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(54) Process of the development of photograhic print material.

(57) A process for the development of photographically exposed silver halide photographic print material which comprises treating the exposed print material in the presence of a isothiouronium or isothiourea compound as a development accelerator.

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Description

PROCESS OF THE DEVELOPMENT OF PHOTOGRAPHIC PRINT MATERIAL

This invention relates to a process for the development of photographic print material.

A large proportion of exposed monochrome print material is developed under red light conditions until visual inspection shows that the print has been developed sufficiently. When prints are developed for an appreciable period of time no image is visible in the material, then an image appears which gradually gets darker. It is during this darkening period that the operator wishes to examine the print so as to stop development if so desired before full or over-development occurs. The time between placing the exposed print material in the developer solution and the moment when an image first appears is called the induction time. It is highly desirable to have as short an induction period as possible to save the processor from inspecting blank print material for some time. In the past it was found possible to reduce the induction period of some exposed print material by altering the ratio of the black and white developing agents in the developing solution. Such a process is described in British Patent specification No. 1358878. However in some of the current black and white print materials the induction time can not be reduced by such processes.

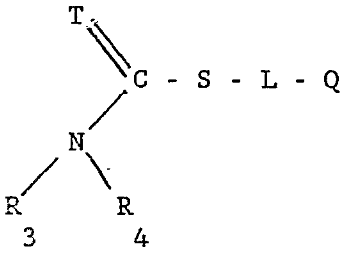
We have found that when certain isothiouronium compounds or isothioureas are added to a black and white developing solution the induction time of print material processed therein is reduced.

Isothiouronium compounds have been proposed to be used in a number of photographic processes and assemblies. For example they are proposed to be used as bleach accelerators in British Patent specification 2033599, U.S. patent specification 4458010 and 4596764, Japanese Kokai 85/76745. They are proposed to be used as image stabilizers in U.S.P. 4500632 and as colour intensifiers in U.S.P. 4469780. However in none of this prior art is it described or implied that isothiouronium compounds can act as development accelerators.

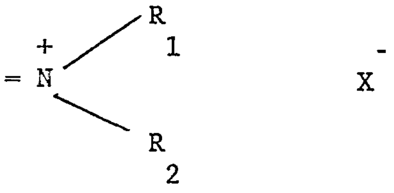
In the British Patent 1067958 there is described photographic silver halide material which comprises as the sensitising agent a combination of sensitisers of two different types. One type consists of either (a) quaternary ammonium compounds containing cyano ethoxyalkyl groups or (b) sulphur substituted thiouronium compounds which are also called isothiouronium compounds. The other group consists of polyethyleneglycol esters either of pentaerythritol esters of phosphoric acid or of amido phosphoric acid. The compounds to be used in the process according to the invention are described and defined in the B.P. 1067958.

Nowhere in B.P. 1067958 does it show that the induction time of print material which contains these sensitisers reduced. Example 5 purports to show that one of the sensitisers can be present in the developing solution but it does not show the use of isothiouronium compounds in a developing solution.

Therefore according to the present invention there is provided a process for the development of photographically exposed silver halide photographic print material which comprises treating the exposed print material with an aqueous solution of a super-additive mixture of black and white silver halide developing agents and an isothiouronium or isothiourea compound of the general formula I :-

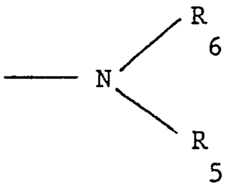


where T is a tertiary amino group of the formula $= N - R_1$ or is a quaternary ammonium group

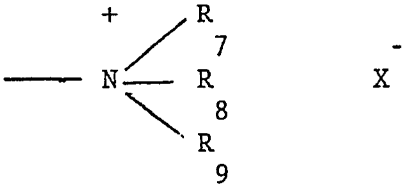


$$=\overset{+}{N}(R_1)(R_2)\quad X^-$$

wherein each of R_1, R_2, R_3 and R_4 are a hydrogen atom or an alkyl group or R_1 and R_2 and/or R_4 and R_3 together represent the atoms necessary to complete a five membered or six membered heterocyclic ring of R_1, R_3 and R_4 together represent the atoms necessary to complete a five or six membered heterocyclic ring, Q is a tertiary amino group of the formula :-



wherein R_5 and R_6 are each a hydrogen atom or an alkyl group or together represent the atoms necessary to complete a five of six membered heterocyclic rings or is a quaternary ammonium salt of the formula



wherein each of R_7, R_8 or R_9 is a hydrogen atom or an alkyl groups or wherein two of R_7, R_8 and R_9 or all three of R_7, R_8 and R_9 represent the atoms necessary to complete a five or six membered heterocyclic ring and X^- is an anion and L is a linking group.

It is an important feature of the present invention that no polyethylene glycol esters either of pentaerythritol esters of phosphoric acid or of amido phosphoric acid are present either in the silver halide photographic material or in the developing solution as undesirable sensitometric effects are observed if they are present.

In the compounds of the general formula I the substituents T and Q denotes a tertiary amino group of the formula $= N - R_1$ or a quaternary ammonium group of the formula $[= N^+R_1\ R_2]\ X^-$. R_1 and R_2 in these formulae are hydrogen or alkyl. Preferred alkyl groups contain 1 to 6 carbon atoms such as methyl, ethyl, propyl, butyl, pentyl and hexyl as well as branched isomers thereof. R_1 and R_2 together with the nitrogen atom to which they are attached form a 5 - or 6 - membered heterocyclic ring such as pyrolidine, piperidine and morpholine.

R_3 and R_4 denote hydrogen or alkyl. Alkyl groups containing 1 to 4 carbon atoms as listed above are preferred.

Further, R_2 and R_3 together with the nitrogen atom to which they are attached form a 5- or 6- membered heterocyclic ring, suitable examples of such rings being listed above.

It is also possible that R_1, R_3 and R_4 together represent the atoms necessary to complete a 5- or 6- membered heterocyclic ring such as pipridine.

Q is a tertiary amino group of the formula $-NR_5R_6$, where R_5 and R_6 are hydrogen or alkyl, preferably the above mentioned alkyl groups having 1 to 6 carbon atoms. Further, R_5 and R_6 may represent the atoms to complete a 5 - or 6 - membered heterocyclic ring such as mentioned above in the definitions of R_1 and R_2. Alternatively, Q denotes a quaternary emmonium group of the formula $[- N^+R_7\ R_8\ R_9]\ X^-$, where R_7, R_8 and R_9 independently of each other are hydrogen or alkyl, preferably the above membraned alkyl groups having 1 to 6 carbon atoms.

Two or all three of R_7, R_8 and R_9 may complete a 5 - or 6 -membered heterocyclic ring such as pyridine.

Most preferably R_1, R_2, R_3 and R_4 are each hydrogen atoms.

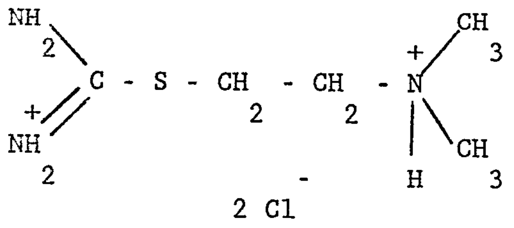
As the isothiouronium compounds are required to be water soluble preferably any alkyl groups present in the compound are lower alkyl groups i.e. alkyl groups having from 1 to 6 carbon atoms.

The preferred alkyl group is methyl

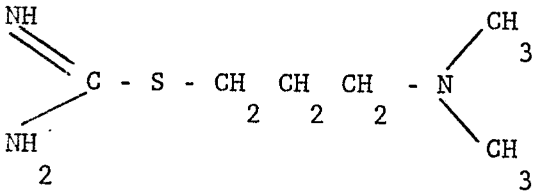
Preferably L is an alkylene or interrupted alkylene chain, that is say an alkyl chain interrupted by for example -0- or -NH-.

Particularly suitable linking groups L are $+CH_2+_2$ and $+CH_2+_3$.

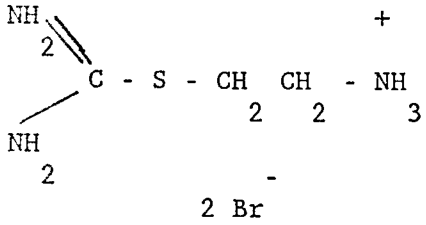
The preferred compounds of formula I for use in the process of the present invention are compound A of the formula :-



compound B of the formula



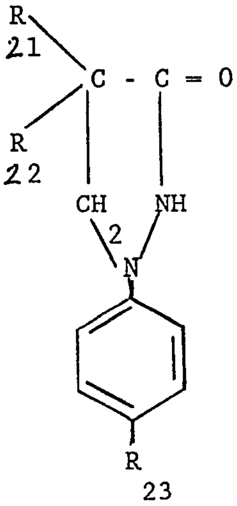
and compound C of the formula



The term superadditive mixture of developing agents means the mixture of two black and white developing agents which exhibit a greater activity than the sum of activities of the two developers when used alone. This term is described in 'Photographic Processing Chemistry' by L.F.A. Mason. Focal Press published in 1975 on pages 29 and 105 to 108. And superadditive mixtures are described in this book.

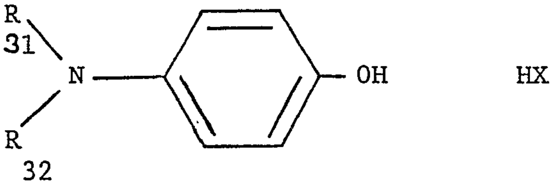
The most useful superadditive mixtures of developing agents for use in the present invention are hydroquinone or a substituted hydroquinone such as chlorohydroquinone, methyl hydroquinone or gentisic acid together with either a 1-phenyl-3-pyrazolidine developing agent or a para-amino phenol developing agent.

The 1-phenyl-3-pyrazolidinone compounds of particular use are of the formula II :-



wherein R_{21} is hydrogen, methyl or ethyl, R_{22} is hydrogen, methyl or $-CH_2OH$ and R_{23} is hydrogen, methyl or ethyl.

The para-aminophenol compounds of particular use are of the formula III :-



where HX is an acid and R_{31} and R_{32} are each hydrogen, alkyl, hydroxyalkyl or substituted alkyl or R_{31} and R_{32} together represent the atoms required to form a five or six membered heterocyclic ring. Suitable five or six membered heterocyclic rings include pyrrolidine, piperidine and morpholine.

The preferred compound is that wherein R_{31} is CH_3 and R_{32} is hydrogen. This is the very well known black and white developing agent metol.

Certain para aminophenol derivatives are also of use. Compounds of both these types are described on page 76 and 77 of the Mason book detailed above.

Secondary silver halide developing agents may also be present for example ascorbic acid.

It is to be understood that the aqueous solution which comprises the super-additive mixture of black and white developing agents and the isothiouronium compound can comprise all the usual ingredients present in a black and white silver halide developing solution.

For example preferably the solution has a pH in the range of 9.5 to 11.5. Most preferably sodium or potassium hydroxide are present in the solution to procure this pH.

Preferably the solution contains a pH buffer to help maintain the pH in the preferred range. Example 5 of suitable buffering substances are metal carbonates, bicarbonates, borates, metaborates and phosphates. Preferably the metals present are sodium or potassium.

Most preferably the solution comprises a sulphite for example sodium sulphite or an amino sulphite for example diethanolamin sulphite. The sulphite is present both as a protection against aerial oxidation and to promote the superadditive action of the developing agents present. Preferably the amount of sulphite ion present in the solution is from 2 to 80 g/litre of developing solution.

Preferably a source of bromide ion is present in the developing solution. Often sodium or potassium bromide are present but an amine bromide for example diethanolamine hydrobromide can be used.

Preferably a development antifoggant is used. Example of suitable antifoggants include benzotriazole, 5-methyl benzotriazole, phenyl mercaptotetrazole and nitro imidazoles for example 6-nitrobenzimidazole.

Anti-sludge and sequestering agents may be present for example complex phosphates and polyphosphates, amino carboxylic acids, for example, E.D.T.A. and organophorphorous compounds.

Water-miscible solvents such as ethylene glycol, diethylene glycol, triethylene glycol, ethylene glycol monomethyl ether and ethylene glycol monoethyl ether may be present as well as amines or ethanolamines. Such compounds may be used to help promote the solubility of the developing agents used or in the case of amines and ethanolamines as buffer promoting additives.

Other additives sometimes present but this list is not meant to be all inclusive, include surface active agents, defoaming agents, gelatin hardening agents, viscosity increasing agents and optical brightening agents.

The processing solution of the present invention proves most effective when the photographic print material with which it is used has as its base for the silver halide emulsion a polyethylene - coated paper base.

The processing solution used in the present invention has been found to be most effective in reducing the development induction time when a so-called dilute developing solution often used for developing print material is used. In so-called dilute developing solutions the total weight of the developing agents present is from 1 to 17 g/litre of developing solution.

The most preferred superadditive combination of developing agents is hydroquinone and 4-methyl, 4-hydroxymethyl-1-phenyl-3-pyrazolidinone. Preferably the amount of hydroquinone used is 1 to 15 g/litre and the amount of pyrazolidinone used is from 0.05 to 2.0 g/litre. The preferred ratio of hydroquinone to pyrazolidinone is from 1:50 to 1:5.

The preferred amount of isothiouronium compound to be present in the developing solution is from 0.001 to 5g/litre.

However the three preferred isothiouronium compound, compounds A, B and C have rather different activities. Thus the preferred range for compound A is from 0.005 to 0.05 g/litre. The preferred range for compound B is from 0.1 to 1.0 g/litre and the preferred range for compound C is from 0.5 to 1.5 g/litre.

The accompanying example will serve to illustrate the invention.

EXAMPLE

A gelatin silver chloro-bromide emulsion containing 55 mole per cent silver chloride and 45 mole per cent silver bromide and of median crystal size 0.31 μ was prepared using the controlled crystal techniques described in British Patent Specification 1,335,925. This emulsion was desalinated and chemically sensitised by the addition of sodium thiosulphate followed by chemical ripening at 55° C until the optimum levels of speed and contrast were obtained.

The emulsion was then coated on to polyethene laminated paper base and dried. The coated paper material was then cut into strips and each of these strips was then imagewise exposed and processed using firstly a developing solution of the basic formula :-

potassium sulphite	15 g
hydroquinone	3.5 g
4-methyl, 4-hydroxymethyl-1-phenyl-3-pyrazolidinone	0.3 g
potassium carbonate	10 g
potassium bromide	0.4 g
potassium hydroxide	2.5 g
benzotriazole	0.04 g
ethylenediamine tetraacetic acid	1.5 g
water to	1 litre
pH	10.8
temperature	20° C

The following developing solutions were prepared.

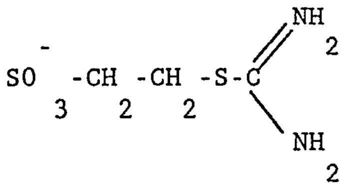
Developer A control - no addition
Developer B 0.01 g of compound A per litre
Developer C 0.4 g of compound B per litre
Developer D 1.0 g of compound C per litre

As a comparative test two compounds which have been proposed to be used in photographic developing solutions of not dissimilar molecular formula to the isothiouronium compounds were also tested as development accelerators.

These were compound D of the formula

$HS\text{-}CH_2\text{-}CH_2\text{-}0\text{-}CH_2\ CH_2\text{-}0\text{-}CH_2CH_2SH$

which is described in U.S.P. 4469780 as used in a colour intensifying bath and compound E of the formula +



which is described in U.S.P. 4500632 as an emulsion sensitiser.

Thus Developer E comprised 0.1 g of compound IV per litre and Developer F comprised 0.1 g of compound V per litre

A strip of the print material prepared and imagewise exposed as described above was processed in each of the developing solutions A to F and the period in seconds for the image to first appear, the induction time, was noted for all the developing solutions. The strips were then kept in the developing solution for 1 minute which was sufficient time for a fully developed image to be obtained.

All the strips were then fixed in a fixing bath, at 20°C for 30 seconds, of the formula :-

ammonium thiosulphate (of 60% w/w solution)	140 ml
boric acid	7 g
sodium hydroxide	2.5 g
sodium metabisulphite	6 g
glacial acetic acid	9 ml
water to	1 litre

The amount of fog present in each print was measured as was the contrast of each print. This is because some of the compounds proposed in the past to be used as developer accelerators have caused unacceptable increases in fog or unacceptable losses in contrast measured against a standard.

The results are set out in the Table below

TABLE

Developing Solution	Induction Time (in seconds)	Fog	Loss of Contrast (log exposure range) *
A (control)	14	zero	zero
B	11	zero	0.04
C	10	zero	0.03
D	11.5	0.02	0.02
E	15	0.01	0.13
F	16	zero	0.12

* Log exposure range is described in I.S.O. Standard No. G846.

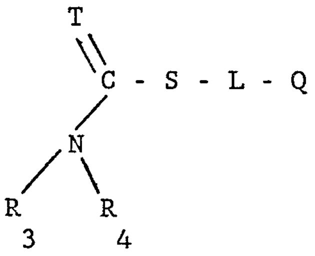
Thus using all the three preferred developing accelerating agents there is an appreciable reduction in the induction time. In the case of compounds A and B (developing solution B and C) no increase in fog but in the case of compound C (developing solution) a very small increase in fog is observed. Using all three compounds there is very small loss of contrast.

In the case of the two comparative compounds D and E (developing solutions E and F)there is no decrease in induction time and in fact there is an increase and also a considerable loss in contrast.

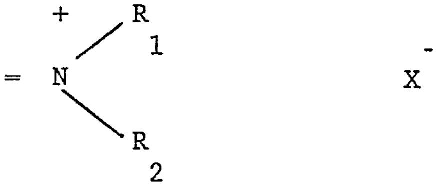
Claims

1. A process for the development of photographically exposed silver halide photographic print material which comprises treating the exposed print material with an aqueous solution of super-additive mixture of

black and white silver halide developing agents and which is characterised in that the aqueous solution comprises at least one isothiouronium or isothiourea compound of the general formula I:-

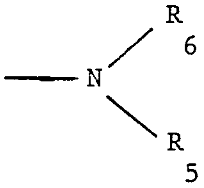


where T is a tertiary amino group of the formula = N - R_1 or is a quaternary ammonium group

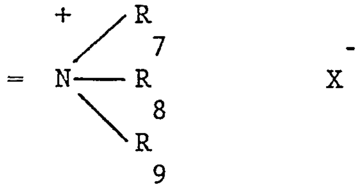


,

wherein each of R_1, R_2, R_3 and R_4 are a hydrogen atom or an alkyl group or R_1 and R_2 and/or R_3 and R_4 together represent the atoms necessary to complete a five membered or six membered heterocyclic ring of R_1, R_3 and R_4 together represent the atoms necessary to complete a five or six membered heterocyclic ring, Q is a teritary amino group of the formula :-



wherein R_5 and R_6 are each a hdyrogen atom or an alkyl group or together represnt the atoms necessary to complete a five or six membered heterocyclic ring or is a quaternary ammonium salt of the formula



wherein each of R_7, R_8 and R_9 is a hydrogen atom or an alkyl groups wherein two of R_7, R_8 and R_9 or all three of R_7, R_8 and R_9 represent the atoms necessary to complete a five or six membered heterocyclic ring, X- is an anion and L is a linking group.

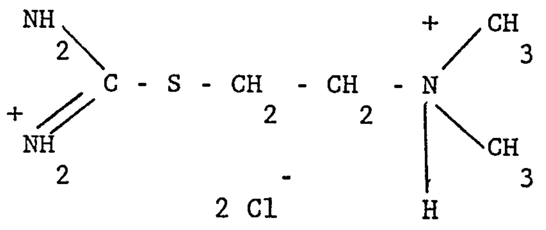
2. A process according to claim 1 characterised in that in formula I R_1, R_2, R_3 and R_4 are each hydrogen atoms.

3. A process according to claim 1 characterised in that in formula I L is an alkylene or interrupted alkylene claim.

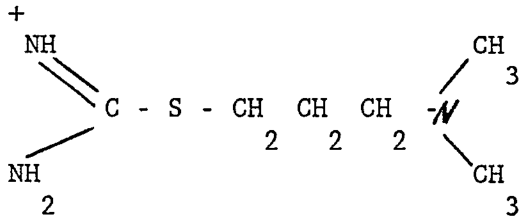
4. A process according to claim 3 characterised in that L is $+CH_2+_2$ or $+CH+_{23}$.

5. A process according to claim 1 characterised in that the compound of formula I is compound A of the

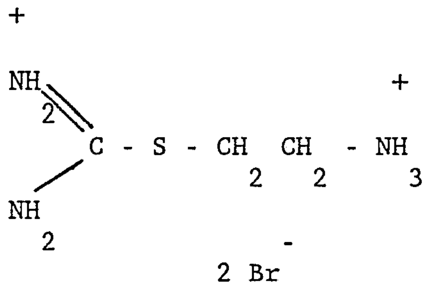
formula



or compound B of the formula

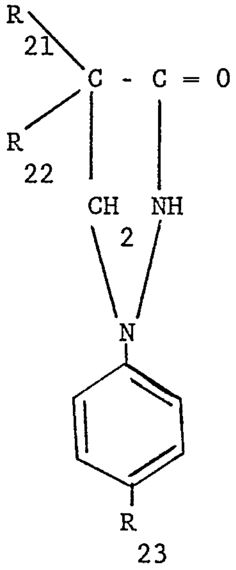


or compound C of the formula



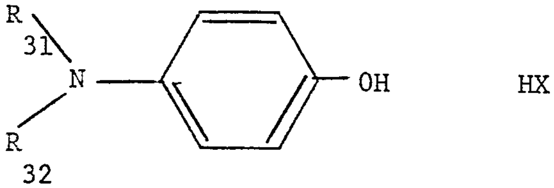
6. A process according to claim 1 characterised in that the superadditive mixture of black and white developing agents used comprises hydroquinone or a substituted hydroquinone together with either a 1-phenyl-3-pyrazolidinone developing agent or a para-amino phenol developing agent.

7. A process according to claim 6 characterised in that the 1-phenyl-3-pyrazolidinone developing agent has the formula



wherein R_{21} is hydrogen, methyl or ethyl, R_{22} is hydrogen, methyl or -CH_2 0H and R_{23} is hydrogen, methyl or ethyl.

8. A process according to claim 6 characterised in that the para-amino phenol developing agent has the formula



where HX is an acid and R_{31} and R_{32} are each hydrogen, alkyl, hydroxyalkyl or substituted alkyl or R_1 and R_2 together represent the atoms required to form a five or six membered heterocyclic ring.

9. A process according to claim 8 characterised in that in the formula for the para-amino phenol developing agent R_1 is -CH_3 and R_2 is hydrogen.

10. Photographic material which in characterised in that it has been prepared using the process claimed in claim 1.