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PHOTOGRAPHIC DIFFUSION TRANSFER PROCESS

Leslie A. Williams, Harrow, England, assignor to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

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9 Claims. (Cl. 96—29)

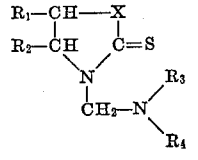
This invention relates to photographic processes for producing direct positive images and to materials for use therein.

In photography, most of the layers in which photographic images are found are themselves originally light-sensitive. However, not all photographic layers used for forming images are light-sensitive and the present invention concerns a class of non-light-sensitive layers, namely, those containing development nuclei for silver salts or substances forming development nuclei at a suitable stage in the photographic process or precipitants for silver salts by double decomposition. Such non-light-sensitive layers are used to form positive silver or silver salt images therein by reaction between the substances in the layers and dissolved silver salts diffusing thereinto from the unexposed areas of contiguous silver halide emulsion layer which has been exposed image-wise and which has been or is being developed to a negative image.

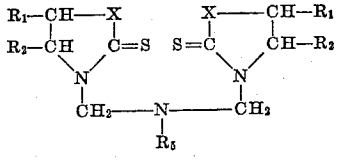
One drawback sometimes encountered in processes of this type is that the positive image produced is of a brownish or other non-acceptable color.

The present invention provides a sheet material comprising a non-light-sensitive photographic layer containing a silver precipitating agent such as development nuclei, or a substance capable of forming development nuclei with dissolved silver salts or a precipitant for silver salt, and al o containing a compound of one of the following general formulas:

(I)



(II)



wherein R_1, R_2 and R_3 may each be hydrogen or a lower alkyl group, R_4 may be a lower alkyl group, or R_3 and R_4 may together represent the non-metallic atoms necessary to complete a heterocyclic ring, R_5 is a lower alkyl group, and X may be O or S.

R_1 and R_2 may be, for example, hydrogen, methyl or ethyl; when R_3 is hydrogen, R_4 may be cyclohexyl; R_3 and R_4 together may complete a piperidyl or morpholinyl ring; and R_5 may be a lower alkyl group such as methyl or isopropyl.

The invention includes the process of preparing a direct positive image which comprises exposing a photographic silver halide emulsion layer to an object or image, developing a negative image in the exposed layer, and during or after development, transferring silver halide by diffusion from the unexposed areas of the emulsion layer to a non-light-sensitive image-receiving layer containing a silver precipitating agent such as development nuclei or a substance capable of forming development nuclei

with dissolved silver halide or a precipitant for silver salts by double decomposition and in effective contact with the emulsion layer, the transfer being effected in the presence of a silver halide solvent and a compound of one of the above general formulas.

By "in effective contact," we mean that dissolved silver salts can diffuse from the emulsion layer to the non-light-sensitive layer. There may be an intermediate layer present between the two aforesaid layers which does not hinder the silver salt diffusion, and the two layers may or may not be coated on the same support.

We have found that the presence of one of the compounds of the present invention has the effect of producing a blacker positive image than would otherwise be produced.

In the process of the invention, the said compound may be present in the receiving layer or in the solution employed for effecting development in the emulsion layer.

An alkaline solution is used to effect development of the exposed layer and the developing agent may be present in either the emulsion layer or in the alkaline solution or both. A mixture of developing agents may be used, if desired.

The silver halide solvent may be present in the developing solution or the receiving layer and is preferably sodium thiosulphate.

It is preferable to employ an antifoggant to prevent the formation of fog in the exposed emulsion layer and this may be present in either the emulsion layer or in the alkaline solution used to effect development. Any of the well-known nitrogen-containing organic antifoggants may be used and it has been found that benztriazoles are very suitable.

The compounds of the invention are preferably employed in the following concentrations: from 8 to 80 mgs./sq. meter, when incorporated in the receiving layer; or from 0.05 to 1.0 gram/liter, when incorporated in the developing solution.

A suitable non-light-sensitive image-receiving layer for use in the present invention comprises a gelatin layer containing a substance constituting development nuclei such as colloidal silver or silver sulphide) or a substance forming development nuclei with dissolved silver salts (such as zinc sulphide), and also containing one of the compounds of the invention.

Such a layer may be coated on a paper support and contacted in the presence of a silver halide solvent with an exposed and developing emulsion layer which may be coated on a separate support, or may be coated on the same support as the emulsion layer. In the latter case, it is preferable to coat the non-light-sensitive layer on a paper support, then to overcoat this layer with a comparatively unhardened emulsion layer. After exposure, development and formation of the direct positive image in the non-light-sensitive layer, the exposed and developed unhardened emulsion layer is removed, for example by washing in warm water.

The following examples illustrate the present invention:

EXAMPLE 1

A high contrast silver chloride emulsion containing the following constituents is coated on a paper support at the mentioned coating rate:

	Grams/sq. m.
Silver chloride	1.4
Diphenyl iodonium-5-methyl benztriazole	0.063
Hydroquinone	0.28
Gelatin	5.6

The resulting emulsion layer is exposed to a subject

such as a document and treated with the following developer:

	Grams
Sodium sulphite (anh.)	75
Hydroquinone	18
Sodium hydroxide	11.5
1-phenyl-3-pyrazolidone	0.5
Water to 1 liter.	

During or after development, the exposed emulsion layer containing developing agent is squeegeed for about 20 seconds into contact with an image-receiving sheet comprising a light weight paper support bearing a nucleated layer as follows:

	Grams/sq. m.
Gelatin	6.1
Sodium thiosulphate (anh.)	1.4
Titanium dioxide	0.63
Colloidal silver sulphide	0.0027
3-cyclohexylaminomethyl-5-methyl-2-thiooxazolidine	0.036

After separating the layer and the sheet, a positive image of a neutral black color was obtained on the receiving sheet.

Similar results were obtained when employing, instead of 3-cyclohexylaminomethyl-5-methyl-2-thiooxazolidine, the following compounds in the specified amounts:

	Grams/sq. m.
3,4'-morpholinylmethyl-5-methyl-2-thiooxazolidine	0.036
3,4'-piperidylmethyl-5-methyl-2-thiooxazolidine	0.036
Isopropyldi-(5-methyl-2-thiooxazolidin-3-ylmethyl)amine	0.021
Methyldi-(5-methyl-2-thiooxazolidin-3-ylmethyl)amine	0.021
Methyldi-(2-thiothiazolidin-3-ylmethyl)amine	0.021

EXAMPLE 2

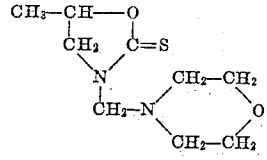
The procedure of Example 1 was repeated with the exception that 3,4'-morpholinylmethyl-5-methyl-2-thiooxazolidine was employed in the developer (0.05 gram/liter) and there was no toning agent in the receiving sheet. A positive image of a neutral-black color was obtained in the receiving sheet.

Similar results were obtained when employing, instead of 3,4'-morpholinylmethyl-5-methyl-2-thiooxazolidine, the following compounds in the specified amounts:

	Grams/liter
Isopropyldi-(5-methyl-2-thiooxazolidin-3-ylmethyl)amine	0.075
Methyldi-(5-methyl-2-thiooxazolidin-3-ylmethyl)amine	0.075
Methyldi-(2-thiothiazolidin-3-ylmethyl)amine	0.075

The compounds referred to in the above examples, may be prepared as described in the following preparations.

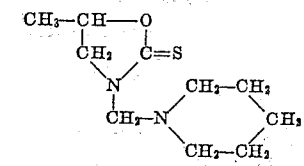
Preparation 1



3,4'-morpholinylmethyl-5-methyl-2-thiooxazolidine

39 grams of 5-methyloxazoline-2-thiol were heated slowly in 37% formalin (27 ccs.). At 50° C. a light brown oil had formed. Ethanol (20 ccs.) was added and the temperature was lowered to 25° C. A solution of morpholine (29 grams) in ethanol (10 ccs.) was then added while cooling under running water. The mixture was stirred vigorously and a white crystalline solid separated. It was recrystallized from aqueous alcohol as colorless needles M.P. 85–86° C.

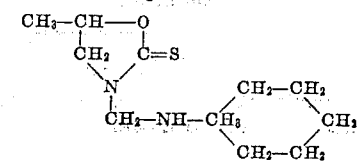
Preparation 2



5-methyl-3,1'-piperidinylmethyl-2-thiooxazolidine

This was made by the procedure of Preparation 1, using instead of morpholine, piperidine (28.4 grams). The resulting solid was collected, dried and recrystallized from benzene/light petroleum (60–80° C.) as colorless needles M.P. 90° C.

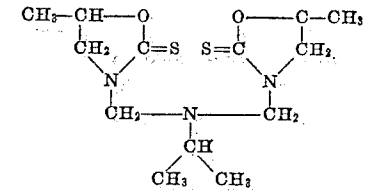
Preparation 3



3-cyclohexylaminomethyl-5-methyl-2-thiooxazolidine

This was made according to the method described in U.S. 2,343,566.

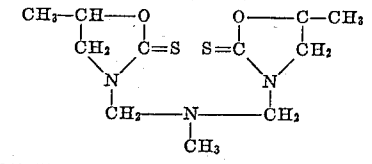
Preparation 4



Iso-propyldi-(5-methyl-2-thiooxazolidin-3-ylmethyl)amine

5-methyloxazoline-2-thiol (131 grams) was heated slowly in 37% formalin (85 ccs.). At 50° C. a light brown oil had formed. Ethanol (20 ccs.) was added and the temperature was lowered to 25° C. A solution of iso-propylamine (32.5 grams) in ethanol (10 ccs.) was then added while cooling under running water. The mixture was stirred vigorously and a white crystalline solid separated. It was twice recrystallized from alcohol as colorless crystals M.P. 140° C. yield 141 grams.

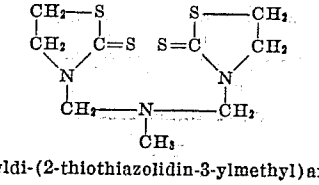
Preparation 5



Methyldi-(5-methyl-2-thiooxazolidin-3-ylmethyl)amine

This was prepared as in the above example, using 5-methyloxazoline -2-thiol (65.5 grams) and 37% formalin (42.5 ccs.); ethanol (10 ccs.) was added at 50° C. At 25° C. 33% alcoholic methylamine solution (51.6 ccs.) was added with cooling. The mixture was stirred rapidly and the resulting oil set aside to chill to give a solid (70 grams) which was recrystallized from ethanol (6 ccs./grams) as colorless needles M.P. 83° C.

Preparation 6

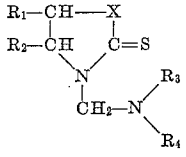


Methyldi-(2-thiothiazolidin-3-ylmethyl)amine

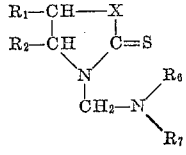
Thiazoline-2-thiol (6 grams) was slowly warmed in 37% formalin (10 ccs.) to 50° C. by which time a clear oil was obtained. To this, ethanol (5ccs.) was added and the solution cooled to 25° C. Methylamine (33% alcoholic solution 5 ccs.) was added with cooling, and after vigorous stirring a solid separated which was recrystallized from acetone as colorless crystals M.P. 212–213° C. Yield 4 grams.

What I claim is:

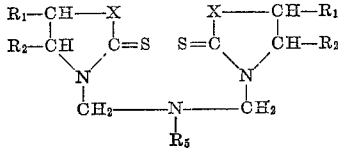
1. A process for preparing a photographic image which comprises exposing a photographic silver halide emulsion layer to a subject, developing the emulsion layer, then transferring the silver halide by diffusion from the undeveloped areas of the emulsion layer to an image-receiving layer containing a silver precipitating agent, the transfer being effected in contiguity with a silver halide solvent and a compound having a general formula of the class consisting of



and



and



wherein R_1, R_2, and R_3 are selected from the class consisting of hydrogen and lower alkyl groups, R_4 and R_5 are selected from the class consisting of lower alkyl groups, and R_6 and R_7 are selected from the class consisting of non-metallic atoms necessary to complete a heterocyclic ring of the class consisting of morpholinyl and piperidyl and X is selected from the class consisting of oxygen and sulfur atoms.

2. A process for preparing a photographic image which comprises exposing a photographic silver halide emulsion layer to a subject, developing the emulsion layer, then transferring the silver halide by diffusion from the undeveloped areas of the emulsion layer to an image-receiving layer containing a silver precipitating agent, the transfer being effected in contiguity with a silver halide solvent and a compound of the class consisting of 3-cyclohexylaminomethyl-5-methyl-2-thiooxazolidine, 3,4'-morpholinylmethyl-5-methyl-2-thiooxazolidine, 3,4'-piperidylmethyl-5-methyl-2-thiooxazolidine, isopropyldi-(5-methyl-2-thiooxazolidin-3-ylmethyl)amine, methyldi-(5-methyl-2-thiooxazolidin-3-ylmethyl)amine and methyldi-(2-thiothiazolidin-3-ylmethyl)amine.

3. A process for preparing a photographic image which comprises exposing a photographic silver halide emulsion layer to a subject, developing the emulsion layer, then transferring the silver halide by diffusion from the undeveloped areas of the emulsion layer to an image-receiving layer containing a silver precipitating agent, the transfer being effected in contiguity with a silver halide solvent and 3-cyclohexylaminomethyl-5-methyl-2-thiooxazolidine.

4. A process for preparing a photographic image which comprises exposing a photographic silver halide emulsion layer to a subject, developing the emulsion layer, then transferring the silver halide by diffusion from the undeveloped areas of the emulsion layer to an image-receiving layer containing a silver precipitating agent, the transfer being effected in contiguity with a silver halide solvent and 3,4'-morpholinylmethyl-5-methyl-2-thiooxazolidine.

5. A process for preparing a photographic image which comprises exposing a photographic silver halide emulsion layer to a subject, developing the emulsion layer, then transferring the silver halide by diffusion from the undeveloped areas of the emulsion layer to an image-receiving layer containing a silver precipitating agent, the transfer being effected in contiguity with a silver halide solvent and 3,4'-piperidylmethyl-5-methyl-2-thiooxazolidine.

6. A process for preparing a photographic image which comprises exposing a photographic silver halide emulsion layer to a subject, developing the emulsion layer, then transferring the silver halide by diffusion from the undeveloped areas of the emulsion layer to an image-receiving layer containing a silver precipitating agent, the transfer being effected in contiguity with a silver halide solvent and isopropyldi-(5-methyl-2-thiooxazolidin-3-ylmethyl)-amine.

7. A process for preparing a photographic image which comprises exposing a photographic silver halide emulsion layer to a subject, developing the emulsion layer, then transferring the silver halide by diffusion from the undeveloped areas of the emulsion layer to an image-receiving layer containing a silver precipitating agent, the transfer being effected in contiguity with a silver halide solvent and methyldi-(5-methyl-2-thiooxazolidin-3-methyl)amine.

8. The process of claim 1 wherein the designated compound is present in the developer solution during the transfer step.

9. The process of claim 1 wherein the designated compound is present in the image-receiving layer during the transfer step.

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