

L106.061



PATENT SPECIFICATION

NO DRAWINGS

L106.061

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Int. Cl.:—G 03 c 5/26



COMPLETE SPECIFICATION

Photographic Development

5 We, EASTMAN KODAK COMPANY, a Com-
pany organized under the Laws of the State
of New Jersey, United States of America,
of 343 State Street, Rochester, New York
14650, United States of America (Assignees
of JAMES LEO GRAHAM) do hereby declare
the invention, for which we pray that a
patent may be granted to us, and the method
by which it is to be performed, to be particu-
larly described in and by the following state-
ment:—

10 This invention relates to photographic
development, and more particularly to a
method of processing multilayer colour films
or papers at elevated temperatures.

15 In multilayer photographic elements used
for colour photography, there are usually
three selectively colour sensitive emulsion
layers coated on one side of a single support.
20 For example, the uppermost layer is gener-
ally blue sensitive, the next layer is generally
green sensitive, while the emulsion layer ad-
jacent the support is generally red sensitive.
25 Between the blue sensitive and green sensitive
layers is usually a filter layer for absorbing
any blue radiation which might be trans-
mitted through the blue sensitive layer and
would otherwise fall in the inherent silver
30 halide sensitivity region of the green and red
sensitive layers. In some such multilayer
photographic elements, dye forming couplers
which react with the oxidation products of
the silver halide developer to form dyes are
included in the sensitive layers. The multi-
35 layer coatings can also include interlayers for
specialized purposes. Such multilayer materi-
als are well known.

40 The processing of multilayer photographic
elements used for colour photography is
generally a relatively time-consuming process
compared with that for monochrome materi-
als so that it has been desirable to find a
more rapid method of processing such film,
particularly those containing incorporated dye
45 forming couplers. Accordingly, since it is

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well known that increasing the temperature
of a photographic developing solution will in-
crease the rate at which it develops a silver
halide emulsion, it has been proposed to pro-
cess multilayer photographic emulsions in a
high temperature colour process to provide
more rapid processing.

Normally a necessary step in processing an
emulsion at a higher temperature is to shorten
the time of development to an appropriate
level to avoid over development. However,
shortening the time of development of a
colour material will not, by itself, give bal-
anced development in the separate sensitive
layers of such a material. If the development
time is adjusted for optimum colour develop-
ment of the top, blue sensitive layer, then the
lower green and red sensitive layers will be
underdeveloped. If the time is adjusted so
that the lower layers are correctly developed,
then the top layer will be greatly over-
developed. Moreover, adjustments in the light
sensitivities of the emulsions in the sensitive
layers will not balance the amounts of
development received in each layer in a multi-
layer system. It is essential therefore, that
the rate of development of each emulsion
layer must be controlled so that all layers
will arrive at optimum development at the
same time for the chosen processing tem-
perature.

According to the present invention the
overdevelopment of the top emulsion layer
can be controlled during high temperature
processing by the presence of a benzothia-
zolum salt.

According to the present invention there
is provided a process for developing a multi-
layer gelatino-silver halide photographic
material comprising treating the layer with a
solution containing a photographic developing
agent when the outermost emulsion layer
contains between 1 to 10 grams of a benzo-
thiazolum salt per mole of silver halide in
said emulsion layer and the benzothiazolum

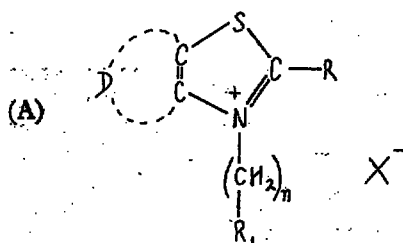
it
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salt has the formula (A) hereinafter illustrated.

These compounds may be incorporated in the emulsion, by incorporating the salt in a layer over the top light sensitive layer, or they may be added in a bath, such as a pre-hardener bath, prior to development.

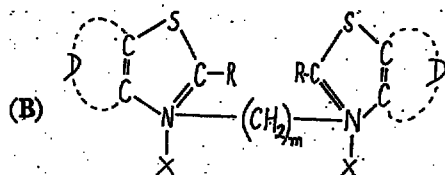
There is also provided a photographic processing bath comprising an aqueous solution free from silver halide developing agents and containing between 1 and 200 mg. per litre of the benzothiazolium salt of the formula (A).

The benzothiazolium salts are represented by the following general formula:



in which R represents a hydrogen atom or an alkyl group containing from 1—2 carbon atoms, R₁ represents a hydrogen atom, an aryl group such as phenyl, *o*-, *m*-, or *p*-tolyl or *o*-, *m*-, or *p*-methoxyphenyl, or an arylenethiazolyl group such as e.g. 2-benzothiazolyl, 3-benzothiazolyl or 2-(β -naphthothiazolyl), D represents the atoms necessary to complete a mono- or multicyclic aromatic hydrocarbon nucleus such as a benzene or naphthalene nucleus which may be substituted by groups such as methyl, ethyl, methoxyl or ethoxyl, n represents a positive integer from 1 to 26 (provided that n is not greater than three when R₁ represents an aryl group) and X represents an acid radical such as perchlorate, bromide, benzenesulphonate, toluenesulphonate, methyl sulphate or ethyl sulphate.

A particularly useful group of quaternary salts embraced by Formula A above includes the compounds represented by the following general formula:



wherein R, D and X each have the values given above, and m represents a positive integer from 1 to 26.

Typical quaternary salts embraced by Formula A above include, for example, the following:

Decamethylene - bis - benzothiazolium perchlorate

3 - Ethylbenzothiazolium - *p* - toluenesulphonate

3 - *n* - Hexylbenzothiazolium - *p* - toluenesulphonate 50

3 - (2 - Benzothiazolylmethyl) - benzothiazolium - *p* - toluenesulphonate

3 - *n* - Nonylbenzothiazolium - *p* - toluenesulphonate 55

Trimethylene - bis - 2 - methylbenzothiazolium bromide

Decamethylene - bis - (2 - methylbenzothiazolium) - perchlorate

3 - (2 - Benzothiazolylmethyl) - 2 - methylbenzothiazolium - *p* - toluene sulphonate 60

2 - Methyl - β - naphthothiazolium metho-*p* - toluenesulphonate

Ethylene - bis - benzothiazolium bromide 65

Pentamethylene - bis - benzothiazolium perchlorate

Hexamethylene - bis - benzothiazolium perchlorate

3 - Benzylbenzothiazolium chloride 70

Heptamethylene - bis - benzothiazolium perchlorate

Nonamethylene - bis - benzothiazolium perchlorate 75

Hexacosane - 1,26 - bis - benzothiazolium perchlorate

The preferred benzothiazolium compounds include:

I 3 - Methylbenzothiazolium iodide 80

II Decamethylene - bis - benzothiazolium perchlorate

III Propane - 1,3 - bis - (3 - methyl - 2 - benzothiazolium paratoluene sulphonate)

IV Pentane - 1,5 - bis - (3 - methyl - 2 - benzothiazolium paratoluene sulphonate) 85

Many of these quaternary compounds have been previously described. For example, the bis compounds represented by Formula B can be prepared according to the methods described in U.S. Patent 2,425,774, as well as by the method described by U.S. Patent 2,694,716. Such methods generally comprise the fusion of a heterocyclic base with an alkylene halide. Such techniques are well known to those skilled in the art. Alkyl esters of organic sulphonic acids can also be fused with thiazole bases to provide the salts used in the method of the invention.

When used in a bath prior to development, from 1—200 milligrams per litre of the bath are employed. This may be a bath containing water and the benzothiazolium salt or the benzothiazolium salt may be used in a pre-hardener bath containing hardening agents which aid in conditioning the photographic element so that it can be processed at relatively high temperatures. The prehardener bath may be at any suitable temperature from 50°F. to 200°F., since the purpose of the bath is to imbibe the benzothiazolium salt into the top emulsion layer of the multilayer 110

element. The developer is preferably at a temperature greater than 100°F., but a useful range is from 85°F. to 200°F.

The amount of benzothiazolium salt, whether incorporated in the bath or in the silver halide emulsion, depends upon the temperature at which the development is carried out within the ranges given above. This can be accomplished in the bath by increasing the concentration of the benzothiazolium salt or by leaving the photographic element in the bath for a longer period of time, or a combination of the two. In a preferred embodiment, the multilayer element is immersed in the bath for two and a half minutes, the bath contains hardeners and the temperature is close to that of the developer solution.

It will be appreciated that any supports customarily used in the art may be used for the silver halide emulsion as well as any customary light sensitive silver halide salts and colloid vehicles such as gelatin which can be hardened chemically.

Various colour emulsions may be used and these emulsions may comprise various layer arrangements. For instance, the support may carry thereon a blue-sensitive layer containing a yellow coupler, an interlayer, a green-sensitive layer containing a magenta coupler and a red sensitive layer containing a cyan coupler and having thereon an overcoat. These couplers may occur in different layers and in different orders as a matter of choice. It will be appreciated that various supports known in the art may be used for the silver halide emulsion and that if a transparent support is used, that one or more light-sensitive layers may be coated on one side and one or more layers on the other side, provided the benzothiazolium salt is used on both sides of the support. Another useful photographic element may have a bleachable filter layer incorporated in the element between two light-sensitive layers or on the support when it is between the light-sensitive layers. In still another useful element, the light-sensitive elements can have one or more strata of the type described in Specification No. 1,021,564. For example, one strata would be a high speed emulsion and the second strata a low speed emulsion both optically sensitized to the same portion of the spectrum and producing the same dye image. Similarly, the second light-sensitive layer can have one or more strata.

The photographic emulsion may contain a

single coupler or a combination of couplers in one or more of the light-sensitive layers.

In the silver halide emulsions in the colour element, various silver salts may be used as the sensitive salts, including silver bromide, silver iodide, silver chloride or silver halide such as silver chlorobromide or silver bromoiodide.

The emulsions can be chemically sensitized by any of the accepted procedures. The emulsions can be digested with naturally active gelatin, or sulphur compounds can be added.

When incorporated in the emulsion or in an overcoat, the benzothiazolium salts may be incorporated as aqueous solutions, alcohol-water solutions, or by any other manner known in the art.

In the following Examples, numbers 1, 2 and 5 illustrate the effect of the benzothiazolium salts on the development rate of blue-sensitive silver halide emulsion layers of the type used as the outermost layer in multilayer photographic materials; Examples 3, 4 and 6 illustrate the process of the invention.

EXAMPLE 1

Four photographic films were prepared consisting of a cellulose acetate support coated with a blue sensitive silver bromoiodide gelatin emulsion containing a ketomethylene yellow colour former α -{3-[α -(2,4-di-t-amylphenoxy)butyramido] benzoyl} 2-methoxyacetanilide). These coatings were alike except for the following addenda.

Coating	Feature
A	Control, no addenda.
B	Compound I added at 6.0 grams/Ag mole
C	Compound III added at 2.0 grams/Ag mole
D	Compound IV added at 2.0 grams/Ag mole

Each coating was given an exposure in a sensitometer and processed to a colour positive in a reversal colour process of the type described in Example 1 of U.S. Patent 2,944,900, except the temperature of the process was 160°F. The change in the rate of development of the emulsion with each of the addenda present is shown by the yellow dye D_{max} obtained.

Coating	Compound Used	160° Δ D _{max}
A	Control	References
B	I	+ .46
C	III	+ .30
D	IV	+ .23

EXAMPLE 2

Three photographic films were prepared consisting of a cellulose acetate support
5 coated with a blue sensitive silver bromo-

iodide gelatin emulsion containing a keto-methylene yellow colour former as described in Example 1. These coatings were alike except for the following addenda.

Coating	Feature
E	Control
F	Compound II added at 3 grams/ Ag mole
G	Compound II added at 6 grams/ Ag mole.

Each coating was exposed in a sensitometer and processed to a colour positive in the process of Example 1 at 75°F. and at 160°F. The change in the rate of develop-

ment is shown here by the D_{maxes} and the relative emulsion speeds at the extreme development temperatures.

Negative Development

Coating	Compound Used	10 min. — 75°F		30 sec. — 160°F		20 sec. 160°F	
		D _{max}	Relative Speed	D _{max}	Relative Speed	D _{max}	Relative Speed
E	—	2.55	100	0.66	not measurable	—	—
F	II	—	—	1.30	69	2.22	91
G	II	—	—	2.36	100	—	—

The figures obtained here show a direct relationship between the control of the rate of development and the temperature at which the development can be carried out. Thus, by control of the rate of development, the temperature of the process may be elevated, giving rapid processing with times of development within practical limits.

The use of the invention with multilayer colour films is shown in the following example.

EXAMPLE 3

Two multilayer films were made each consisting of a cellulose acetate support coated with a red sensitive silver bromiodide gelatin emulsion containing a phenolic cyan colour former over which was coated a gelatin inter-

layer. Next, a green sensitive silver bromiodide emulsion layer was coated containing a pyrazolone magenta colour former and over this a yellow filter layer. Over the entire film a blue sensitive silver bromiodide emulsion was then coated containing a keto-methylene yellow colour former and finally a gelatin overcoat.

The films were alike except for the following changes.

Coating	Feature
H	No further change
I	Like H except Compound IV added to the blue sensitive layer only at 4.85 grams/Ag mole.

Each coating was exposed in a sensitometer and processed to a colour positive in the reversal process of Example 1 at 75°F. and 160°F. The time of development in the negative developer of the high temperature

process was adjusted so that the film with the controlled rate of development would approximate the speed of the control film in the standard temperature process.

Coating	Process Temp.	Red		Green		Blue	
		D _{max}	Relative Speed	D _{max}	Relative Speed	D _{max}	Relative Speed
H	75°F	2.94	100	3.44	100	4.04	100
	160°F	2.87	100	3.29	100	2.08	not measurable, over-developed
I	75°F	3.14	100	3.74	91	<4.00	23
	160°F	3.08	100	3.73	100	<3.76	100

This example shows that the control of rate of development at high processing temperatures of a particular layer of a multilayer film can be achieved by incorporating a benzothiazolium salt in that layer.

The rate of development control shown above by these compounds is also applicable to multilayer colour films which are developed directly to a negative such as in a paraphenylenediamine-type developer process.

EXAMPLE 4

A negative multilayer coating J was prepared consisting of a cellulose acetate support coated with a red sensitive layer silver bromiodide gelatin emulsion containing a phenolic cyan colour former and 0.05 gram/

Ag mole of Compound I over which was coated a gel interlayer. Next, a green-sensitive silver bromiodide emulsion layer was coated containing a pyrazolone magenta colour former and 0.225 gram/Ag mole of Compound I and over this a yellow filter layer. Over the entire film a blue-sensitive silver bromiodide emulsion was coated containing a keto-methylene yellow colour former and 2.25 grams/Ag mole of Compound I.

This coating J was compared with a product coating K of similar structure but containing no compound I. Each coating was exposed in a sensitometer and processed to a colour negative in a negative process referred to below in the article by Hanson et al. The following results were obtained.

Coating	Process Temp.	Red		Green		Blue	
		D _{min}	Relative Speed	D _{min}	Relative Speed	D _{min}	Relative Speed
K	75°F	.13	100	.56	100	1.18	100
	115°F	.23	100	.81	72	1.82	100
J	115°F	.26	115	.68	100	1.10	100

A typical negative colour process as referred to is described in detail by W. T. Hanson, Jr. and W. I. Kisner in an article in the "Journal of the Society of Motion Picture and Television Engineers", Vol. 61, (1953), pages 667—701.

EXAMPLE 5

Twelve photographic films were made consisting of a cellulose acetate support each

coated with a blue-sensitive silver bromiodide gelatin emulsion containing a keto-methylene yellow colour former. These coatings were alike except for the features listed below.

Each coating was exposed in a sensitometer and processed to a colour positive in the process of Example 1 either at 75°F. or at 160°F. The change in the rate of development of the emulsions with each of the addenda present is shown by the dye D_{maxes}.

Feature	75°F D _{max}	160°F D _{max}
Control	2.24	1.18
Compound I at 0.1 gram/Ag mole	—	0.99
Compound I at 0.5 gram/Ag mole	—	1.09
Compound II at 0.1 gram/Ag mole	—	1.04
Compound II at 0.5 gram/Ag mole	—	1.24
Compound V* at 0.1 gram/Ag mole	—	1.29
Compound V* at 0.5 gram/Ag mole	—	1.52

* Compound V at 0.5 gram/Ag mole also shows a speed loss of approximately 1.10 log E compared to the control.

* Compound V is 1-phenyl-5-mercaptotetrazole.

Feature	75°F D _{max}	160°F D _{max}
Control	2.52	1.40
Compound III at 0.1 gram/Ag mole	—	1.08
Compound III at 0.5 gram/Ag mole	—	1.31
Compound IV at 0.1 gram/Ag mole	—	1.00
Compound IV at 0.5 gram/Ag mole	—	1.22

These results show that when the compounds are used in an antifoggant amount such as 2—8 mg. per 100 ml. of photographic emulsion, that they are ineffective in reducing the rate of development at elevated temperatures. Two to eight mg. per 100 ml. of emulsion corresponds to about 300 mg./Ag mole. The use of a conventional antifoggant, compound V, is also ineffective, since it results in a speed loss.

EXAMPLE 6

A multilayer film of the type described in Example 3, identified as H, was immersed in a prehardener bath containing 20 milligrams per litre of N-methyl-benzothiazolium-p-toluene sulphonate for two and a half minutes. It was then passed through a neutralizer bath and processed as in Example 3 with similar results to those obtained with coating I, in which the compound was incorporated in the emulsion.

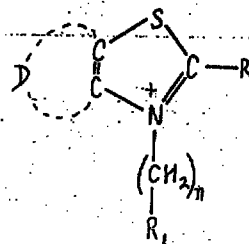
The prehardener bath was prepared as follows: 800 ml. of water at 90°F. was used to dissolve 4.30 ml. of dimethoxytetrahydrofuran (DMTF), 5.41 ml. of 18 N sulphuric acid and 0.5 gram of the sodium salt of para-toluenesulphonic acid. This solution was stirred for 10 minutes at 90°F. whereby the DMTF became hydrolyzed to succinaldehyde. 153 grams of sodium sulphate and 2 grams of sodium bromide were then added and the composition was mixed for 20 minutes. There was then added 20 grams of sodium acetate and 27 ml. of formalin, the

volume was then brought to one litre with water and the pH was adjusted to 4.8 at 80°F.

Incorporation of the same amount of N-methyl-benzothiazolium-p-toluene sulphonate in the negative developer at 160°F. had no appreciable effect in restraining the development. Overdevelopment occurred in the top layer.

WHAT WE CLAIM IS:—

1. A process for developing a multilayer gelatino-silver halide photographic material comprising treating the layer with a solution containing a photographic developing agent when the outermost emulsion layer contains between 1 and 10 grams of a benzothiazolium salt per mole of silver halide in said emulsion layer and the benzothiazolium salt has the formula:



in which R is a hydrogen atom or an alkyl group containing one or two carbon atoms.

R₁ is a hydrogen atom, an aryl group or an arylbenzothiazolyl group.

D represents the atoms necessary to complete a monocyclic or multicyclic aromatic



Feature	75°F D _{max}	160°F D _{max}
Control	2.24	1.18
Compound I at 0.1 gram/Ag mole	—	0.99
Compound I at 0.5 gram/Ag mole	—	1.09
Compound II at 0.1 gram/Ag mole	—	1.04
Compound II at 0.5 gram/Ag mole	—	1.24
Compound V* at 0.1 gram/Ag mole	—	1.29
Compound V* at 0.5 gram/Ag mole	—	1.52

* Compound V at 0.5 gram/Ag mole also shows a speed loss of approximately 1.10 log E compared to the control.

* Compound V is 1-phenyl-5-mercaptotetrazole.

Feature	75°F D _{max}	160°F D _{max}
Control	2.52	1.40
Compound III at 0.1 gram/Ag mole	—	1.08
Compound III at 0.5 gram/Ag mole	—	1.31
Compound IV at 0.1 gram/Ag mole	—	1.00
Compound IV at 0.5 gram/Ag mole	—	1.22

These results show that when the compounds are used in an antifoggant amount such as 2—8 mg. per 100 ml. of photographic emulsion, that they are ineffective in reducing the rate of development at elevated temperatures. Two to eight mg. per 100 ml. of emulsion corresponds to about 300 mg./Ag mole. The use of a conventional antifoggant, compound V, is also ineffective, since it results in a speed loss.

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A multilayer film of the type described in Example 3, identified as H, was immersed in a prehardener bath containing 20 milligrams per litre of N-methyl-benzothiazolium-p-toluene sulphonate for two and a half minutes. It was then passed through a neutralizer bath and processed as in Example 3 with similar results to those obtained with coating I, in which the compound was incorporated in the emulsion.

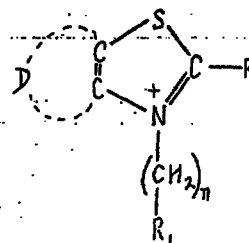
The prehardener bath was prepared as follows: 800 ml. of water at 90°F. was used to dissolve 4.30 ml. of dimethoxytetrahydrofuran (DMTF), 5.41 ml. of 18 N sulphuric acid and 0.5 gram of the sodium salt of paratoluenesulphonic acid. This solution was stirred for 10 minutes at 90°F. whereby the DMTF became hydrolyzed to succinaldehyde. 153 grams of sodium sulphate and 2 grams of sodium bromide were then added and the composition was mixed for 20 minutes. There was then added 20 grams of sodium acetate and 27 ml. of formalin, the

volume was then brought to one litre with water and the pH was adjusted to 4.8 at 80°F.

Incorporation of the same amount of N-methyl-benzothiazolium-p-toluene sulphonate in the negative developer at 160°F. had no appreciable effect in restraining the development. Overdevelopment occurred in the top layer.

WHAT WE CLAIM IS:—

1. A process for developing a multilayer gelatino-silver halide photographic material comprising treating the layer with a solution containing a photographic developing agent when the outermost emulsion layer contains between 1 and 10 grams of a benzothiazolium salt per mole of silver halide in said emulsion layer and the benzothiazolium salt has the formula:



in which R is a hydrogen atom or an alkyl group containing one or two carbon atoms.

R₁ is a hydrogen atom, an aryl group or an arylmethiazolyl group.

D represents the atoms necessary to complete a monocyclic or multicyclic aromatic



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hydrocarbon nucleus which may be substituted,

X represents an acid radical,
and n represents a positive integer from 1 to 26,

excepting that when R_1 is an aryl group, n is not greater than 3.

2. Process as claimed in claim 1 wherein the material is developed at a temperature between 85°F and 200°F.

3. Process as claimed in claim 2 wherein the emulsion is developed at a temperature greater than 100°F.

4. Process as claimed in any of the preceding claims wherein the benzothiazolium salt is incorporated in the outermost silver halide emulsion layer prior to coating on the support.

5. Process as claimed in claim 4 wherein the silver halide emulsion layer furthest from the support is sensitive to or sensitized to the blue region of the spectrum.

6. Process as claimed in any of the claims 1 to 3 wherein the benzothiazolium salt is incorporated in a layer coated over the silver halide emulsion layer prior to exposure.

7. Process as claimed in any of the claims 1 to 3 wherein the exposed silver halide emulsion layer is treated with a solution containing the benzothiazolium salt, prior to development, for sufficient time to imbibe between 1 and 10 grams of the benzothiazolium salt per mole of silver halide into the outermost layer.

8. Process as claimed in claim 7 wherein the solution contains between 1 mg and 200 mg per litre of the benzothiazolium salt.

9. Process as claimed in either claim 7 or claim 8 wherein the solution comprises a gelatin hardening agent or agents.

10. Process as claimed in any of the claims 7, 8 or 9 wherein the exposed silver halide emulsion layer is treated with the solution for 2½ minutes at a temperature between 85°F and 200°F.

11. Process as claimed in any of the preceding claims wherein the benzothiazolium salt is benzothiazole methiodide.

12. Process as claimed in any of the preceding claims 1 to 10 wherein the benzothiazolium salt is decamethylene-bis benzothiazolium perchlorate.

13. Process as claimed in any of the preceding claims 1 to 10 wherein the benzothiazolium salt is propane-1,3-bis-(3-methyl-2-benzothiazolium p-toluene sulphonate).

14. Process as claimed in any of the preceding claims 1 to 10 wherein the benzothiazolium salt is pentane-1,5-bis-(3-methyl-2-benzothiazolium p-toluene sulphonate).

15. Processes for developing a multilayer gelatino-silver halide photographic material as claimed in claim 1 as herein described.

16. Photographic reproductions compris-

ing developed silver halide emulsion layers whenever developed by the method of any of the claims 1 to 15.

17. A multilayer photographic material comprising a support carrying two or more light sensitive silver halide emulsion layers and the outer layer contains between 1 and 10 grams of a benzothiazolium salt having the formula (A) illustrated herein per mole of silver halide.

18. A photographic material as claimed in claim 17 in which the support carries three silver halide emulsion layers and the outermost layer contains the benzothiazolium salt.

19. A photographic material as claimed in claim 18 in which the outermost silver halide emulsion layer is sensitive or sensitized to the blue region of the spectrum.

20. A photographic material as claimed in any of the claims 17 to 19 in which the benzothiazolium salt is benzothiazole methiodide.

21. A photographic material as claimed in any of the claims 17 to 19 in which the benzothiazolium salt is decamethylene-bis-benzothiazolium perchlorate.

22. A photographic material as claimed in any of the claims 17 to 19 in which the benzothiazolium salt is propane-1,3-bis-(3-methyl-2-benzothiazolium p-toluene sulphonate).

23. A photographic material as claimed in any of the claims 17 to 19 in which the benzothiazolium salt is pentane-1,5-bis-(3-methyl-2-benzothiazolium p-toluene sulphonate).

24. A photographic processing bath for use in the process as claimed in claim 8 comprising an aqueous solution free from silver halide developing agents and containing between 1 and 200 mg. per litre of the benzothiazolium salt having the formula (A) herein.

25. A bath as claimed in claim 24 in which the benzothiazolium salt is benzthiazole methiodide.

26. A bath as claimed in claim 24 in which the benzothiazolium salt is decamethylene-bis-benzothiazolium perchlorate.

27. A bath as claimed in claim 24 in which the benzothiazolium salt is propane-1,3-bis-(3-methyl-2-benzothiazolium p-toluene sulphonate).

28. A bath as claimed in claim 24 in which the benzothiazolium salt is pentane-1,5-bis-(3-methyl-2-benzothiazolium salt is p-toluene sulphonate).

29. A bath as claimed in claim 24 in which the benzothiazolium salt is N-methyl-benzothiazolium p-toluene sulphonate.

30. A bath as claimed in any of the claims 24 to 29 comprising a gelatin hardening agent or agents.

31. Photographic processing baths as claimed in claim 24 as herein described.



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Agent for the Applicants.

ghe.

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