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SILVER HALIDE PHOTOGRAPHIC EMULSIONS

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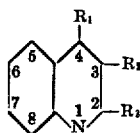
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1943

14 Claims. (Cl. 95—6)

This invention relates to silver halide photo-
graphic emulsions and particularly to gelatino
silver chloride photographic emulsions such as
are used in development papers for contact print-
ing, i. e. the so-called "gaslight" printing papers.

It is well known that the colour of developed
images obtained from gelatino silver chloride de-
velopment emulsions can be controlled to some
extent by the addition of certain substances to
the emulsion or to the developer. In the absence
of any special additions the developed images may
vary from a greenish to a fairly neutral black.
It is generally preferred that the developed
images should be on the bluer side of neutral
black rather than on the greener side, and various
suggestions have hitherto been made for obtain-
ing the desired blue-black images. Thus it is
known to include in the emulsion a small quan-
tity of a quinine salt, which has the effect of
yielding developed images of a good blue-black
colour. Various other substances have been sug-
gested as emulsion additions for the same pur-
pose, but none of those hitherto proposed is so
satisfactory as the quinine salts. Many com-
pounds have likewise been suggested as developer
additions, but from both manufacturers' and
users' standpoints, it is better to include the blue-
black toning substance in the emulsion since the
products can then be developed with standard
developers.

According to the present invention silver chlo-
ride emulsions which yield images of excellent
blue-black colour on development are obtained by
including in the emulsion, during its manufac-
ture, a quinoline compound of the general formu-
la:



where R_1 is an alkyl or aralkyl group, R_2 is a hy-
drogen atom or an alkyl or aralkyl group, or R_1
and R_2 together form the residue of an alicyclic
nucleus, and R_3 is a hydrogen atom or a lower
alkyl group. These compounds may be further
substituted in the carbocyclic ring and may be
applied in the form of their mineral acid salts.

Thus the compounds employed are essentially
4-alkyl quinolines or 4-aralkyl quinolines which
may or may not contain other substituent groups.
It is found that any substituents may be present
in the carbocyclic ring, e. g. halogen atoms, hy-
drocarbon groups or alkoxy, aryloxy or aralkyl-
oxy groups, or benz groups fused to the carbo-
cyclic ring, though lower alkyl substituents and
lower alkoxy substituents are preferred. Com-
pounds containing benz groups fused to the carbo-
cyclic ring, e. g. in the 5:6- or 7:8-positions,

though operative, are generally less satisfactory
than those without such groups.

The group R_1 may be any alkyl or aralkyl group,
e. g. methyl, ethyl or higher alkyl, or benzyl. The
group R_2 may be a hydrogen atom or any alkyl
or aralkyl group as specified above. The group R_3
may be a lower alkyl group, but it is strongly pre-
ferred that it be a hydrogen atom, i. e. that the
2-position in the nitrogen ring should be unsub-
stituted. It is found that in general compounds
of the above general formula in which R_3 is a
lower alkyl group are less effective for the pur-
poses of this invention than the corresponding
compounds in which the 2-position is unsubsti-
tuted; for example, 2:4-dimethyl quinoline,
though effective, is considerably less effective
than 4-methyl quinoline.

Specific compounds which are of particular
value are 4-methyl quinoline containing no other
substituent group, and 4-methyl quinolines con-
taining the following additional substituent
groups: 3-methyl, 3-ethyl, 6-methyl, 7-methyl, 6-
methoxy, 6-ethoxy, 8-ethoxy, and combinations
of such groups. Other compounds of particular
value are the corresponding compounds where the
4-methyl group is replaced by a 4-ethyl, 4-higher
alkyl or 4-benzyl group. Particularly valuable
compounds of the type where R_1 and R_2 in the
formula form an alicyclic ring are 3:4-tetra-
methylene quinoline and corresponding com-
pounds containing alkyl or alkoxy groups in the
carbocyclic ring of the quinoline nucleus.

As indicated above, the compounds can be used
either as the free bases or as mineral acid salts.
Thus, for example, the compounds may be used
as the hydrochlorides or bisulphates.

The proportion of compound added to the
emulsion will depend on the particular compound
used and on the precise nature of the emulsion.

In general a good blue-black tone can be obtained
using the compounds of this invention in propor-
tions of the order of 25 ccs. of a 1% solution of
the compound per pound of emulsion, though
lower proportions or higher proportions can be
used, e. g. of the order of 5 to 50 ccs. of a 1% so-
lution per pound of emulsion.

Many substances when added to photographic
emulsions have undesirable effects on the qualities
of an emulsion, i. e. loss of speed, increased tend-
ency to the formation of fog (i. e. developed silver
not arising from the exposure) and on the con-
trast of the developed images. It is a particular
merit of the compounds used as blue-black toners
according to the present invention that they do
not have any serious adverse effect in respect of
any of these properties.

The following examples illustrate the invention:

Examples

A gelatino silver chloride emulsion of the "gas-

light" type was prepared and to portions of it were added proportions of different compounds according to this invention. A control sample containing quinine bisulphate as the blue-black toning agent was also prepared. The quinine bisulphate and other compounds were each added in the proportion of 25 ccs. of a 1% solution per pound of smulsion. The samples were coated on paper base, exposed, developed in a standard metol-hydroquinone developer, and the photographic properties of the images obtained were studied. The image colours compared with the quinine control were as follows:

Example No.	Compound	Image colour
Quinine control.	Quinine bisulphate.....	Standard blue.
1.....	4-methyl quinoline.....	Shade less blue than standard.
2.....	6-ethoxy-4-methyl quinoline hydrochloride.	Similar to standard.
3.....	6-methoxy-4-methyl quinoline hydrochloride.	Bluer than standard.
4.....	4:6-dimethyl quinoline hydrochloride.	Slightly bluer than standard.
5.....	8-ethoxy-4-methyl quinoline hydrochloride.	Shade bluer than standard.
6.....	3:4-dimethyl-quinoline hydrochloride.	Distinctly bluer than standard.
7.....	6-ethoxy-3:4-dimethyl quinoline bisulphate.	Trace less blue than standard.
8.....	4:7-dimethyl quinoline hydrochloride.	Slightly bluer than standard.
9.....	3:4-dimethyl quinoline bisulphate.	Distinctly bluer than standard.
10.....	3-ethyl-4-methyl quinoline hydrochloride.	Similar to standard but slaty blue.
11.....	3:4-tetramethylene quinoline bisulphate.	Do.

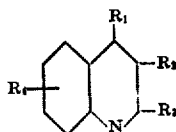
The solutions of the compounds of the examples were made in ethyl alcohol or water according to convenience. It will be noted that all of the compounds effect a very substantial blueing of the image colour, always comparable with that obtained by the use of quinine, and in some cases even greater than that obtained by the use of quinine. Moreover, the speed loss resultant on the use of the compounds was in no case very serious, and in most cases was not very much different from the speed loss resultant on the use of quinine.

The compounds did not lead to any substantial increase in the fog level of the emulsion, and did not affect the contrast characteristics of the emulsion to any marked extent. All the compounds therefore are very valuable substitutes for quinine.

It is to be understood that in the foregoing description and in the following claims the expression "silver chloride photographic emulsion" means a photographic emulsion in which the predominant silver salt is silver chloride and includes the possibility of a small proportion of other silver halide being present.

What we claim is:

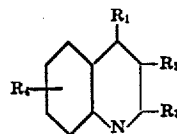
1. Silver-chloride photographic emulsions containing a compound selected from the class consisting of compounds of the general formula:



where R_1 is selected from the class consisting of alkyl, aralkyl and, with R_2 and the two carbon atoms of the heterocyclic ring attached thereto, an alicyclic nucleus; R_2 is selected from the group consisting of hydrogen, alkyl, aralkyl, and, with R_1 and the two carbon atoms of the heterocyclic

ring attached thereto, an alicyclic nucleus; R_3 is selected from the group consisting of the hydrogen atom and lower alkyl groups; R_4 is a member of the group consisting of the hydrogen atom, halogen atoms, hydrocarbon, alkoxy, aralkoxy, aralkyloxy and a hydrocarbon radical which forms a benzene ring with two adjacent carbon atoms of the carbocyclic ring; and the mineral acid salts of any such compounds.

2. A photographic element comprising a support bearing a gelatino silver chloride emulsion layer containing a compound selected from the class consisting of compounds of the general formula



where R_1 is selected from the class consisting of alkyl, aralkyl, and, with R_2 and the two carbon atoms of the heterocyclic ring attached thereto, an alicyclic nucleus; R_2 is selected from the group consisting of hydrogen, alkyl, aralkyl and, with R_1 and the two carbon atoms of the heterocyclic ring attached thereto, an alicyclic nucleus; R_3 is selected from the group consisting of the hydrogen atom and lower alkyl groups; R_4 is a member of the group consisting of the hydrogen atom, halogen atoms, hydrocarbon, alkoxy, aryloxy, aralkyloxy and a hydrocarbon radical which forms a benzene ring with two adjacent carbon atoms of the carbocyclic ring; and the mineral acid salts of any of such compounds in an amount of the order of 5-50 ccs. of a 1% ethyl alcohol solution per pound of emulsion.

3. Gelatino silver chloride photographic emulsions containing a 4-alkyl quinoline which is unsubstituted in the 2-position and in which the group attached to the carbon atom in the 3-position is selected from the class consisting of the hydrogen atom and alkyl and aralkyl groups.

4. Gelatino silver chloride photographic emulsions containing a 4-methyl quinoline which is unsubstituted in the 2-position and in which the group attached to the carbon atom in the 3-position is selected from the class consisting of the hydrogen atom and alkyl and aralkyl groups.

5. Gelatino silver chloride photographic emulsions containing a 4-alkyl quinoline which is unsubstituted in the 2-position and which contains an alkoxy substituent in the carbocyclic ring and in which the group attached to the carbon atom in the 3-position is selected from the class consisting of the hydrogen atom and alkyl and aralkyl groups.

6. Gelatino silver chloride photographic emulsions containing a 4-methyl quinoline which is unsubstituted in the 2-position and contains a lower alkoxy substituent in one of the 6 and 8 positions and in which the group attached to the carbon atom in the 3-position is selected from the class consisting of the hydrogen atom and alkyl and aralkyl groups.

7. Gelatino silver chloride photographic emulsions containing a 4-alkyl quinoline which is unsubstituted in the 2-position and contains a lower alkyl substituent in the 3-position.

8. Gelatino silver chloride photographic emulsions containing a 4-methyl quinoline which is unsubstituted in the 2-position and contains a lower alkoxy substituent in one of the 6 and 8 positions and a lower alkyl substituent in the 3-position.

9. Gelatino silver chloride photographic emulsions containing a mineral acid salt of a 4-alkyl quinoline which is unsubstituted in the 2-position and in which the group attached to the carbon atom in the 3-position is selected from the class consisting of the hydrogen atom and alkyl and aralkyl groups.

10. Gelatino silver chloride photographic emulsions containing a mineral acid salt of a 4-alkyl quinoline which is unsubstituted in the 2-position and contains a lower alkoxy substituent in one of the 6 and 8 positions and in which the group attached to the carbon atom in the 3-position is selected from the class consisting of the hydrogen atom and alkyl and aralkyl groups.

11. Gelatino silver chloride photographic emulsions containing a mineral acid salt of a 4-alkyl quinoline which is unsubstituted in the 2-position and contains a lower alkyl substituent in the 3-position.

12. A photographic element comprising a support bearing at least one gelatino silver chloride emulsion layer which layer contains a 4-methyl quinoline which is unsubstituted in the 2-position and in which the group attached to the carbon atom in the 3-position is selected from the class consisting of the hydrogen atom and alkyl and aralkyl groups.

13. A photographic element comprising a support bearing at least one gelatino-silver chloride emulsion layer which layer contains a small amount of 6-methoxy-4-methyl-quinoline hydrochloride.

14. A photographic element comprising a support bearing at least one gelatino-silver chloride emulsion layer which layer contains a small amount of 3,4-dimethyl quinoline hydrochloride.

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Certificate of Correction

Patent No. 2,397,015.

March 19, 1946.

JOHN DAVID KENDALL ET AL.

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Page 2, first column, line 8, for "smulsion" read *emulsion*; and second column, line 13, for "consisitng" read *consisting*; line 55, for "corbon" read *carbon*; page 3, second column, line 8, claim 12, after "groups" and before the period insert *in an amount of the order of 5-50 ccs. of a 1% ethyl alcohol solution per pound of emulsion*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 28th day of May, A. D. 1946.

[SEAL]

LESLIE FRAZER,
First Assistant Commissioner of Patents.

9. Gelatino silver chloride photographic emulsions containing a mineral acid salt of a 4-alkyl quinoline which is unsubstituted in the 2-position and in which the group attached to the carbon atom in the 3-position is selected from the class consisting of the hydrogen atom and alkyl and aralkyl groups.

10. Gelatino silver chloride photographic emulsions containing a mineral acid salt of a 4-alkyl quinoline which is unsubstituted in the 2-position and contains a lower alkoxy substituent in one of the 6 and 8 positions and in which the group attached to the carbon atom in the 3-position is selected from the class consisting of the hydrogen atom and alkyl and aralkyl groups.

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