United States Patent

[11] **3,615,525**

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[33] **Great Britain**
[31] **24,191**

[54] DERIVATIVE OF 6-AMINO-1,2,3,4-TETRAHYDROQUINOLINE AS SUPERADDITIVE IN DEVELOPING COMPOSITION

6 Claims, No Drawings

[52] **U.S. Cl.** **96/66.3,** 96/29, 96/66
[51] **Int. Cl.** **G03c 5/30**
[50] **Field of Search** 96/66, 66.3, 29

[56] **References Cited**

UNITED STATES PATENTS

727,358	8/1966	Willems et al.	96/66

OTHER REFERENCES

Willems, et al. (II): Photographic Science and Engineering, Vol. 10, pages 306–313 (1966)

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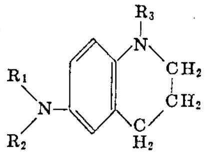
ABSTRACT: Photographic developing compositions comprising hydroquinone and a quinoline derivative having the formula



wherein R_1 is an alkyl group comprising from one to five carbons atoms, R_2 is an alkyl group comprising from one to five carbon atoms, and R_3 is hydrogen, or an alkyl group comprising from one to five carbon atoms, at most one of R_1, R_2 and R_3 being substituted alkyl are described. These compositions provide super-additive development in photographic processes.

DERIVATIVE OF 6-AMINO-1,2,3,4-TETRAHYDROQUINOLINE AS SUPERADDITIVE IN DEVELOPING COMPOSITION

The invention relates to a process for the development of photographic materials, containing exposed silver halide, and to developing compositions used therein.

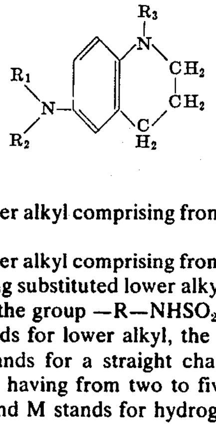
It is known that the developing activity of a developing solution contains a mixture of several developing substances can be higher than the sum of the developing activities of the separate developing solutions of each of these developing substances used in the same concentration as in the solution of that mixture. This phenomenon is called the superadditive development.

The most common example of superadditive development is that of the combination of p-monomethylaminophenol hemisulfate and hydroquinone, which has been described by G. Pizzighelli, *Lietfaden der praktischen Photographie, Auflage* 14 (Paul Nanneke) p. 177.

It is further known from British Pat. specification No. 542,502 that the combination of hydroquinone and 1-phenyl-3-pyrazolinone has a more intense developing action than the combination of hydroquinone and p-monomethylaminophenol hemisulfate.

In our British Pat. specification No. 989,383 it has been described that developing baths with a mixture of hydroquinone and particular p-phenylene diamine derivatives selected from N,N'-tetraalkyl-p-phenylene diamines of which one of the alkyl groups may be substituted by water-solubilizing groups such as hydroxyl and sulfo, 6-amino-1,2,3,4-tetrahydroquinoline and 6-amino-1-alkyl-tetrahydroquinolines have a higher developing activity than the combination of hydroquinone and p-monomethylaminophenol hemisulfate and show the advantage over the combination of hydroquinone and 1-phenyl-3-pyrazolidinone of being stable to hydrolysis even in strong alkaline medium.

It has now been found that an exceptional superadditive developing activity is obtained when using, in the development of exposed silver halide emulsion layers, a combination of developing agents consisting of hydroquinone and a compound corresponding to the general formula:



wherein

- R_1 stands for lower alkyl comprising from one to five carbon atoms,
- R_2 stands for lower alkyl comprising from one to five carbon atoms including substituted lower alkyl e.g. hydroxyalkyl, carboxyalkyl, the group $—R—NHSO_2R_4$ wherein each of R and R_4 stands for lower alkyl, the group $—X—SO_3M$ wherein X stands for a straight chain or branched alkylene radical having from two to five carbon atoms in straight line and M stands for hydrogen, an alkali metal atom such as sodium or potassium, ammonium or an amine and
- R_3 stands for hydrogen, lower alkyl comprising from one to five carbon atoms including substituted lower alkyl e.g. alkyl substituted as exemplified for R_2.

at most one of R_2 and R_3 being substituted alkyl.

The combinations of developing agents according to the invention show as compared with the developing combinations described in our British Pat. specification No. 989,383 a markedly higher development activity. In most cases they even have a higher activity than the developing combination of hydroquinone and 1-phenyl-3-pyrazolidinone. Moreover, the developing compositions of the invention have the further advantage of being stable to hydrolysis, even in strong alkaline medium whereas compositions with 1-phenyl-3-pyrazolidinone hydrolyse in strong alkaline baths. Thus with the developing combinations of the invention very stable developing solutions are obtained which is particularly interesting for preparing liquid developers.

The compounds corresponding to the above general formula can be added to the developing bath in the form of free bases as well as in the form of their salts e.g. as hydrochloride, as sulfate, etc.

The following are examples of compounds corresponding to the above general formula:

1. 6-diethylamino-1,2,3,4-tetrahydroquinoline dihydrochloride;
2. 1-ethyl-6-diethylamino-1,2,3,4-tetrahydroquinoline dihydrochloride;
3. 1-(4-sulfobutyl)-6-diethylamino-1,2,3,4-tetrahydroquinoline
4. 1-(2-hydroxyethyl)-6-dimethylamino-1,2,3,4-tetrahydroquinoline dihydrochloride;
5. 1-ethyl-6-(N-ethyl-nN-3-sulfopropyl-amino)-1,2,3,4,-tetrahydroquinoline;
6. 1-(3-sulfopropyl)-6-(N-ethyl-N-methylamino)-1,2,3,4-tetrahydroquinoline,
7. 1-(2-methylsulfonylamino-ethyl)-6-diethylamino-1,2,3,4-tetrahydroquinoline dihydrochloride;
8. 1-(3-carboxypropyl)-6-dimethylamini-1,2,3,4-tetrahydroquinalone.

The 6-amino-tetrahydroquinoline derivatives of use according to the present invention can be prepared by alkylation of 6-amino-tetrahydroquinolines or by alkylation of 6-dialkylamino-tetrahydroquinolines. The 6-dialkylamino-tetrahydroquinolines are prepared by hydrogenation of the 6-dialkylaminoquinolines, which in their turn can be prepared as described in *Bull. Soc. Chim. Fr.* 27 (1920) 430.

The following preparations illustrate more particularly how the 6-amino-tetrahydroquinoline derivatives of use according to the invention can be prepared.

Preparation 1: Compound 1

A solution of 80 g. (0.4 mole) of 6-diethylamino-quinoline in 400 ml. of anhydrous ethanol is hydrogenated, using 8 ml. of Raney nickel as catalyst, in a sealed tube at 70° C. and a hydrogen pressure of 1,500 p.s.i. The uptake of hydrogen is complete after 90 min. The catalyst is filtered off and the filtrate is treated with 200 ml. of concentrated hydrochloric acid. After evaporation of the alcohol the residue is recrystallized from a mixture of ethanol and ethyl acetate. Melting point: 160° C.

Preparation 2: Compound 2

40.4 g. (0.2 mole) of 6-diethylamino-1,2,3,4-tetrahydroquinoline and 18.2 g. (0.1 mole) of triethylphosphate are heated for 3 hours in an oil bath at 200° C. After having been cooled to 50° C. a solution of 15 g. of sodium hydroxide in 50 ml. of water is added and heating is continued for 90 min. The reaction mixture is treated with water and extracted with ether. After evaporation of the ether the residue is distilled. The 1-ethyl-6-diethylamino-1,2,3,4-tetrahydroquinoline has a boiling point of 184°-187° C./14 mm. It is converted into its dihydrochloride by treating the base, dissolved in ethanol, with alcoholic hydrochloric acid. Melting point: 172° C. (after recrystallization from a mixture of ethanol and ethyl acetate).

Preparation 3 : Compound 3

80.8 g. (0.4 mole) of 6-diethylamino-1,2,3,4-tetrahydroquinoline and 54.4 g. (0.4 mole) of butane sultone are heated for 3½ hours, in an oil bath at 170° C. The reaction mixture is dissolved in 750 ml. of water and treated with 16 g. (0.4 mole) of sodium hydroxide dissolved in 75 ml. of water. The aqueous layer is extracted three times with ether. Then the aqueous layer is treated with 160 ml. of 2.5N hydrochloric acid and evaporated. The residue is boiled with 500 ml. of anhydrous ethanol. The undissolved sodium chloride is filtered off and the ethanol filtrate is evaporated. The product is dried in vacuum over phosphorus penta-oxide.

In addition to the 6-amino-tetrahydroquinoline derivatives corresponding to the above general formulas and hydroquinone, a developing bath according to this invention may also contain ingredients such as buffer compositions which may comprise salts such as carbonates, borates, phosphates, bisulfites, metabisulfites, sulfites, and acids such as boric acid and citric acid. The developing bath may further contain potassium bromide, water-softening agents such as polyphosphates or derivatives of ethylene diamine tetraacetic acid, antifogging agents and moistening agents, as well as other compounds known in the developing technique.

The pH of the baths can vary within wide limits, preferably between eight and 11, so that a rapid or slow development can be obtained at will resulting in high-contrast and low-contrast images respectively.

The ratio of hydroquinone to a 6-amino-tetrahydroquinoline derivative used in the present invention, can be chosen in such a way that the bath composition is suited for the development of all kinds of materials including materials having silver chloride emulsion layers of low sensitivity as well as materials having sensitive silver bromoiodide emulsion layers.

The ratio of hydroquinone to the 6-amino-tetrahydroquinoline derivatives used in the present invention can vary within wide limits. The amounts are, however, generally chosen in such a way that the hydroquinone strongly outweighs the said derivatives. A strong superadditive effect is already obtained with a ratio of 50 mg. of a said derivative used in this invention to 5 g. of hydroquinone per liter. Generally the amount of hydroquinone is comprised between 1 and 30 g. per litre and the amount of 6-amino-tethydroquinoline derivative between 5 mg. and 2 g. per liter.

Combinations of developing agents used in this invention may also be applied in the treating solution and/or in the light-sensitive material and/or in the image-receiving material used in the application of the silver complex diffusion transfer process, the principle of which is described in British Pat. specification Nos. 614,155 and 654,630 and in German Pat. specification No. 887,733. For more details concerning the silver complex diffusion transfer process, the different embodiments of the materials and apparatus used therein, there can be referred to "Progress in Photography" 1955–1958, p. 24–36 and the patent literature cited therein.

The following examples illustrate the present invention.

Example 1

Strips of a photographic material comprising a light-sensitive silver bromoiodide emulsion layer, coated on material comprising triacetate support, are exposed through a grey filter with light-quantity (E) which corresponds to the shoulder part of the density/log E curve.

One of these film strips is developed in a bath A having the following composition:

sodium carbonate	20.0 g.
sodium hexametaphosphate	1.0 g.
sodium sulfite	20.0 g.
potassium bromide	0.5 g.
hydroquinone	4.4 g.
water up to	1,000 ml.

The other strips are developed in baths having the same composition as bath A but moreover containing an equivalent amount of a developing agent as listed in table 1 given hereinafter.

The results of these developing tests are listed in table 1. The densities are determined after a development time of 30, 6060 and 90 sec.

Table 1

Developing bath	Density after a developing time of		
	30 sec.	60 sec.	90 sec.
bath A	0.04	0.04	0.10
bath A+85 mg. of compound 1	0.80	>2	
bath A+95 mg. of compound 2	0.90	>2	
bath A+105 mg. of compound 3	0.10	0.90	1.90
bath A+70 mg. of 1-methyl-6-amino-1,2,3,4-tetrahydroquinoline oxalate	0.10	0.40	1.10
bath A+107 mg. of N,N-diethyl-N'-propyl-N'-3-sulphopropyl-p-phenylene diamine	0.13	0.20	0.40

From these results it clearly appears that the developing combination of the invention has a higher activity than the developing combinations of our British Pat. specification No. 989,383.

Example 2

Strips of a photographic material comprising a light-sensitive silver bromoiodide emulsion layer coated on a cellulose triacetate support, are exposed through a grey filter with a light-quantity (E) which corresponds to the shoulder part of the density/log E curve.

Each of these exposed strips is developed at 20° C. in separate developing baths. One of them is developed in a bath B containing as developing agent only hydroquinone and having the following composition:

boric acid	5.0 g.
borax	10.0 g.
sodium hexametaphosphate	1.0 g.
sodium sulfite	20.0 g.
potassium bromide	0.5 g.
hydroquinone	4.4 g.
water up to	1,000 ml.

The other strips are developed in developing baths having the same composition as bath B, but containing moreover an equivalent amount of a developing agent as listed in table 2 given hereinafter.

The densities are determined after 1, 3 and 5 respectively

Table 2

Developing bath	Density after a developing time of		
	1 min.	3 min.	5 min.
bath B	0.04	0.04	0.04
bath B+85 mg. of compound 1	0.20	1.20	1.60
bath B+95 mg. of compound 2	0.80	1.45	1.70
bath B+105 mg. of compound 3	0.05	0.84	1.25
bath B+70 mg. of 1-methyl-6-amino-1,2,3,4-tetrahydroquinoline oxalate	0.05	0.46	1.00
bath B+107 mg. of N,N-diethyl-N'-propyl-N'-3-sulphopropyl-p-phenylene diamine	0.05	0.17	0.58
bath B+50 mg. of 1-phenyl-3-pyrazolidinone	0.05	0.46	1.10

From these results it appears that the developing activity of the combination of developing agents according to the invention is not only higher than that of the developing combinations of our British Pat. specification No. 989,383 but even higher than that of the combination of 1-phenyl-3-pyrazolidinone and hydroquinone.

Example 3

Strips of a photographic material comprising a silver bromoiodide emulsion layer were exposed through a step wedge and developed for 2 minutes in a developing bath C having the following composition:

sodium carbonate	20.0 g.
sodium sulfite	20.0 g.
potassium bromide	1.0 g.
hydroquinone	4.5 g.
water up to	1,000 ml.

Other strips were developed in baths having the same composition as bath C but moreover containing an equivalent amount of a developing agent as listed in table 3, hereinafter. These baths were used either directly after their preparation or after having been stored for some time in closed containers at 80° C. The results of the developing tests before and after storage are listed in table 3.

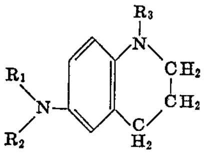
Table 3

Developing bath	Storage time	Relative sensitivity	Gradation
Bath C+0.63 g. of compound 3	0	110	1.67
	20 hours	110	1.63
	130 hours	110	1.43
Bath C+0.3 g. of 1-phenyl-3-pyrazolidinone	0	100	1.59
	20 hours	62	1.18
	40 hours	5.9	0.70

From these results it appears, that compound 3 is much more stable against hydrolysis than 1-phenyl-3-pyrazolidinone and for this reason is interesting for preparing liquid developers.

What we claim is:

1. Photographic developing composition comprising hydroquinone and a derivative of 6-amino-1,2,3,4-tetrahydroquinoline corresponding to the following general formula, in the form of the free base or in its salt form



wherein

R_1 is an alkyl group comprising from one to five carbon atoms,

R_2 is an alkyl group comprising from one to five carbon atoms, and

R_3 is hydrogen, or an alkyl group comprising from one to five carbon atoms,

at most one of R_1, R_2 and R_3 being substituted alkyl.

2. Photographic developing composition according to claim 1, wherein one of R_1, R_2 and R_3 is a hydroxyalkyl group, a carboxyalkyl group, or the group $-R-NHSO_2R_4$ wherein each of R and R_4 is a lower alkyl group, the group $-X-SO_3M$ wherein X is a straight or branched alkylene group having from two to five carbon atoms in straight line, and M is hydrogen, an alkali metal, ammonium or an amine.

3. Photographic developing composition according to claim 1, wherein each of R_1 and R_2 is a lower alkyl group having from one to five carbon atoms, and R_3 is hydrogen, a lower alkyl group having from one to five carbon atoms or the group $-X-SO_3M$ wherein X is a straight or branched alkylene group having from two to five carbon atoms in straight line, and M is hydrogen, an alkali metal, ammonium or an amine.

4. Photographic-developing composition according to any of claim 1, wherein the said hydroquinone is present in an amount of from 1 to 30 g. per litre and the said 6-amino-1,2,3,4-tetrahydroquinoline derivative in an amount of from 5 mg. to 2 g. per litre.

5. Photographic-developing method comprising developing and exposed silver halide emulsion layer of a photographic material an means of hydroquinone and a 6-amino1,2,3,4tetrahydroquinoline derivative as defined in claim 1.

6. Photographic-developing method according to claim 5, for application in the silver complex diffusion transfer process wherein the exposed light-sensitive material is developed with an aqueous alkaline solution in the presence of hydroquinone and a 6-amino-1,2,3,4-tetrahydroquinoline derivative as defined in claim 1.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,615,525 Dated October 26, 1971

Inventor(s) JOZEF FRANS WILLEMS ET AL

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Title page under References Cited, United States Patents, "727,358" should read -- 3,265,502 --. Column 1, line 9, "contains" should read -- containing --. Column 2, line 17 (No. 5), "-(N-ethyl-nN-3-sulfopropylamino)-" should read -- -(N-ethyl-N-3-sulphopropyl-amino)- --; Column 2, lines 24 - 25 (No. 8), "-6-dimethylamini-1,2,3,4-tetrahydroquinalone" should read -- -6-dimethylamino-1,2,3,4-tetrahydroquinoline --. Column 3, line 16, after "having" insert -- highly --; Column 3, lines 43 - 44, "material comprising" should read -- a cellulose --; Column 3, line 45, after "with" insert -- a --; Column 3, line 61, "6060" should read -- 60 --. Column 4, line 28, after "5" insert -- min. --. Column 6, lines 20 - 21, claim 4, after "according to" delete -- any of --; Column 6, line 26, claim 5, "and" should read -- an --; Column 6, line 27, claim 5, "an" should read -- by --; Column 6, line 28, "amino 1,2,3,4tetrahydroquinoline" should read -- amino-1,2,3,4-tetrahydroquinoline --.

Signed and sealed this 18th day of December 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

RENE D. TEGTMEYER
Acting Commissioner of Patents