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Schlunke et al.

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[45] **Oct. 23, 1973**

[54] PHOTOGRAPHIC COLOUR MATERIAL

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[73] Assignee: **Ciba-Geigy AG,** Basel, Switzerland

[22] Filed: **Aug. 31, 1971**

[21] Appl. No.: **176,689**

[30] **Foreign Application Priority Data**
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[52] **U.S. Cl.** **96/53,** 96/20
[51] **Int. Cl.** **G03c 7/16**
[58] **Field of Search** 96/53, 20, 99, 73

[56] **References Cited**

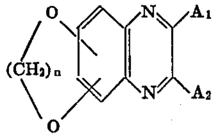
UNITED STATES PATENTS

3,656,953	4/1972	Schlunke et al.	96/20
2,669,517	2/1954	Mueller	96/53
3,615,494	10/1971	Watanabe et al.	96/53

Primary Examiner—Norman G. Torchin
Assistant Examiner—Richard L. Schilling
Attorney—Harry Goldsmith et al.

[57] **ABSTRACT**

A photographic light-sensitive material for the silver bleaching process which comprises on a support in at least one layer a quinoxaline of formula



(1)

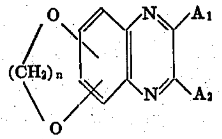
wherein A_1 and A_2 are each an alkyl-, aralkyl-, aryl, or heterocyclic group and *n* is 1 or 2, whereby the oxygen-containing ring is connected with the quinoxaline group in the 5,6- or 6,7-position as a colour bleaching catalyst as well as quinoxalines of the formula given above are disclosed.

11 Claims, No Drawings

PHOTOGRAPHIC COLOUR MATERIAL

This invention relates to photographic material which contains quinoxalines as colour bleaching catalysts.

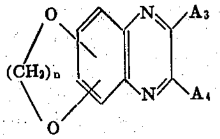
According to the present invention these is provided a photographic eight-sensitive material for the silver bleaching process which comprises on a support in at least one layer a quinoxaline of formula



(1)

wherein A_1 and A_2 each represent an alkyl group with at most of 5 carbon atoms, an at most bicyclic aralkyl group with 1 to 5 carbon atoms in the alkyl portion, an at most bicyclic aryl group or a 5 or 6-membered heterocyclic group having N, O or S as heteroatoms and n represents 1 or 2, whereby the oxygen-containing ring is connected with the quinozaline group in the 5,6 or 6,7-position, as colour bleaching catalysts.

Advantageously quinoxalines of formula



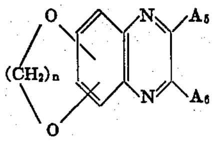
(2)

are used, wherein A_3 and A_4 each represent an alkyl group with at most 5 carbon atoms or an optionally substituted benzene group and *n* represents 1 or 2, whereby the rings are interconnected in the indicated manner.

Groups A_1 and A_2 or A_3 and A_4 as well as groups A_5 and A_6 of the following formula (3) can be the same or different. Alkyl groups with 1 to 5, preferably 1 to 3 carbon atoms which can be used are e.g. amyl, n-sec. or tert. butyl, n or isopropyl, ethyl or in particular methyl groups. As at most bicyclic aralkyl groups are mentioned e.g. the naphthenyl or benzyl group. The at most bicyclic aryl groups are naphthalene, diphenyl or benzene groups, having optionally further substituents such as, e.g., lower alkyl, lower alkoxy, hydroxy, substituted amines, amine or halogen. Particularly lower alkyl groups can be used as substituents for the amine. Heterocyclic 5 or 6-membered groups which can be used are, e.g., pyridyl, furyl or thienyl groups.

Depending on whether *n* is 1 or 2 the compounds of formula (1) are dioxolo or dioxano quinoxalines.

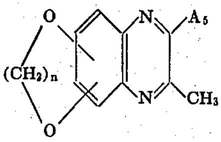
Of particular interest are quinoxalines of formula



(3)

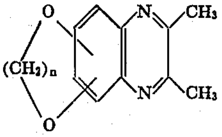
wherein A_5 and A_6 each represent a methyl or phenyl group and *n* is 1 or 2, whereby the rings are interconnected in the indicated manner.

Among these quinoxalines those of formula



(4)

and particularly of formula



(5)

wherein A_5 is a methyl or phenyl group and *n* is 1 or 2, whereby the rings are interconnected in the indicated manner, are particularly suitable.

The quinoxalines of formula (1) can be used as colour bleaching catalysts in a processing bath, preferably in a colour bleaching bath and/or in a layer of the photographic material.

The reduction products of the quinoxalines of formula (1) can also be used for so-called bleach development, by themselves acting as hydrogen developers in an acid medium.

Such processes are known, e.g., from French Pat. No. 1,565,800.

The quinoxalines of formula (1) can be used either alone or in the presence of other conventional colour bleaching catalysts. It is also possible to use various quinoxalines of formula (1) simultaneously in the colour bleaching bath. Finally the quinoxalines of formula (1) can also be used together with other bleaching-promoting measures, e.g., together with an irradiation or bubbling with a gas of the colour bleaching bath or in additon of organic solvents to the colour bleaching bath.

The quinoxalines of formula (1) can therefore be incorporated into a coating free from bleachable image dye. The multi-layer material can therefore have for example an additional gelatin layer containing only the catalyst located directly on the emulsion carrier or between two colour layers. In the latter case the catalyst-containing layer also acts as a separating layer. In addition, the catalyst can also be incorporated into colloidal silver or layers containing filter or antihalo dye or covering coatings. These filter layers as well as the coatings with the image dyes advantageously contain gelatin as the layers colloid.

However, the quinoxalines of formula (1) can also be incorporated directly into a layer containing image dye. Furthermore, the mjlti-layer material can have the conventional composition. Colour-photographic images can be produced in per se known manner with the photographic materials of tje indicated composition.

The colour bleaching catalysts of formula (1) can, as already indicated, e.g. be added to the colour bleaching bath where they then directly exert their action. They can also be added to a previous treatment bath, e.g., the developer, a hardening bath, a stop bath or a special bath preceeding the silver bleaching bath. In this way a certain portion of the catalyst quantity introduced is absorbed and retained by the photographic coating material until it can act in the colour bleaching bath. Depending on the particular use the quantity of catalyst used can vary within wide limits. Generally it suffices for a strong action to add 0.001 to 0.1g of catalyst to 1 litre of a colour bleaching bath of normal composition containing a silve complex constituent such as, e.g., alkali metal bromide or iodide or thiourea and optionally an anti-oxidising agent such as e.g. sodium hypophosphite and for giving the necessary pH-value a stong organic or inorganic acid such as, e.g., benzenesulphonic acid, hydrochloric acid, sulphuric acid, phosphoric acid or sodium bisulphate.

Further objects of the invention are therefore a photographic, light-sensitive material for the silver dye-bleach process containing on a carrier in at least one layer as a colour bleaching catalyst a quinoxaline of formula (1) and photographic processing baths, particularly colour bleaching baths, characterised in that as the colour bleaching catalyst they contain at least a quinoxaline of formula (1).

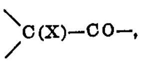
A further object of the invention is a process for producing colour photographic images according to the silver dye-bleach process on materials containing on a substrate at least one silve halide emulsion layer with a bleachable image dye by exposure, developing the silver image and colour bleaching, characterised in that the colour bleaching is performed in the presence of at least one quinoxaline of formula (1) as the colour bleaching catalyst.

The hitherto known compounds used in the silver bleaching process as colour bleaching catalysts have a widely different action on azo dyes of differing constitution. Whereas they can be very effective with one class of azo dyes, they may have only a very slight bleaching-promoting action with another class. Thus, there is a need for compounds which alone or in combination bring about a uniform bleaching of all three layer dyes of a multi-layer material.

It has been found that quinoxalines of formula (1) are admirably suited for this purpose. They are characterised by a very favourable position of their redox potentials and good solubility in the colour bleaching bath in the requisite concentrations. Particularly if the groups A_1 and A_2 of formula (1) each represent a methyl group the quinoxalines according to the invention of formula (1) have a good activity and lead to a favourable gradation. In addition, when they are present and appropriately used bleach couplings between the individual image dye-containing layers are largely eliminated.

Quinoxalines of formula (1) are appropriately prepared in per se known manner (cf J.C.E. Simpson, Condensed Pyridazine and Pyrazine Rings in A. Weissberger, The Chemistry of Heterocyclic Compounds, J. Wiley & Sons, New York, 1953, 203ff) by condensation of the corresponding aromatic 1,2-diamine with a 1,2-dicarbonyl compound. Instead of diamine it is possible to use the corresponding more stable o-nitroaniline or the corresponding o-dinitro compound, which can be reduced to the desired diamine and then without intermediate separation reacted to give quinoxaline. The corresponding benzofuroxans or their reduction products (benzofurazans) can also be reduced to 1,2-diamines via intermediate stages (F.B. Mallory S.P. varimbi, J. Org. Chem., 28, 1656ff, 1963) and condensed to quinoxalines.

Instead of the 1,2-dicarbonyl compound it is also possible to react an α-substituted halogeno ketone of formula



$$>C(X)-CO-,$$

wherein X is a nucleophilic group, e.g. -I, -Br, -Cl, or -OH with the o-diamine to give the corresponding 1,2-dihydroquinoxaline (J. Figueras, J. Org. Chem., 31, 803ff, 1966), which is then oxidised in situ to quinoxaline.

The quinoxalines are obtained in better yield and greater purity if the condensation is performed under nitrogen.

α-Oximinoketones can also be reacted with 1,2-diamines to give quinoxalines (cf. J.C.E. Simpson, loc. cit.).

As starting materials for one of the indicated syntheses can, e.g., be used the compounds given in the following table.

1,2-Dicarbonyl compounds, α-halogenoketones, α-Oximinoketones

diacetyl
3-bromobutanone-2
3-chlorobutanone
3-iodbutanone
3-oximinobutanone-2
hexandione-3,4
benzil
benzoin
bromodesoxybenzoin
1-phenylpropandione-1,2
1-phenyl-2-oximinopropanone-1
bromopropiophenone
chloropropiophenone
2′-hydroxypropiophenone
di-(α-naphthyl)-diketone
di-(β-naphthyl)-diketone
α-pyridil
γ-pyridil
di-(2-thienyl)-diketone
di-(2-furyl)-diketone

o-dinitrobenzenes, o-nitroanilines, 1,2-diamines

[4,5-d]-dioxolo-1,2-dinitrobenzene
[4,5-d]-dioxolo-1-amino-2-nitrobenzene
[4,5-d]-dioxolo-1,2-diaminobenzene
[3,4-d]-dioxolo-1,2-dinitrobenzene
[3,4-d]-dioxolo-1-amino-2-nitrobenzene
[3,4-d]-dioxolo-1-nitro-2-aminobenzene
[3,4-d]-dioxolo-1,2-diaminobenzene
[4,5-b]-dioxano-1,2-dinitrobenzene
[4,5-b]-dioxano-1-amino-2-nitrobenzene
[4,5-b]-dioxano-1,2-diaminobenzene
[3,4-b]-dioxano-1,2-dinitrobenzene
[3,4-b]-dioxano-1-amino-2-nitrobenzene
[3,4-b]-dioxano-1-nitro-2-aminobenzene
[3,4-b]-dioxano-1,2-diaminobenzene

benzofuroxans, benzofurazans

[5,6-d]-dioxolobenzofuroxan
[5,6-d]-dioxolobenzofurazan
[4,5(6,7)-d]-dioxolobenzofuroxan
[4,5-d]-dioxolobenzofurazan
[5,6-b]-dioxanobenzofuroxan
[5,6-b]-dioxanobenzofurazan
[4,5(6,7)-b]-dioxanobenzofuroxan
[4,5-b]-dioxanobenzofurazan

The quinoxalines of formula (1) are new and can serve as intermediates, e.g., in the preparation of pharmaceutically active compounds.

The percentages in the following preparation instructions and examples are percentages by weight.

Preparation Instructions

General instructions

An appropriate o-dinitro derivative is dissolved in a suitable solvent, e.g., methanol, ethanol, glacial acetic acid or dimethyl formamide or also only suspended with 1 to 10 percent by weight of hydrogenation catalyst e.g., a 10 percent palladium-carbon catalyst and hydrogenated under normal pressure, optionally with initial heating. When the reaction is terminated the catalyst is filtered off under N_2 and the filtrate under N_2 is mixed with an at least equimolar quantity of distilled or recrystallised diketone or a solution of the diketone in a suitable solvent, whereby in most cases a colour deepening occurs and the temperature rises. Subsequently the mixture is refluxed until the end of the reaction and the desired substance is isolated after cooling. The product can be purified by recrystallising from a suitable solvent by distillation or if necessary by chromatography or sublimation. Instead of the dinitro derivative it is possible in some cases to use the corresponding o-nitroamino compound.

If the o-diamino compound is single and obtainable with sufficient purity it can be reacted directly or in the form of its salt (hydrochloride, hydrosulphate, hydroperchlorate, etc.) with the corresponding diketone in a suitable solvent under nitrogen. When using a salt it is recommended that an equivalent quantity of sodium or potassium acetate be added to saturate the liberated acid.

For the synthesis of the 2,3-asymetrical compounds the α-diketone is replaced by α-bromopropiophenone. The thus formed 1,2-dihydroquinoxaline is then oxidised with m-nitrobenzenesulphonic acid Na salt in the presence of an aqueous sodium hydroxide solution to give quinoxaline.

The redox potentials are determined in the usual manner by means of polarography. The solvent used is in all cases a mixture of dimethylformamide-2N sulphuric acid in a ratio of 1:1. The potential is measured relative to an Ag/AgCl electrode of known potential and then converted to the potential relative to a normal hydrogen electrode. Whereas in certain cases two single electron transitions, characterised by that two polarographic waves are observed in other cases only one polarographic wave is observed, corresponding to the average redox potential.

The melting points and analysis results of the quinoxalines of formula (1) are given in the table.

A [6,7-d]-dioxolo-2,3-dimethylquinoxaline

20g (94.5mmol) of [4,5-d]-dioxolo-1,2-dinitrobenzene are dissolved in 200ml of methanol and after adding 1g of 10 percent palladium/animal charcoa hydrogenated under normal pressure, whereby the internal temperature rises to 60°C; hydrogen consumption 14.1 litres = 100 percent of theory. The catalyst is filtered off under nitrogen and the filtrate is mixed with 8.6g (100mmol) of diacetyl under N_2. The reaction mixture is stirred for 45 minutes at room temperature and then evaporated to dryness. After recrystallising from a little methanol 15.7g (=84 percent of theory) of compound A are obtained, whereby the thin layer chromatogram in toluene:acetone 9:1 is uniform. The IR spectrum and nuclear magnetic resonance spectrum conform with the structure.

B [6,7-d]-dioxolo-2-methyl-3-phenylquinoxaline

31.5g (149mmol) of [4,5-d]-dioxolo-1,2-dinitrobenzene are hydrogenated as described in Example A; H_2 consumption 21 litres = 100 percent of theory. The filtrate is mixed with 15g of crystallised sodium acetate and 33.25g of freshly distilled bromopropiophenone and refluxed for 3 hours. The hot solution is mixed with a freshly prepared solution of 36.5g of 95 percent sodium-m-nitrobenzenesulphonate and 66g (1.45mol) of sodium hydroxide in 287ml of H_2O and 45ml of ethanol and refluxed for 2 hours. After cooling overnight 300ml of water are added and the solution distilled to 500ml. The residue from which already part of the desired product is precipitated is continuously extracted for 12 hours with 500ml of ethyl acetate.

After treating the organic phase with animal charcoal and filtering, the solvent is removed under reduced pressure. The residue is dissolved in a minimum of ethanol, again treated with animal charcoal and the filtrate agitated in 500ml of hot water. After slowly cooling to 0°C., 8.7g (=22 percent of theory) of compound B are finally obtained. The thin-layer chromatogram in toluene:acetone 9:1 reveals in addition to the main quantity four slight impurities. The IR and NMR spectra show the characteristic strips for the required structure.

C [5,6-d]-dioxolo-2,3-dimethylquinoxaline

1. [4,5-d]-dioxolacetanilide

51.4g (308mmol) of [4,5-d]-dioxolonitrobenzene are dissolved in 500ml of ethanol and hydrogenated in the presence of 1.5g of 10 percent palladium/carbon under normal pressure at room temperature. After filtering off the catalyst and evaporating the solvent there remain 41.1g (=95 percent of theory) of the amino compound as a brown oil which in the thin-layer chromatogram with toluene:acetone 9:1 as the solvent system reveals in addition to the main zone two small impurities. This oil is mixed with 44ml of glacial acetic acid and 35ml of acetic anhydride and after adding 0.55g of zinc powder is refluxed for 1 hour. The still hot solution is poured onto 200ml of an ice-water mixture. The resulting crystals are filtered off and dried at 60°C in vacuo. Yield 47.8 = 85 percent of theory (based on the nitro compound) of m.p. 134.1°C. The thin-layer chromatogram in trichloromethane:methanol 9:1 as the solvent system reveals a main spot, whilst the IR and NMR spectra show the strips characteristic of the structure.

2. [4,5-d]-dioxolo-2,3-dinitroacetanilide

47.8g (266mmol) of [4,5-d]-dioxolacetanilide are added portionwise accompanied by virorous stirring at 5°–10°C. to a mixture of concentrated $HNO_3(d=1.4)$ and 166ml of fuming $HNO_3(d=1.54)$. On termination of the addition the reaction mixture is stirred for a further 10 minutes and then poured onto an ice-water mixture. After neutraliSing the solution to pH=6 the aqueous phase is extracted with ethylacetate, the organic phases are dried together and the solvent removed under reduced pressure. The remaining yellow crystals (16g) are dissolved in a minimum of methanol and treated with activated charcoal. The filtrate is mixed with 1,000ml of the water-ice mixture. The resulting yellow needles are suction filtered and dried;

yield 8.4g = 11 percent of theory of m.p. 179.1°C. The thin-layer chromatogram in toluene:acetone 6:4 reveals in addition to the main zone two negligible impurities. The IR and NMR spectra conform with the structure.

3. [4,5-d]-dioxolo-2,3-dinitroaniline

9.6g (35mmol) of [4,5-d]-dioxolo-2,3-dinitroacetanilide are refluxed for 3 hours in 40ml of ethanol and 4g of 37 percent hydrochloric acid. After cooling to 0°C. 7.1g (=90 percent of theory) of the amine found to be thin-layer chromatographically (solvent system toluene:acetone 7:3) uniform. The IR and NMR spectra show the absorptions to be expected from the structure.

4. [3,4-d]-dioxolo-1,2-dinitrobenzene

7.1g (31mmol) of [4,5-d]-dioxolo-2,3-dinitroaniline suspended in 215ml of glacial acetic acid are diazotised with 7.4g (107mmol) of sodium nitrite in 70ml of 96 percent sulphuric acid at 15°C. After stirring for 2 hours at room temperature the reaction mixture is poured into 142ml of ethanol. After adding 0.45g of copper powder stirring takes place at room temperature with the end of gas evolution (3 hours). The reaction mixture is poured onto ice-water. On leaving to stand almost colourless needles are precipitated, which are dissolved in a minimum of methanol and treated with activated charcoal. After adding water 4.7g (74 percent of theory) of slightly yellowish and fine needles are obtained. The thin-layer chromatogram in toluene-:acetone 7:3 reveals in addition to the main spot one slight impurity. The IR and NMR spectra conform with the structure.

5. [5,6-d]-dioxolo-2,3-dimethylquinoxaline

3.1g (15 mmol) of [3,4-d]-dioxolo-1,2-dinitrobenzene are, as described in Example A, hydrogenated in 50 ml of ethanol as the solvent. After adding 1.3g (15mmol) of diacetyl the reaction mixture is refluxed for 1 hour. The thus obtained residue is taken up in 30ml of methanol, again treated with animal charcoal and finally cooled to −50°C. Thereby 1g (=33 percent of theory) of almost colorless crystals are obtained, which in the thin-layer chromatogram with toluene:acetone 9:1 as the solvent system reveal in addition to the main spot one slight impurity. The IR and NMR spectra reveal the characteristic strips expected from the structure.

D. [5,6-b]-dioxano-2,3-dimethylquinoxaline

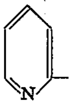
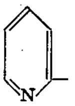
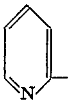
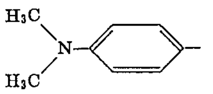
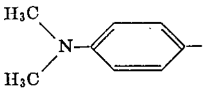
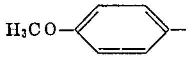
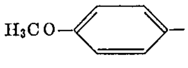
9.0g (40mmol) of [3,4-b]-dioxano-1,2-dinitrobenzene, dissolved in 250ml of ethanol are hydrogenated in the presence of Raney nickel (activity W5) and 0.5g of 10 percent palladium/carbon at room temperature and normal pressure; H_2 consumption 5300ml = 90 percent of theory. After filtering off the catalyst and adding 3.5ml (40mmol) of diacetyl the solution is refluxed for 1 hour and evaporated to about 50ml under reduced pressure. The residue is treated with activated charcoal and the filtrate cooled to −10°C, whereby 2.9g = 33 percent of theory of cOmpound D are obtained. The thin-layer chromatogram in toluene:acetone 8:2 as the solvent system reveals no impurities. The IR and NMR spectra conform with the structure.

E. [6,7-b]-dioxano-2,3-diphenylquinoxaline

9.0g (40mmol) of [4,5-b]-dioxano- 1,2-dinitrobenzene, dissolved in 250ml of ethyl acetate are hydrogenated as described under D. The filtrate is mixed with 8.4g (40mmol) of benzil and refluxed for 1 hour. After cooling to room temperature the solvent is removed under reduced pressure, the residue is taken up in 300 ml of acetone: trichloromethane 10:1, treated with activated charcoal and finally evaporated to about half the volume. After cooling to 0°C. 5.9g (= 43 percent of theory) of compound E are obtained. The thin-layer chromatogram in toluene:acetone 9:1 reveals in addition to the desired substance E an insignificant impuritY. The IR and NMR spectra conform with the structure.

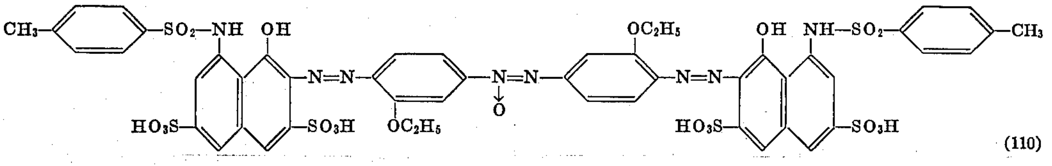
The other compounds shown in Table I were prepared analogously to one of the hereinbefore described instructions.

TABLE I

	In Formula (1)					Analysis					
						Percent C		Percent H		Percent N	
Compound	A₁	A₂	n	Connection point	Melting point, ° C.	Calc.	Found	Calc.	Found	Calc.	Found
A	CH_3	CH_3	1	6.7	213.3	65.34	65.47	4.98	5.03	13.85	13.95
B	CH_3	C_6H_5	1	6.7	125.2	72.72	72.61	4.58	4.51	10.60	10.48
C	CH_3	CH_3	1	5.6	154.5	65.34	65.52	4.98	5.25	13.85	13.92
D	CH_3	CH_3	2	5.6	141.3	66.65	66.58	5.59	5.54	12.96	12.84
E	C_6H_5	C_6H_5	2	6.7	225.0	77.63	77.53	4.74	4.77	8.23	8.04
F	C_6H_5	C_6H_5	1	6.7	152.7	77.29	77.43	4.32	4.44	8.58	8.25
G	C_6H_5	C_6H_5	1	5.6	136.9	77.29	77.37	4.32	4.51	8.58	8.30
H	CH_3	CH_3	2	6.7	189.9	66.65	66.36	5.59	5.63	12.96	13.10
I	CH_3	C_6H_5	2	6.7	105.6	73.37	73.52	5.07	4.98	10.07	9.90
J	C_6H_5	C_6H_5	2	5.6	192.2	77.63	77.79	4.74	4.72	8.23	8.00
K			1	6.7	203.1	69.50	69.24	3.68	3.72	17.07	16.71
L			2	6.7	195.7	70.16	70.12	4.12	4.15	16.37	16.35
M			1	6.7	276.0	72.80	73.25	5.86	6.03	13.58	13.59
N			1	6.7	170.2	71.49	71.63	4.70	4.73	7.25	6.94

Example 1

On a 13 × 18cm glass plate is cast a solution of 3.3ml of 6 percent gelatin, 2.0ml of a 1 percent solution of the hardener 2,4-dichloro-6-phenylamino-1,3,5-triazino-3′-sulphonic acid, 0.5ml of a 2.10^{-3} molar solution of compound G in acetone and 4.2ml of water. After drying, on this is cast a solution of 3.3ml of 6 percent gelatin, 3.3ml of a silver bromide emulsion containing 5.3g of silver per 100g of emulsion, 2.0ml of the above hardener, 0.3ml of a 1percent solution of the blue-green dye of formula


(110)

and 1.1ml of water. After drying the thus obtained laminar bond a step wedge is copied thereon (50 lux, 3 sec.) and then the copy is developed as follows:

1. develop for 6 minutes in a bath containing per litre 50g of anhydrous sodium sulphite, 0.2g of 1-phenyl-3-pyrazolidone, 6g of hydroquinone, 35g of anhydrous sodium carbonate, 4g of potassium bromide and 0.3g of benzotriazole;
2. fix for 2 minutes with a solution of 200g of sodium thiosulphate, 10g of sodium sulphite, 20g of sodium acetate and 10ml of glacial acetic acid per litre of water;
3. rinse for 4 minutes;
4. colour bleach for 6 minutes with a solution of 10g of potassium iodide in 1 litre of 1N-sulphuric acid;
5. rinse for 2 minutes;
6. bleach the remaining silver for 2 minutes with a bath containing 150ml of 37 percent hydrochloric acid, 25g of copper sulphate and 30g of potassium bromide per litre;
7. rinse for 2 minutes;
8. fix for 4 minutes as under 2);
9. rinse for 10 minutes.

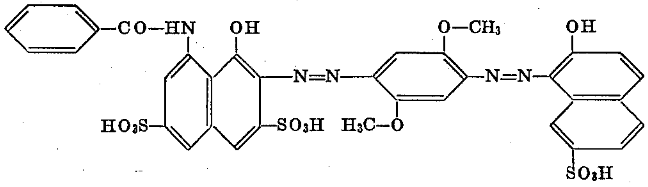
After drying the clean colourless bleached photograph is obtained with a clearly graduated gradation of the wedge used as the original.

Example 2

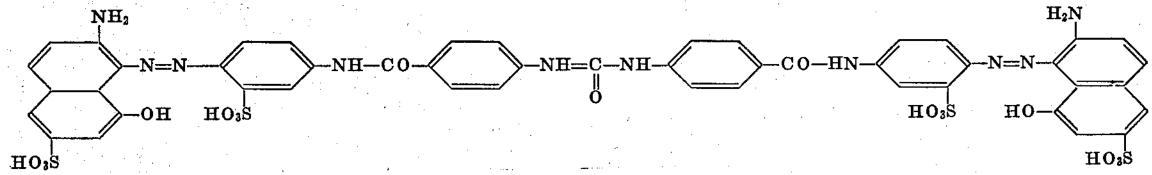
If instead of compound G compound E dissolved in dimethyl formamide is used, then proceeding as described in Example 1 again a clean positive image of the exposed wedge is obtained. If instead of compound G compound J is used as an acetic solution, then proceeding as described in Example 1 once again a clean positive image is obtained of the wedge used as the original.

EXAMPLE 3

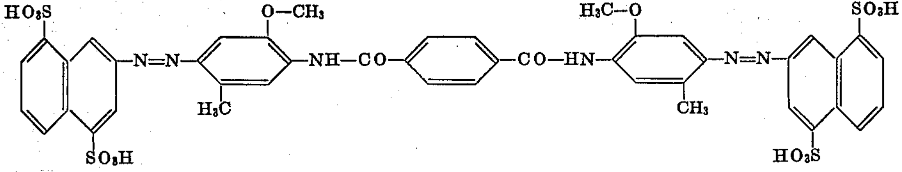
A photographic material with three colour layers contains on a white-opaque cellulose acetate film a red-sensitive silver bromide emulsion with the blue-green dye of formula


(102)

thereover an empty gelatin separating layer and then a green-sensitive silver bromide emulsion with the purple dye of formula

(103)


After a further separating layer follows a layer with a yellow filter dye or colloidal silver acting as a yellow filter, over which there is a silver bromide layer with the yellow dye of formula


(104)

and a covering layer. All these layers are hardened with a halogenotriazine compound such as 2,4-dichloro-6-phenylamino-1,3,5-triazino-3′-sulphonic acid.

This copying material is successively exposed under a step wedge into the three spectral areas blue (Kodak Wratten filter 2B+49), green (Kodak Wratten filter 16+61) and red (Kodak Wratten filter 2×29) and, as described in Example 1 developed for 7 minutes and fixed. Subsequently bleaching takes place in a silver bleaching bath containing per litre 27ml of 96percent sulphuric acid, 10g of potassium iodide and 10ml of a 4.10^{-2} molar solution of compound A in glacial acetic acid. After a brief rinsing the remaining silver is, as described in Example 1 under (6), oxidised, rinsed and fixed as described above. After thorough washing-out and drying a white-bleached neutral wedge is obtained, opposite to the original in its gradation.

EXAMPLE 4

Instead of compound A as in Example 3, it is possible to use compound B or any other quinoxaline indicated in Table I dissolved in a suitable photographically inactive, water-miscible solvent. Proceeding as described in Example 3, with appropriate balancing once again the positive-grey image of the original used, cleanly bleached on white at the corresponding points is obtained.

Example 5

A photographic material as described in Example 3 is as stated exposed into the three spectral areas. Subsequently the copy is developed as follows:

1. develop for 7 minutes in a bath containing per litre 50 g of anhydrous sodium sulphite, 0.2g of 1-phenyl-3-pyrazolidone, 6g of hydroquinone, 35g of anhydrous sodium carbonate, 4g of potassium bromide, 0.3g of benzotriazole and 20ml of a 4.10^{-2} molar solution of compound C in acetone;
2. fix for 2 minutes with a solution of 20g of sodium thiosulphate, 10g of anhydrous sodium sulphite and 10ml of glacial acetic acid per litre;
3. rinse for 2 minutes;
4. colour-bleach for 10 minutes with a solution of 10g of potassium iodide in 1 litre of sulphuric acid;
5. rinse for 2 minutes;
6. bleach the remaining silver for 8 minutes with a bath containing per litre 150ml of 37 percent hydrochloric acid, 25g of copper sulphate and 30g of potassium bromide;
7. rinse for 2 minutes;
8. fix for 3 minutes, as under 2);
9. rinse for 10 minutes.

After drying a neutral wedge is obtained with a clean white and clearly graduated gradation.

Example 6

On a 13 × 18cm glass plate is cast a solution with the following composition: 3.3ml of a 6 percent gelatin, 3.3ml of a silver bromide emulsion containing 5.3g of silver per 100g of emulsion, 1.0ml of a 1 percent solution of the hardener described in Example 1, 0.3ml of a 1 percent solution of the blue-green dye of formula (101) and 2.1ml of water. After drying on the thus obtained layer is copied a step wedge and the plate is then treated as follows:

1. develop for 10 minutes in a bath containing per litre 20g of anhydrous sodium sulphite, 1g of 4-methylaminophenolsulphate, 4g of hydroquinone, 10g of anhydrous sodium carbonate, 2g of potassium bromide and 3g of sodium thiocyanate;
2. rinse for 2 minutes;
3. oxidise for 2 minutes with a solution of 5g of potassium bichromate and 5ml of 96 percent sulphuric acid per litre of solution;
4. rinse for 4 minutes;
5. rinse for 5 minutes with a solution of 50g of anhydrous sodium sulphite per litre;
6. rinse for 3 minutes;
7. develop for 4 minutes with a solution consisting of 2g of Calgon, 50g of anhydrous sodium sulphite, 10g of hydroquinone, 50g of anhydrous sodium carbonate, 2g of 1-phenyl-3-pyrazolidone and 20 ml of a 1 percent t-butyl-aminoborane solution per litre:
8. rinse for 2 minutes;
9. colour bleach for 6 minutes with a colour bleaching bath cOntaining per litre 27ml of 96 percent sulphuric acid, 10g of potassium iodide and 10ml of a 4.10^{-2} molar solution of compound D in ethanol;
10. rinse for 2 minutes;
11. bleach for 2 minutes of the residual silver as described in Example 1 under 6);
12. rinse for 2 minutes;
13. fix for 4 minutes as described in Example under 2);
14. rinse for 10 minutes;

After drying a clear, bleached colourless image of the wedge used with opposite gradation is obtained.

Instead of compound D it is possible to use compound C or another quinoxaline described in the table in a suitable photographically inactive, water-miscible solvent. Proceeding as described in this example, once again a clean bleached colourless image of the exposed wedge with opposite gradation is obtained.

Example 7

A solution consisting of 3.3ml of 6 percent gelatin, 3.3ml of a silver bromide solution containing 5.3g of silver per 100g of emulsion, 1.0ml of a 1 percent solution of the hardener described in Example 1, 0.3ml of a 1 percent solution of the blue-green dye of formula (101) described in Example 1, 0.5ml of a 4.10^{-2} molar solution of compound G in acetone and 1.6ml of water is cast on a 13 × 18cm glass plate. After drying on the thus obtained layer a step wedge is copied (50 lux, 10 sec.) and the copy processed further as described in Example 1. After drying a clean bleached colourless positive image is obtained of the wedge used as the original.

Example 8

A photographic material as described in Example 3 is, as described in Example 3, exposed into the three spectral areas. The copy is then treated as follows:

1. develop 7 minutes in a bath containing per litre 20g of anhydrous sodium sulphite, 10g of anhydrous sodium carbonate. 4g of hydroquinone, 1g of 4-methylaminophenol-sulphate, 2g of potassium bromide and 10ml of a 4.10^{-2} molar solution of compound G in acetone;
2. fix for 2 minutes with a solution of 200g of sodium thiosulphate, 15g of anhydrous sodium sulphite, 25g of crystallised sodium acetate and 13ml of glacial acetic acid per litre;
3. rinse for 2 minutes;
4. colour bleach for 10 minutes with a solution containing 10g of potassium iodide, 27ml of 96 percent sulphuric acid and 5ml of a 4.10^{-2} molar solution of compound G in acetone per litre;
5. rinse for 2 minutes;
6. bleach the remaining silver for 8 minutes, as described in Example 5 under 6);
7. rinse for 2 minutes;
8. fix for 3 minutes as under 2);
9. rinse for 10 minutes.

After drying a clean, white bleached positive image of the original is obtained.

Example 9

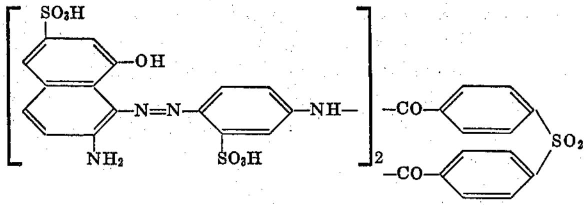
On a 13 × 18cm glass plate is cast a solution of 3.3ml of 6 percent gelatin, 2.0ml of a 1 percent solution of the hardener described in Example 1, 3.3ml of a silver bromide emulsion containing per 100g of emulsion, 5.3g of silver, 0.3ml of a 1 percent solution of the blue-green dye of formula (101) and 1.1ml of water. After drying, a step wedge is copied thereon (501lux, 3 sec.) and the copy is treated as follows:

develop for 6 minutes;
fix for 2 minutes;
rinse for 4 minutes as described in Example 1;
colour bleach for 6 minutes with a solution containing per litre 27ml of 96 percent sulphuric acid, 10g of potassium iodide and 10ml of a 4.10^{-2} molar solution of one of the compounds H or I in dimethyl formamide.

After rinsing for 2 minutes the remaining silver is oxidised as described in Example 1 under 6), rinsed and fixed as described hereinbefore. The copy is thoroughly washed and dried. In all cases, a clean bleached colourless blue-green wedge is obtained, whose gradation is parallel to the original.

Example 10

A solution consisting of 3.3ml of gelatin, 1.0ml of a 1 percent solution of the purple dye of formula



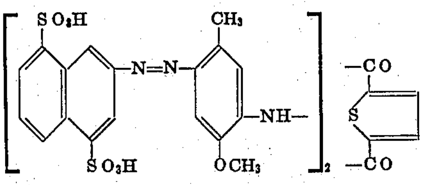
(105)

2.0ml of a 1 percent solution of the hardener described in Example 1, 3.3ml of a silver bromide emulsion containing 5.3g of silver per 100g of emulsion and 0.4ml of water is cast on a 13 × 18cm glass plate. After drying a step wedge is copied thereon (50 lux, 5 sec.) and the copy is treated as follows:

Develop and fix as described in Example 1, colour bleach for 6 minutes with a solution containing per litre 10g of potassium iodide, 27ml of 96 percent sulphuric acid and 10ml of a 4.10^{-2} molar solution of compound A, B, C or H in ethanol or in another suitable water-miscible, photographically inactive solvent. After briefly rinsing, the remaining silver is oxidised as described hereinbefore, rinsed and fixed. After thorough washing-out and drying in all cases a clean bleached colourless image of the original used is obtained with a clearly graduated gradation.

Example 11

A 13 × 18cm glass plate is coated with a solution of 3.3ml of 6 percent gelatin, 2.0ml of a 1 percent solution of the hardener described in Example 1, 3.3ml of a silver bromide emulsion containing 5.3g of silver per 100g of emulsion, 0.5ml of the yellow dye of formula



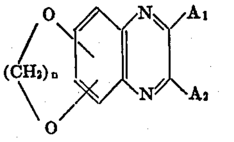
and 0.9ml of water. After drying a step wedge is copied thereon (50 lux, 5 sec.) and treated analogously to Examples 9 and 10, whereby instead of the compounds contained therein the colour bleaching bath contains 10ml of 4.10^{-2} molar solution of one of the substances B, F and J in acetone or another suitable, water-miscible photographically inactive solvent. After drying a clean bleached colourless yellow image of the original used is obtained.

Example 12

On a photographic material as described in Example 10 a step wedge is exposed (500 lux, 10 sec.). The strip is well moistened with a 1N-sulphuric acid containing 10^{-2} mol of compound B per litre and subsequently brought into close contact with a polished iron plate. After briefly rinsing, fixing takes place followed by thorough rinsing. After drying a silver wedge corresponding to the original and a colour wedge opposite to the original are obtained. By proceeding as described hereinbefore and oxidising the silver formed as described in Examples 5 and 6, then rinsing, fixing and rinsing again a purple wedge is obtained having an opposite gradation to the original.

We claim:

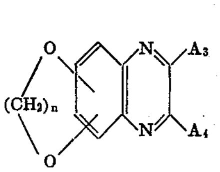
1. Photographic, light-sensitive material for the silver bleaching process which comprises on a support in at least one layer a quinoxaline of formula



(1)

wherein A_1 and A_2 are each an alkyl group with at most 5 carbon atoms, an at most bicyclic aralkyl group with 1 to 5 carbon atoms in the alkyl portion, an at most bicyclic aryl group or a 5 or 6-membered heterocyclic group having as hetero atoms N, O or S, and *n* is 1 or 2, whereby the oxygen- containing ring is connected with the quinoxaline group in the 5,6 or 6,7-position, as a colour bleaching catalyst.

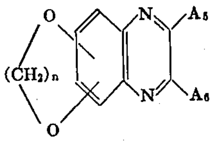
2. Photographic material according to claim **1**, which comprises a quinoxaline of formula



(2)

wherein A_3 and A_4 are each an alkyl group with at most 5 carbon atoms, benzene, lower alkyl-benzene, lower alkoxy-benzene, hydroxybenzene, aminobenzene or halobenzene, and *n* is 1 or 2 as a colour bleaching catalyst.

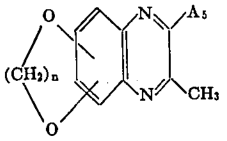
3. Photographic material according to claim **2**, which comprises a quinoxaline of formula



(3)

wherein A_5 and A_6 are each a methyl or phenyl group and *n* is 1 or 2 as a colour bleaching catalyst.

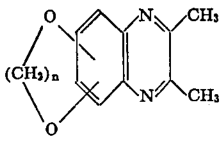
4. Photographic material according to claim **3**, which comprises a quinoxaline of formula



(4)

wherein A_5 is a methyl or phenyl group and *n* is 1 or 2 as a colour bleaching catalyst.

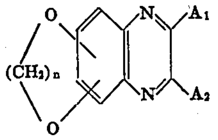
5. Photographic material according to claim **4**, which comprises a quinoxaline of formula



(5)

wherein *n* has the meaning given in claim **4**, as a colour bleaching catalyst.

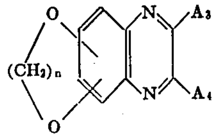
6. A process for producing a colour photographic image by the silver dye-bleach process using a material which carries on a substrate, at least one silver halide emulsion layer with a bleachable image dye, by exposing the material, developing the silver image and colour bleaching the image dye in accordance therewith, characterised in that the colour bleaching is performed in the presence of at least one quinoxaline of formula



(1)

wherein A_1 and A_2 are each an alkyl group with maximum 5 carbon atoms, an at most bicyclic aralkyl group with 1 to 5 carbon atoms in the alkyl portion, an at most bicyclic aryl group or a 5 or 6-membered heterocyclic group having as hetero atoms N, O or S, and *n* is 1 or 2, whereby the oxygen-containing ring is connected with the quinoxaline ring in the 5,6 or 6,7-position as the colour bleaching catalyst.

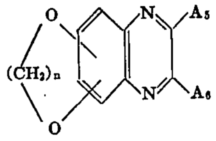
7. Process according to claim **6**, characterised in that as the colour bleaching catalyst a quinoxaline of formula



(2)

is used, wherein A_3 and A_4 are each an alkyl group with maximum 5 carbon atoms, benzene, lower alkylbenzene, lower alkoxy-benzene, hydroxybenzene, aminobenzene or halobenzene, and *n* is 1 or 2.

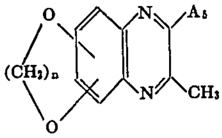
8. Process according to claim **7**, characterised in that as the colour bleaching catalyst a quinoxaline of formula



(3)

is used, wherein A_5 and A_6 are each a methyl or phenyl group and *n* is 1 or 2.

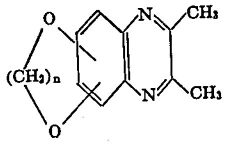
9. Process according to claim **8**, characterised in that as the colour bleaching catalyst a quinoxaline of formula



(4)

is used, wherein A_5 is a methyl or phenyl group and n is 1 or 2.

10. Process according to claim **9**, characterised in that as the colour bleaching catalyst a quinoxaline of formula



(5)

is used, wherein *n* is 1 or 2.

11. Process according to claim **6**, characterised in that the quinoxaline is in the colour bleaching bath.

* * * * *