R_8 also denotes an H_2N— group or an HO— group.

The carbocyclic 6-membered rings of Formulae V, VI and VII formed by R_1 and R_2 together with two carbon atoms of the diazine ring may contain further substituents for example methyl or methoxy groups or halogen atoms or may preferably be free from such substituents.

Some examples of diazines whose reduction products of the type mentioned may be used in the present process are as follows:

Phenazines

(1)



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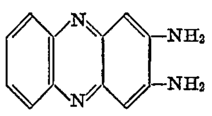

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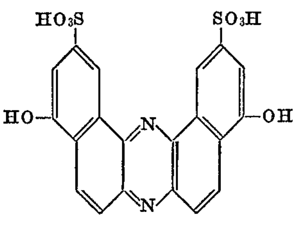

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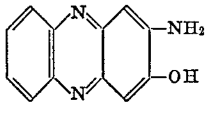

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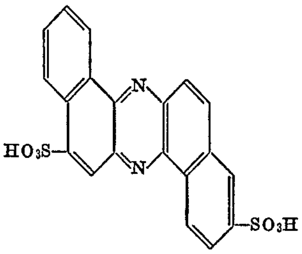

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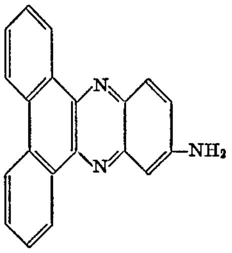

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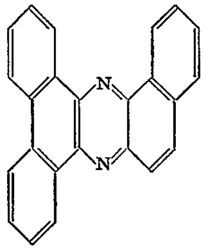

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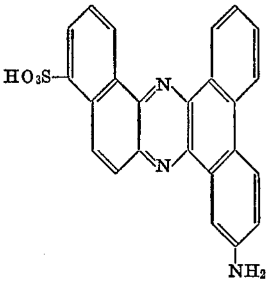

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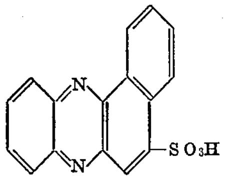

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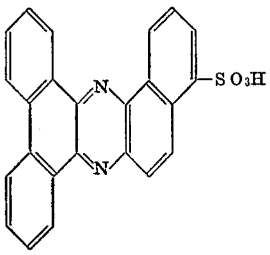

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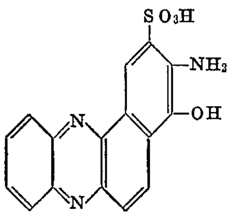

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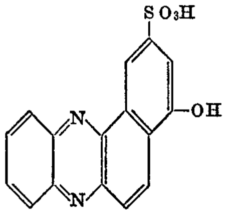

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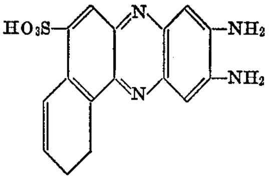

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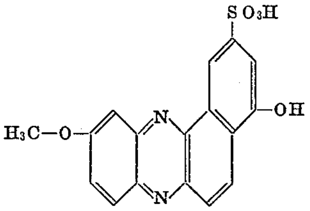

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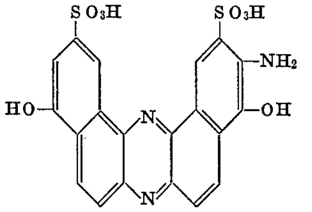

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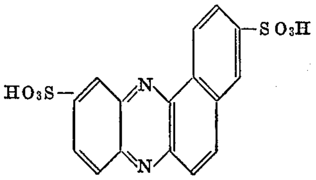
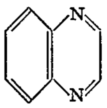


Quinoxalines

(17)



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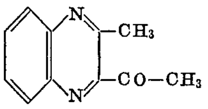

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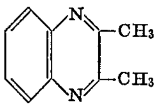

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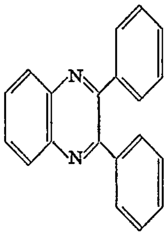

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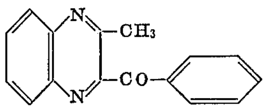

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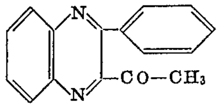

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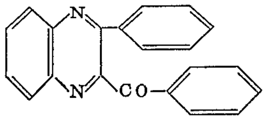

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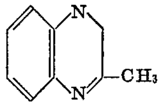

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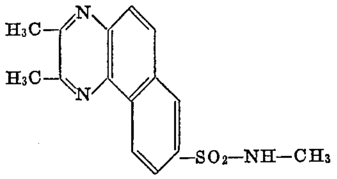

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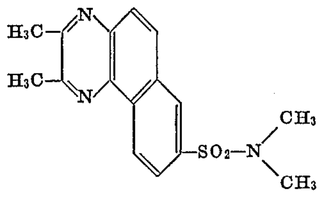

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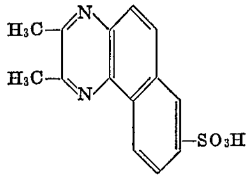

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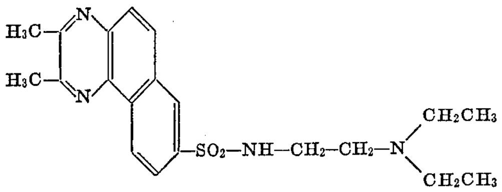

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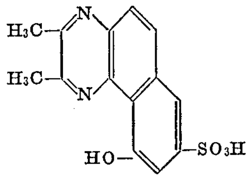

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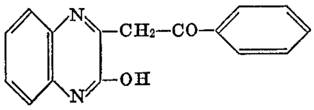

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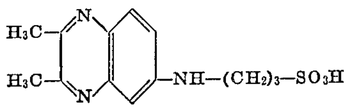

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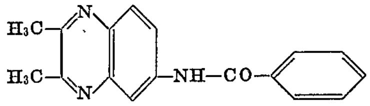

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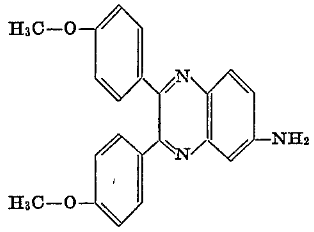

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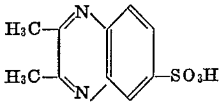

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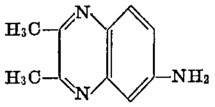

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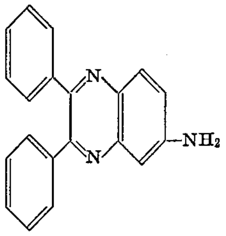

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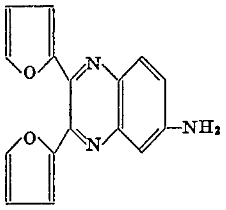

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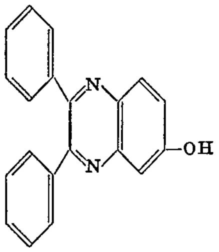

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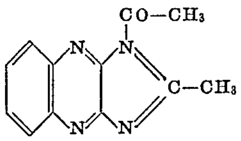

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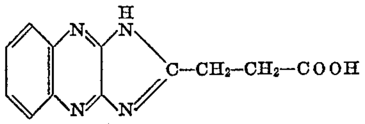

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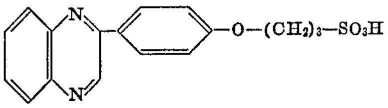

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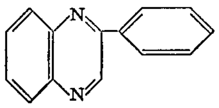

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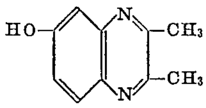

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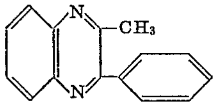

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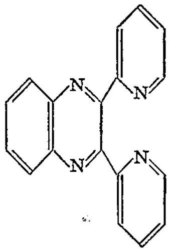

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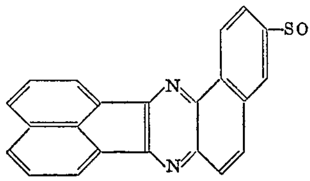

Pyrazines

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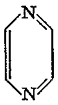

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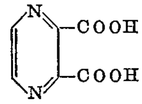

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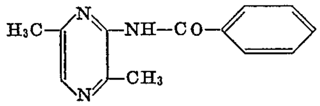

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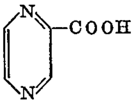

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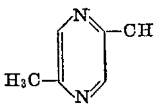


Materials which are particularly suitable for the development process according to the present invention are for example the reduction products of pyrazine-2-carboxylic acid, quinoxaline, 2-phenylquinoxaline (advantageously used as 3-phenyl-1,2-dihydroquinoxaline), 2-methyl-3-acetylquinoxaline and phenazine.

The present process is preferably carried out in aqueous medium which has been rendered acid with a suitable acid or a buffer mixture, advantageously to a pH-value of between 0 and 4. The speed of development and the gradation may be varied within wide limits as a function of the pH-value. As suitable acids and buffer substances the following may be mentioned: aliphatic, aromatic or heterocyclic monocarboxylic and dicarboxylic acids, which may also contain substitutents for example chlorine, bromine and iodine atoms, hydroxyl, nitro, amino or acylamino groups, and also aliphatic or aromatic sulphonic acids, phosphoric acids, ammonium ions for example NH_4^+ or NH_3alkyl^+, HSO_4^-, HF/HCl, HBr, $HClO_4$, H_2CO_3, H_3PO_4, H_2SO_4, HSO_3^-, SO_2,

$$[Al(H_2O)_6]^{3+}$$

HBF_4, $Na_2S_2O_7$ and $Na_2S_2O_5$.

As has been mentioned, the developers are preferably employed in the form of aqueous solutions. At the same time the requisite reduction stage of the diazine compound may also be produced directly in the developing solution, for example by mixing the components, by electrolytic reduction of the diazine compound or may be produced in other ways from stable derivatives of the developer substances. The developers may also be caused to act on the silver salt by impregnating an absorbent strip with the solutions or by incorporating them in suspension or droplets of a high-boiling crystalloid solvent or in capsules of the light-sensitive layer or of an adjacent layer which can be broken open by pressure or change of pH, or by disposing them in containers which can be torn open between the layers of film packs for the diffusion transfer process. The temperature range for development may also be varied within wide limits.

The developer solution may also contain reduction products of a mixture of two or more diazines of the type mentioned or other reducing or oxidising substances for setting up the desired redox equilibrium. Thus a certain quantity of diazine may be added, particularly to a developer which has been freshly charged with a dihydrodiazine, in order to have the radical monohydrodiazine, which under certain circumstances is particularly desirable, already available at the beginning of the development.

Furthermore the developer solution may contain silver halide solvents for example bromide ions, thiocyanate ions or thiourea at a suitable concentration. Haze preventatives for example benzotriazole or phenylmercaptotetrazole may also be added. Hardeners for gelatine, toning substances for producing a bluish black silver image and surface-active substances for uniform wetting may also be added to the developer solution.

The developer solutions to be used in accordance with the invention are suitable for the development of any desired silver halide emulsion, for example emulsions of silver chloride, silver bromide, silver chlorobromide or silver bromoiodide. The emulsions furthermore may contain in the usual layer-forming agents, preferably in gelatine, the usual additives for example sensitisers and surface-active substances and can be sensitive to the most diverse radiation of corpuscular and electromagnetic nature. Silver salts vaporised onto a substrate and free from binders may also be developed in accordance with the invention.

The term "development" is here generally to be understood to mean the reduction of silver salts in layer materials, that is to say not only the selective reduction of silver halide crystals which have been exposed imagewise, but also the reduction of silver salts in layers which have been exposed to diffuse light and the reduction of silver salts which can be developed without exposure to light, for example rehalogenated silver or silver salt with haze nuclei, which are present for example in chemically hazed emulsions. Similarly, the second development in the reversal process, the physical development in the metal diazo process or the reduction of dissolved silver salts in the positive layer of the silver salt transfer process, where silver salts are reduced in contact with colloidal metal or sulphide, may be carried out according to the present reduction process. Mono-baths for the so-called stabilisation process may also be employed in accordance with the invention. Furthermore the process is advantageous for surface development by direct positive methods which depend on the principle of a latent internal image; such methods are for example described in U.S.A. patent specifications Nos. 2,456,953 and 2,479,875 and in Dutch patent applications Nos. 66.05890 and 66.05891.

Special importance attaches to those development methods in which the developed silver image, the undeveloped silver salt image which is complementary to the developed silver image, or the distribution of unconsumed developer which corresponds to the silver salt image are utilised for effecting further chemical reactions, whereby images are produced which are based on dyestuff formation, dyestuff destruction, differences in the degree of polymerisation of the layer colloid, differing electrical conductivity, or differing ease of diffusion or sublimation. The manufacture of coloured images is here particularly important.

This is because the developer solutions of the invention are at the same time suitable for the reduction of azo dyestuffs which are used as image dyestuffs in the silver colour bleaching process. By choosing suitable reduction conduitions it is possible, in a layer which in addition to silver halide simultaneously contains a reducible azo dyestuff, preferentally to reduce the silver halide in the exposed areas whilst the dyestuff is reduced in the unexposed areas. In this way a corrected dyestuff image is produced alongside the silver image. In place of the azo dyestuffs, other reducible substances for example diazonium salts, nitro compounds or quinones can also be reduced imagewise in the unexposed areas.

Furthermore many new possibilities result from the combination of the present process with known development processes which take place in an alkaline medium. Thus for example in the case of a chromogenic reversal process the first development may be carried out in accordance with the invention in an acid medium using the reducing 1,4-diazine compounds and the chromogenic development may be carried out according to known methods. Other novel effects may be achieved by combining layer colloids having different swelling and diffusion characteristics depending on the pH-value or by using filter cover layers which are only soluble in an alkaline medium, which after the acid first development still retain their optical effectiveness and are only dissolved off in a later process stage.

The present process has a series of significant advantages over the conventional development methods which are tied to an alkaline medium:

(1) When the images manufactured according to known processes are inadequately soaked, a gradual yellowing takes place since the conventional developer substances yield coloured oxidation products. This danger does not exist with the present process, since developers can be used whose oxidation products are colourless.

(2) Alkaline developer solutions cause a strong swelling of the gelatine used as the binder. By contrast, development may be effected according to the present process near the isoelectric point of the gelatine at which point the gelatine shows a minimum swelling.

(3) The diffusion of colour coupling agents or image dyestuffs is much stronger in alkaline solutions than in acid solutions.

(4) The known developers are irreversibly oxidised by atmospheric oxygen; by contrast, the compounds to be used in accordance with the present invention can in part be electrolytically regenerated.

The following examples illustrate the invention:

EXAMPLE 1

2.48 g. (0.02 mol) of pyrazine-2-carboxylic acid are dissolved in 100 ml. of ethanol and 900 ml. of 0.1 N sulphuric acid. The solution is freed of atmospheric oxygen by introducing a stream of nitrogen and is then reduced by adding 200 ml. of an 0.1 molar solution of $CrSO_4$ ($pH=1.1$) containing sulphuric acid.

A photographic silver bromide enlargement paper of the commercially available type which has been exposed behind a grey wedge is developed in this solution for 5 minutes at a temperature of 24° C. The paper is then briefly soaked and fixed in the usual manner in a 20% sodium thiosulphate solution. A negative copy of the grey wedge used for the exposure is obtained. The silver density (haze) developed in the unexposed areas, the sensitivity and the gradation are similar to that obtained by using a conventional 1-methylamino-4-hydroxybenzene/hydroquinone developer of pH-value 10.8.

Other commercially available materials which are used in black and white photography, for example negative films, dispositive films and the like, may also be developed with this solution.

EXAMPLE 2

2.48 g. (0.02 mol) pyrazine-2-carboxylic acid are dissolved in 200 ml. of dimethylformamide and 600 ml. of 0.1 N sulphuric acid. The solution is freed of atmospheric oxygen by introducing a stream of nitrogen and is then reduced by adding a solution of 0.02 mol of $CrSO_4$ in 200 ml. of 0.1 N sulphuric acid.

Thereafter a photographic silver bromide enlargement paper is exposed, developed and fixed as described in Example 1 and a similar result is obtained. Other commercially available materials as mentioned in Example 1 may also be developed with this solution.

Similar results are obtained when 0.01 molar solutions of the following substances are used:

	Solvent	Concentration of Solvent, in percent by volume
Substance of Formula No.:		
2	Dimethylformamide	30
4	do	40
11	do	50
15	do	10
18	Ethanol	50
19	do	20
21	do	50
22	do	50
23	do	50
27	Dimethylformamide	50
32	do	50
35	Ethanol	20
43	Dimethylformamide	20
45	do	20
46	do	50
48	do	25

All solutions are 0.1 molar in sulphuric acid. Because of the different solubility of the individual substances different solvents are used at different concentrations.

EXAMPLE 3

2.60 g. of quinoxaline are dissolved in 100 ml. of ethanol and 900 ml. of 0.1 N sulphuric acid. The solution is hydrogenated using palladium charcoal as catalyst until 0.02 mol of hydrogen has been taken up.

A photographic negative film of commercially available type containing silver bromide-iodide microcrystals which has been exposed behind a grey wedge, is developed in this solution for 5 minutes, the temperature of the solution being 24° C. After development the film is soaked in running water and fixed for 5 minutes in a 20% sodium thiosulphate solution in the usual manner. A negative image of the grey wedge used for the exposure is obtained.

The solution is also suitable for the development of other photographic materials containing silver halide, for example commercially available copying papers, enlargement papers, diapositive films and the like.

EXAMPLE 4

0.01 mol of 2-methyl-3-acetylquinoxaline is dissolved in 500 ml. of dimethylformamide and hydrogenated with palladium charcoal as catalyst until 0.01 mol of hydrogen has been taken up. The palladium charcoal is filtered off and the filtrate is added to 500 ml. of 0.2 N sulphuric acid.

Thereafter a photographic negative film is exposed, developed and fixed as described in Example 3 and a similar result is obtained. Other photographic materials as mentioned in Example 3 may also be developed with this solution.

Instead of 0.01 mol of 2-methyl-3-acetylquinoxaline, 0.01 mol of the compounds of Formulae Nos. 1, 4, 11, 21, 22 or 23 may be used with equally good results.

EXAMPLE 5

0.01 mol of compound (45) is dissolved in 500 ml. of glacial acetic acid and hydrogenated using platinum oxide as the catalyst until 0.01 mol of hydrogen has been taken up. A photographic negative film is then exposed, developed and fixed exactly as described in Example 3. A similar result is obtained. Other photographic materials as mentioned in Example 3 may also be developed with this solution.

Instead of 0.01 mol of the compound of Formula 45 0.01 mol of the compound of Formula 44 may also be used.

EXAMPLE 6

The following developer baths are prepared: (a) 1.2 g. of 3-phenyl-1,2-dihydroquinoxaline, 50 ml. of dimethylformamide and 950 ml. of 0.1 N sulphuric acid, (b) 2.0 of 3-phenyl-1,2-dihydroquinoxaline, 100 ml. of acetone and 900 ml. of 0.1 N sulphuric acid.

The 3-phenyl-1,2-dihydroquinoxaline is manufactured according to J. Figueras, J. Org. Chem. 31, 803 [1966].

The solutions (a) and (b) are used for the development of any desired commercially available photographic material for black and white photography, the development time being between 5 and 10 minutes at 25° C.

EXAMPLE 7

The procedure of Example 6 is followed but a developing bath of the following composition is used: 4.0 g. of 2-methyl-3-acetyldihydroquinoxaline and 1,000 ml. of 0.1 N sulphuric acid.

EXAMPLE 8

1 g. of potassium thiocyanate is dissolved in developer solution (a) described in Example 6, and 0.5 g. of potassium bromide is dissolved in developer solution (b).

When a commercial highly sensitive negative film is developed for 10 minutes at 24° C. in these solutions, the gradation becomes about 20% steeper in comparison with development according to Example 6.

EXAMPLE 9

The developer solution (b) mentioned in Example 6 is used and 200 mg. of phenylmercaptotetrazole are dissolved therein.

When a commercially available photographic negative film which has been exposed behind a grey wedge is developed in this solution, a blackening curve having a gradation of 4.0 is obtained.

When the same film is developed in a conventional metel-hydroquinone developer of pH 10.8, a gradation of 1.5 is obtained at the same threshold sensitivity (density 0.1 above haze).

EXAMPLE 10

A solution of the following composition is prepared: 2.0 g. of 3-phenyl-1,2-dihydroquinoxaline, 150 ml. of ethyl alcohol and 850 ml. of Britton-Robinson buffer solution of pH=2.0.

The Britton-Robinson buffer solution consists of a solution which contains 0.04 M each of phosphoric acid, boric acid and acetic acid and which has been adjusted to the desired pH-value with 0.2 N sodium hydroxide solution.

A commercially available photographic negative film is developed in the solution described in the first paragraph for 10 minutes at 24° C. The results are similar to those obtained when development is carried out according to Example 4, but the haze is somewhat greater.

Instead of 2.0 g. of 3-phenyl-1,2-dihydroquinoxaline 3 g. of dihydrophenazine may be used in 100 ml. of ethanol and 900 ml. of buffer solution. The dihydrophenazine is manufactured from phenazine by reduction with sodium dithionite (E. Tomaroff, Annales de Chimie 13, 124 [1956]).

EXAMPLE 11

1,000 g. of a silver bromide-silver iodide emulsion consisting of 96 mol percent of AgBr and 4 mol percent of AgI and containing 35 g. of Ag are mixed with a solution of 35 g. of 3-phenyl-1,2-dihydroquinoxaline in acetone. The dihydroquinoxaline precipitates in a finely dispersed form. After adding the usual casting additives for example wetting agents and hardens the silver halide emulsion is applied to a transparent triacetate film substrate. Amount of silver applied: 4 g. Ag. m.$^{-2}$.

The film manufactured in this way is exposed behind a grey wedge. In order to develop it, the film is bathed for 5 minutes at 24° C. in a solution of 100 ml. of dimethylformamide in 900 ml. of 0.1 N sulphuric acid, briefly rinsed with water and then fixed in the usual manner. A negative image of the grey wedge used for the exposure is obtained.

EXAMPLE 12

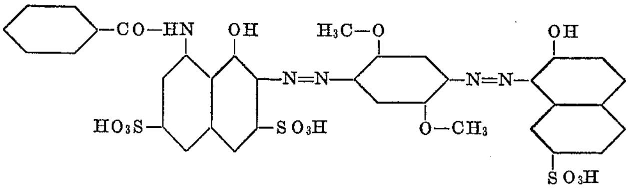
A solution of the following composition is prepared: 2.48 g. of reduced pyrazine-2-carboxylic acid (as in Example 1) 100 ml. of ethanol, 60 ml. of 100% acetic acid, 82 g. of anhydrous sodium acetate and 900 ml. of water.

The pH-value of the bath is 4.7.

A commercially available photographic silver bromide enlargement paper which has been exposed behind a grey wedge is developed for 5 minutes at 24° C. in this solution. In comparison with the development according to Example 1, higher haze values and a significantly lower sensitivity are obtained.

EXAMPLE 13

An emulsion layer sensitised to red light and containing per 1 m.^{2} of layer support, 1.5 g. of silver in the form of silver bromo-iodide (96 mol percent of AgBr and 4 mol percent of Ag) and 0.2 g. of the bluish-green dyestuff of formula



is exposed to red light behind a grey wedge. The exposed layer is treated for 4 minutes at 20° C. in a solution (a) of the following composition: 6 g. of 2-methyl-3-acetyldihydroquinoxaline, 500 ml. of 0.1 M potassium hydrogen phthalate and 495 ml. of 0.1 N sulphuric acid (pH-value of the solution: 2.20).

Instead of using solution (a), the exposed layer may also be treated with solution (b): 1 g. of 3-phenyl-1,2-dihydroquinoxaline, 1 g. of 2-methyl-3-acetylquinoxaline, 200 ml. of dimethylformamide, 300 ml. of 0.1 N potassium hydrogen phthalate solution and 500 ml. of 0.1 N sulphuric acid (pH-value of the solution:2.0 to 2.1).

A silver image which is negative relative to the original, and at the same time a bluish-green coloured image which is negative relaitve to the original, are produced.

After a brief soaking the layer is treated for 5 minutes with a silver bleaching bath of the following composition: 25 g. of $CuSO_4 \cdot 5H_2O$, 30 g. of KBr, 150 ml. of 37% HCl and 1,000 ml. of water, and thereafter fixed with a thiosulphate solution in the usual manner. A bluish-green colour image of the grey wedge used for the exposure is then obtained which is negative relative to the original.

EXAMPLE 14

35 g. of gelatine are dissolved in 500 ml. of water at 40° C. and to this solution are added 10 mg. of commercial colloid-silver dissolved in 20 ml. of water, 10 ml. of an alcoholic solution of 1-phenyl-5-mercaptotetrazole

(1%) and 3 ml. of formaldehyde solution (10%). The solution is applied in a thin layer to a baryta paper, dried and used as the image-receiving layer for producing an image according to the silver salt diffusion process.

A text original is exposed onto a commercially available negative paper for the silver salt diffusion process, predominantly containing silver chloride. The exposed negative paper together with the receiving layer is passed through a roller development apparatus of the type used in the silver salt diffusion process, the development apparatus being filled with a developer of the following composition: 0.1 mol of 2-methyl-3-dihydroquinoxaline, 500 ml. of dimethylformamide, 500 ml. of 0.2 N sulphuric acid and 0.4 g. of thiourea.

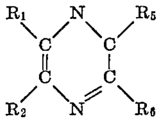
In the development apparatus, the two layers are impregnated with the developer solution and brought into contact with one another. After 10 seconds contact time the two layers are pulled apart and one obtains on the receiving layer a copy of the original exposed onto the negative paper, which can be dried without further treatment. No yellowing or fading of the silver image occurs even on prolonged storage of the copy.

The same developer solution may also be used for the development of film packs which produce images by the silver salt diffusion process, described for example in U.S. patent specification No. 2,543,181.

We claim:

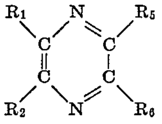
1. A process for the development of a photographic silver image from a silver salt, which comprises liberating the silver from the silver salt in an acid medium in the presence of a reduction product of a 1,4-diazine compound which has at most been reduced to the dihydro stage.

2. A process for the development of a photographic silver image from a silver salt as claimed in claim **1**, which comprises liberating the silver from the silver salt in an acid medium in the presence of a reduction product of a basic diazine compound of the formula



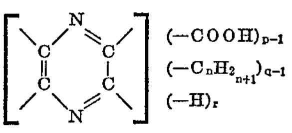
in which R_1 and R_2 together form a 6-membered aromatic-carbocyclic ring and R_3 and R_4 each denotes a member selected from the group consisting of a hydrogen atom, an alkyl group, a phenyl radical and a heterocyclic ring.

3. A process for the development of a photographic silver image from a silver salt as claimed in claim **1**, which comprises liberating the silver from the silver salt in an acid medium in the presence of a reduction product of a basic diazine compound of the formula



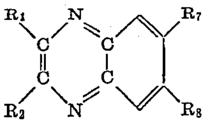
in which R_1 and R_2 together form a 6-membered aromatic-carbocyclic ring, R_5 is a member selected from the group consisting of a hydrogen atom, an alkyl group and a phenyl radical and R_6 is an acetyl group or a benzoyl group.

4. A process for the development of a photographic silver image from a silver salt as claimed in claim **1**, which comprises liberating the silver from the silver salt in an acid medium in the presence of a reduction product of a diazine compound of the formula



in which *n*, *p* and *q* each denotes an integer having a value of at most 3, and $r=6-p-q$.

5. A process for the development of a photographic silver image from a silver salt as claimed in claim **1**, which comprises liberating the silver from the silver salt in an acid medium in the presence of a reduction product of a diazine compound of the formula



in which R_1 and R_2 together form a 6-membered aromatic-carbocyclic ring, R_7 denotes a member selected from the group consisting of a hydrogen atom and an H_2N-group and R_8 denotes a member selected from the group consisting of a hydrogen atom, an H_2N-group and an HO-group.

6. A process for the development of a photographic silver image from a silver salt as claimed in claim **1**, which comprises liberating the silver from the silver salt in an acid medium having a pH-value of at most 4 in the presence of a reduction product of a 1,4-diazine compound which has at most been reduced to the dihydro stage.

7. A process for the development of a photographic silver image from a silver salt as claimed in claim **1**, which comprises liberating the silver from the silver halide in an acid medium having a pH-value of at most 4 in the presence of a reduction product of a 1,4-diazine compound which has at most been reduced to the dihydro stage.

8. A process for the development of a photographic silver image from a silver salt as claimed in claim **1**, which comprises liberating the silver from a silver halide which is distributed in a photographic layer and is exposed image-wise by reduction in an acid medium having a pH-value of at most 4 in the presence of a reduction product of a 1,4-diazine compound which has at most been reduced to the dihydro stage.

9. A process for the development of a photographic silver image from a silver salt, which comprises liberating the silver from a silver halide which is distributed in a photographic layer and is exposed image-wise by reduction in an acid medium in the presence of a reduction product of a 1,4-diazine compound lying between the diazine stages and the monohydro stage.

10. A process for the development of a photographic silver image from a silver salt, which comprises liberating the silver from a silver halide which is distributed in a photographic layer and is exposed image-wise by reduction in an acid medium in the presence of a reduction product of a 1,4-diazine compound lying between the monohydro stage and the dihydro stage.

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U.S. Cl. X.R.

96—66.5, 56.2