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3,843,372

**GELATINO SILVER HALIDE EMULSION LAYER CONTAINING A HALOGEN SUBSTITUTED HETEROCYCLIC NITROGEN COMPOUND, AS HARDENER AND A CYSTEINE, METHIONINE OR CYSTEINE AS LATENT IMAGE REGRESSION INHIBITING AGENT**

Robin Jefferson, Ilford, England, assignor to Ilford Limited, Ilford, Essex, England

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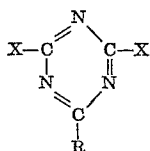
U.S. Cl. 96-109

8 Claims

**ABSTRACT OF THE DISCLOSURE**

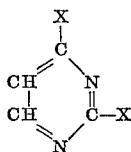
This invention relates to the hardening of photographic material by means of a halogen substituted heterocyclic nitrogen compound. To avoid latent image regression the hardening is carried out in the presence of cysteine, methionine, cystine or similar compounds.

Photographic silver halide materials usually comprise a colloid binder for the silver halide and the most common of these colloid binders is gelatin. It is usual to add a hardening agent for the colloid to the aqueous silver halide emulsion coating mixture when emulsion is coated onto the base support. A great amount of time has been expended in searching for suitable colloid hardeners and a number of very useful compounds and classes of compounds have been discovered. However each of these hardeners and classes of hardeners suffer from certain inherent defects but nevertheless these compounds are used because it has been impossible to discover a hardening agent which has no deleterious side effects. One class of hardening agents which are commonly used are halogen substituted 6-membered heterocyclic rings which comprise, two or three nitrogen atoms in the ring system. Examples of such hardening agents are compounds of the formula I to III:



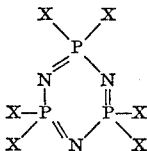
where X is a chlorine or bromine atom and R is a substituent group for example a methoxy group (preferably dichloro substituted triazines).

II



where X is a chlorine or bromine atom;

III



where X is a chlorine or bromine atom.

The effect of such compounds is often increased by adding a base to the heterocyclic nitrogen compounds in the hardening mixture. For example 1,4-diaza-dicyclo-(2,2,2)-octane (Dabco) is often used with the triazine of

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the above formula I, in order to increase its hardening action.

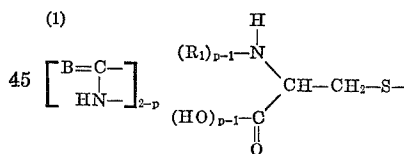
However it has been found that when halogen substituted 6-membered heterocyclic compounds having two or three ring nitrogen atoms are used as hardening agents in photographic materials there is apparent in the photographic materials after exposure and processing a latent image regression.

Latent image regression manifests itself as an apparent decrease in the sensitivity of exposed material. Usually the longer the period over which exposed material is kept before development the greater the apparent decrease in sensitivity of the material. This apparent decrease in sensitivity is enhanced by storing the material at elevated temperatures. With colour photographic material containing several emulsion layers the consequences of latent image regression are more serious because they are more obvious since it generally arises that the regression is not uniform for the several emulsion layers and there is consequently a shift in the colour balance as well as an apparent loss of sensitivity. Nevertheless because of the very desirable hardening actions obtained with the above defined heterocyclic nitrogen compounds it is often required to use these hardening agents in spite of their inherent tendency to produce latent image regression in photographic materials.

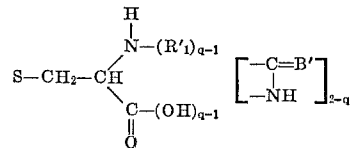
It is the object of the present invention to provide a process to minimise the effect of the above defined nitrogen-containing heterocyclic hardening agents producing latent image regression when these compounds are used to harden the colloid in photographic materials.

According to the present invention in a process for the production of photographic silver halide material wherein the colloid binder of a silver halide emulsion layer of the material is hardened by means of a hardening agent which is a halogen substituted 6-membered heterocyclic ring which comprises two or three ring nitrogen atoms there is provided the step of adding to the silver halide emulsion an aqueous solution of a compound which, in its free amino acid state if it is an amino acid, corresponds to one of the formulae

(1)



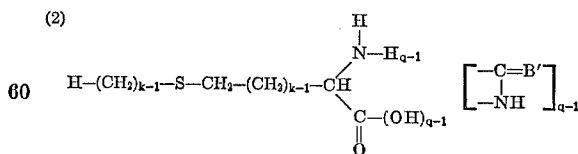
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and

(2)



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wherein R<sub>1</sub> and R'<sub>1</sub>, independently from one another, represent a hydrogen atom, an alkyl group, a substituted alkyl group, an aralkyl group, a substituted aralkyl group, an allyl group, an alkyl-oxy-carbonyl group, an aralkyl-oxy-carbonyl group or an acyl group of the formula R<sub>2</sub>-CO- where R<sub>2</sub> is an alkyl or substituted alkyl group, an aralkyl or substituted aralkyl group or an aryl or substituted aryl group, B and B' represent an oxygen or sulphur atom and p, q and k each is 1 or 2.

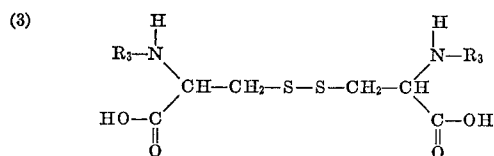
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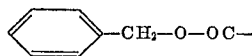
The compounds of formulae (1) and (2) wherein  $p$  and/or  $q$  are 2 contain at least one amino group and at least one carboxylic acid group. Such amphoteric compounds are capable of forming salts with strong acids and with bases such as alkali metals. Therefore the compounds may be used for the present process in the form of salts, provided the salts are soluble in water.

An example of a substituted alkyl group is hydroxymethyl. An example of a substituted alkyl group in the  $R_3$  position is trifluoromethyl. An example of a substituted aralkyl group is hydroxymethyl benzyl. An example of a substituted aryl group is parachlorophenyl.

In a preferred embodiment of the invention the compounds in their free amino acid state correspond to the formula

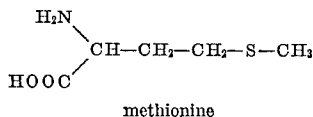


wherein  $R_3$  represents the radical

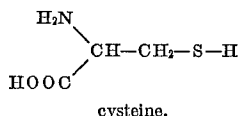


or preferably a hydrogen atom.

In another preferred embodiment the compound in its free amino acid state corresponds to the formula



and in the most preferred embodiment it corresponds in its free amino acid state to the formula



Some of the compounds of formula (1) are advantageously added to the silver halide emulsion as a dilute aqueous alkaline solution. An example of such a compound is cystine. Cysteine or methionine are with advantage added as an aqueous solution of the hydrohalide or as an aqueous alkaline solution.

The preferred amount of the compound of formula (1) or (2) to be added to the silver halide emulsion is from 0.01 to 2.5 millimoles per mole of silver halide present in the emulsion. The quantities of these compounds to be present is very small but they are very efficacious in preventing latent image regression as illustrated in the Examples which follow.

However if more than 2.5 millimoles of the compound is used a certain fogging of the emulsion is obtained on development.

#### Example 1

A fast iodobromide emulsion was prepared, in gelatin solution, having 3.2 mole percent of silver iodide. This emulsion was digested at an elevated temperature to maximum sensitivity in the presence of sodium thiosulphate and a gold salt. The emulsion was then stabilised by the addition of a tetraazaindene compound and cooled. A wetting agent was then added to the emulsion which was reheated, brought to a pH of 6 and divided into portions. One portion was coated onto film strips without any further additions being made to it. This was the control emulsion.

To another portion of the emulsion there was added an aqueous solution containing 7 g. of 4(2,4-dichloro-1,3,5-triazinylamino) benzenesulphonic acid (which is a compound of formula 1) per 250 g. of emulsion together with 0-35 g. Dabco as a hardening combination.

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To the third portion of the emulsion there was added, a dilute aqueous alkaline solution containing 7 g. of the triazine compound used above together with 0.35 g. Dabco and 0.2 g. cystine to 250 g. of emulsion.

In each test one strip of the control emulsion and the strips of the test emulsions were all exposed through a step-wedge and then incubated for 7 days at 60% R.H. at 42° C. such conditions being chosen to accelerate latent image regression.

All the strips were then processed for 8 minutes at 20° C. in a metol/hydroquinone based developer. The relative log speed measured at a density 0.1 above fog of all the strips was then determined and compared with the relative log speed at 0.1 above fog of identical strips which after coating were stored for seven days at room temperature, exposed through a stepwedge and then at once processed as above.

The results obtained are set out in Table I below. Also shown is the comparative hardness of the coated emulsion layer expressed in arbitrary units of scratch resistance.

TABLE I

Emulsion	Sol. 1	Comparative Hardness
Control emulsion.....	-0.04	48
Emulsion together with triazine and Dabco.....	-0.60	128
Emulsion together with triazine, Dabco and cystine (0.2 g.).....	-0.18	138

The figures set out in Table I show the difference in speeds between the set of strips exposed, incubated and then processed compared with the set of strips, incubated, then exposed and processed. The higher the minus figure the greater the latent image regression. Thus the greatest latent image regression is shown in the emulsion which contained the triazine+Dabco hardener combination but no cystine. However when the cystine was also present the latent image regression was very considerably reduced.

#### Example 2

A medium speed iodo-bromide emulsion containing 6.4 mole percent of silver iodide was prepared and digested in a manner similar to that of Example I. To this emulsion was then added wetting agents and an alkaline solution of the colour former 3-*p*-methoxybenzoylacetyl-amino-4-(*N*-methyl-*N*-octadecylamino)benzoic acid (105 g. per 1½ moles of silver halide). The pH was adjusted to 9.7 and the emulsion divided into portions. One portion was coated onto film strips without further addition. This was the control emulsion.

To another portion of the emulsion there was added an aqueous solution containing the triazine compound of Example 1, (40.0 g./1.5 moles silver halide) together with Dabco (4.0 g./1.5 moles silver halide) as the hardening combination.

To a third portion was added an aqueous solution containing the hardening combination used above together with *N,N'*-dicarbobenzoxy-1-cystine (1.25 g./1½ moles silver halide).

In each latent image test, strips of the control emulsion and strips of the test emulsions were all exposed through a step-wedge and stored for 7 days at room temperature. They were then processed together with similar strips exposed just prior to processing, and developed in a conventional colour negative developer. The relative log speeds measured at a density of 0.1 above fog were determined and compared. The results obtained are set out in Table II below.

TABLE II

Emulsion	Sol. 1	Comparative Hardness
Control emulsion.....	-0.12	13
Emulsion together with triazine and Dabco.....	-0.27	139
Emulsion together with triazine, Dabco and <i>N,N'</i> -dicarbobenzoxy-1-cystine.....	-0.12	126

The figures set out show the difference in speeds between the sets of strips exposed, stored 7 days, and then processed compared with the set of strips exposed just prior to processing. The higher the minus figure, the greater the latent image regression. Thus the greatest latent image regression is shown in the emulsion which contained the triazine+Dabco hardener combination but no  $N_1N'$ -dicarbobenzoxy-1-cystine. When the  $N_1N'$ -dicarbobenzoxy-1-cystine-1-cystine was also present, the latent image regression was considerably reduced.

#### Example 3

A medium speed iodo-bromide emulsion containing 6.4 mole percent of silver iodide was prepared and digested in a manner similar to that of Example 1. To this emulsion was then added wetting agents and an alkaline solution of the colour former 3-*p*-methoxybenzoylacetyl-amino-4-(*N*-methyl-*N*-octadecylamino) benzoic acid (105 g. per 1½ moles of silver halide). The pH was adjusted to 9.7 and the emulsions divided into portions. One portion was coated onto film strips without further addition. This was the control emulsion.

To another portion of the emulsion there was added an aqueous solution containing 2,4-dichloro-6-methoxy-1,3,5-triazine (20.6 g./1.5 moles silver halide) together with Dabco (4.0 g./1.5 moles silver halide) as the hardening combination.

To a third portion was added a dilute aqueous alkaline solution containing the hardening combination used above together with 1-cystine 0.05 g. per 1½ moles of silver halide.

In each latent image test, strips of the control emulsion and strips of the test emulsions were all exposed through a step-wedge and stored for 7 days at room temperature. They were then processed together with similar strips exposed just prior to processing, and developed in a conventional colour negative developer. The relative log speeds measured at a density of 0.1 above fog were determined and compared. The results obtained are set out in Table III below.

TABLE III

Emulsion	Sol. 1	Comparative Hardness
Control emulsion.....	-0.07	26
Emulsion together with triazine and Dabco.....	-0.26	193
Emulsion together with triazine, Dabco and cystine.....	-0.04	215

The figures set out show the difference in speeds between the sets of strips exposed, stored 7 days and then processed compared to the set of strips exposed just prior to processing. The higher the minus figure, the greater the latent image regression. Thus the greater latent image regression is shown in the emulsion which contained the triazine+Dabco hardener combination but no 1-cystine. When the 1-cystine was also present, the latent image regression was considerably reduced.

#### Example 4

A medium speed iodo-bromide emulsion containing 6.4 mole percent of silver iodide was prepared in gelatin solution. This emulsion was digested at an elevated temperature to maximum sensitivity in the presence of sodium thiosulphate and a gold salt. The emulsion was then stabilised by the addition of a tetrazaindene compound and cooled. To this emulsion were then added wetting agents and an alkaline solution of the colour former 3-*p*-methoxy benzoylacetyl-amino-4-(*N*-methyl-*N*-octadecylamino) benzoic acid (105 g. per 1½ moles of silver halide). The pH was adjusted to 9.7 and the emulsion divided into portions. One portion was coated onto film strips without further addition. This was the control emulsion.

To another portion of the emulsion there was added an aqueous solution containing 4(2,4-dichloro-1,3,5-triazinyl-amino benzenesulphonic acid (40.0 g./1.5 moles silver

halide) together with Dabco (4.0 g./1.5 moles silver halide) as the hardening combination.

To a third portion was added an aqueous solution containing the hardening combination used above together with cysteine hydrochloride (0.4 g./1½ moles silver halide).

In each latent image test, strips of the control emulsion and strips of the test emulsions were all exposed through a step wedge and stored for 7 days at room temperature. They were processed together with similar strips exposed just prior to processing, and developed in a colour negative developer. The relative log speeds measured at a density of 0.1 above Log were determined and compared. The results obtained are set out in Table IV below.

TABLE IV

Emulsion	Sol. 1	Comparative Hardness
Control emulsion.....	-0.12	13
Emulsion together with triazine and Dabco.....	-0.27	139
Emulsion together with triazine, Dabco and cysteine.....	-0.09	155

These figures show the difference in speeds between the sets of strips exposed, stored 7 days and then processed compared with the set of strips exposed just prior to processing. The higher the minus figure, the greater the latent image regression. Thus the greatest latent image regression is shown in the emulsion which contained the triazine+Dabco hardener combination but no cysteine. When the cysteine was also present, the latent image regression was considerably reduced.

#### Example 5

A medium speed iodo-bromide emulsion containing 6.4 mole percent of silver iodide was prepared and digested in a manner similar to that of Example 4. To this emulsion were then added wetting agents and an alkaline solution of the colour former 3-*p*-methoxy benzoylacetyl-amino-4-(*N*-methyl-*N*-octadecylamino) benzoic acid (105 g. per 1½ moles of silver halide). The pH was adjusted to 9.7 and the emulsion divided into portions. One portion was coated onto film strips without further addition. This was the control emulsion.

To another portion of the emulsion there was added an aqueous solution containing 2,4-dichloro-6-methoxy-1,3,5-triazine (20.6 g./1.5 moles silver halide) together with Dabco (4.0 g./1.5 moles silver halide) as the hardening combination.

To a third portion was added an aqueous alkaline solution containing the hardening combination used above together with methionine (6.4 g./1½ moles silver halide).

In each latent image test, strips of the control emulsion and strips of the test emulsions were all exposed through a step wedge and stored for 7 days at room temperature. They were then processed together with similar strips exposed just prior to processing, and developed in a conventional colour negative developer. The relative log speeds measured at a density of 0.1 above Log were determined and compared. The results obtained are set out in Table V below.

TABLE V

Emulsion	Sol. 1	Comparative Hardness
Control emulsion.....	-.07	26
Emulsion together with triazine and Dabco.....	-.26	193
Emulsion together with triazine, Dabco and methionine.....	-.03	173

The figures set out show the difference in speeds between the sets of strips exposed, stored 7 days, and then processed compared with the set of strips exposed just prior to processing. The higher the minus figure, the greater the latent image regression. Thus the greatest latent image regression is shown in the emulsion which contained the triazine+Dabco hardener combination but

no methionine. When the methionine was also present, the latent image regression was considerably reduced.

The colour developer used in the foregoing Examples was of the formulae:

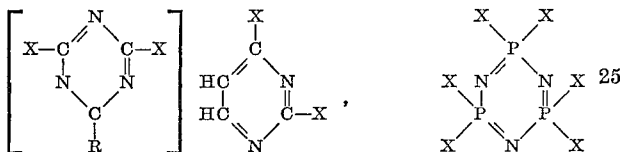
Sodium Hexametaphosphate .....	2.00	5
Sodium Metaborate .....	80.00	
Sodium Hydroxide .....	1.00	
Sodium Sulphite (anhydrous) .....	2.00	
Potassium Bromide .....	1.00	10
Hydroxylamine Sulphate .....	2.60	
Developing Agent <sup>1</sup> .....	4.70	
Water to 1 litre		

pH 10.70±0.05

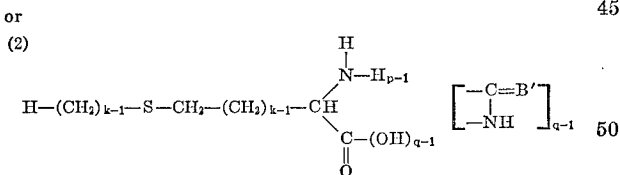
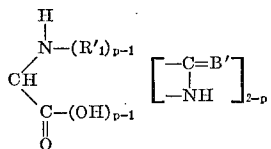
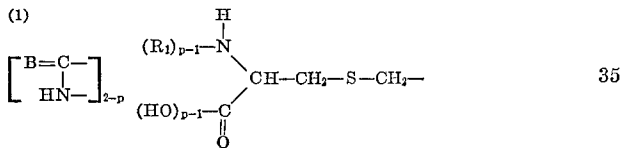
<sup>1</sup> Developing agent is 4-amino-N-ethyl-N-(2-hydroxy-ethyl)-aniline sulphate.

I claim:

1. A hardened silver halide emulsion layer which comprises silver halide, a gelatin binder and a hardener selected from the group consisting of compounds of the formula

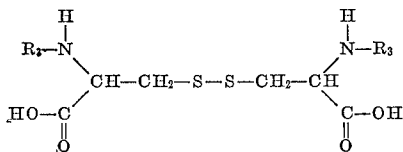


or a dichloro or dibromo substituted triazene wherein X represents a chlorine or bromine atom and a latent image regression inhibiting compound of the formula

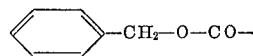


wherein R<sub>1</sub> and R'<sub>1</sub>, independently from one another, represent a hydrogen atom, an alkyl group, a hydroxymethyl group, an aralkyl, a hydroxymethyl benzyl group, an allyl group, an alkyl-oxy-carbonyl group, an aralkyl-oxy-carbonyl group or an acyl group of the formula R<sub>2</sub>-CO— where R<sub>2</sub> is an alkyl or trifluoromethyl group, an aralkyl or hydroxymethyl benzyl group or an aryl or p-chlorophenyl group, B and B' represent an oxygen or sulphur atom and p, q and k each is 1 or 2, or a water-soluble salt of a sulphur compound of formula (1) or (2) the sulphur compound being present in an amount ranging from 0.01 to 2.5 millimoles per mole of silver halide present in the emulsion.

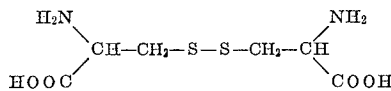
2. A silver halide emulsion layer according to claim 1 which comprises as the latent image regression inhibiting compound:



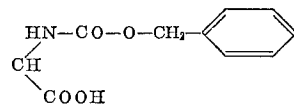
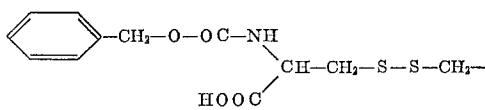
wherein R<sub>3</sub> represents a hydrogen atom or the radical



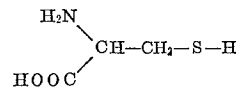
or a water-soluble salt thereof.  
3. A silver halide emulsion layer according to claim 1 which comprises as the latent image regression inhibiting compound:



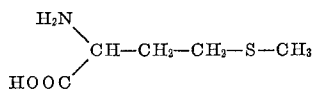
or a water-soluble salt thereof.  
4. A silver halide emulsion layer according to claim 1 which comprises as the latent image regression inhibiting compound:



or a water-soluble salt thereof.  
5. A silver halide emulsion layer according to claim 1 which comprises as the latent image regression inhibiting compound:



or water-soluble salt thereof.  
6. A silver halide emulsion layer according to claim 1 which comprises as the latent image regression inhibiting compound:



or a water-soluble salt thereof.  
7. A silver halide emulsion layer according to claim 1 which comprises employing as the hardening agent 4-(2,4-dichloro-1,3,5-triazinylamino)-benzene sulphonic acid or 2,4-dichloro-6-methoxy-1,3,5-triazine.

8. A silver halide emulsion layer according to claim 1 which comprises employing the hardening agent together with 1,4-diaza-dicyclo-(2,2,2)-octane.

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RONALD H. SMITH, Primary Examiner

W. H. LOUIE, JR., Assistant Examiner

U.S. Cl. X.R.

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