

# United States Patent

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[54] **SILVER DIFFUSION TRANSFER  
PROCESS WITH MERCAPTO-PURINE  
ANTIFOGGANT**

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[51] Int. Cl. ....G03c 5/54

[58] Field of Search .....96/29, 95, 109, 66.5

[56] **References Cited**

**UNITED STATES PATENTS**

2,647,056 7/1953 Land .....95/88

2,956,876	10/1960	Spath.....	96/22
3,353,957	11/1967	Blake.....	96/29
2,566,659	9/1951	Fry.....	96/109
2,933,388	4/1960	Knott.....	96/61
3,017,270	1/1962	Tregillus et al. ....	96/58 X
3,053,657	9/1962	Goodchild et al. ....	96/29

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[57] **ABSTRACT**

Mercapto-substituted purines are utilized in diffusion transfer photographic processes to give positive transfer prints of high quality over a very broad range of processing temperatures.

**12 Claims, No Drawings**

## SILVER DIFFUSION TRANSFER PROCESS WITH MERCAPTO-PURINE ANTIFOGGANT

### BACKGROUND OF THE INVENTION

This invention relates to photography and, more particularly, relates to diffusion transfer processes wherein an exposed silver halide emulsion is developed and an image-wise distribution of unexposed silver halide is formed and transferred, at least in part, to an image-receiving layer.

In silver diffusion transfer processes, a latent image in a photoexposed silver halide emulsion is developed with a silver halide developing agent in the presence of a silver halide solvent. Almost simultaneously with the development of the latent image, the silver halide solvent reacts with the silver halide in the unexposed and undeveloped areas of the emulsion to form a soluble, diffusible silver complex. The soluble silver complex is, at least in part, transferred to an image-receiving stratum where the silver thereof is precipitated to form a positive print.

It is desirable that such processes operate to give prints of good quality over a wide temperature range. In a diffusion transfer process performed at elevated temperatures, the reactions of solution, transfer and development which are balanced at 70° F. are accelerated nonuniformly. The photographic result of such behavior is a print of low contrast with grey background instead of rich blacks. The highlights will be dull and grey with no "crispness."

It has been proposed to counteract these effects by employing certain compounds used in conventional "Tray" or "wet development" photography to counteract the tendency of a silver halide emulsion to "fog," i.e., to become developable without photoexposure, when developed at temperatures above room temperature. (The term "antifoggants" has frequently been used as a class designation for compounds found to be useful in counteracting such fogging tendencies.) These compounds frequently are not suitable for use in diffusion transfer processes and, if effective under high temperature-rapid development conditions in these processes, they usually have an adverse effect on the quality of prints produced in the cold. For example, transfer prints processed at temperatures slightly above freezing tend to have excessive contrast with poor definition of detail in the shadows.

### SUMMARY OF THE INVENTION

It is, therefore, the primary object of the present invention to provide diffusion transfer processes and processing compositions useful therein that produce positive prints having improved contrast and whiter highlights at processing temperatures ranging from about 34° F. up to and in excess of 100° F.

Other objects of the present invention will in part be obvious and will in part appear hereinafter.

It has now been found according to the present invention that the above and other objects may be accomplished if the diffusion transfer process is carried out in the presence of a purine compound containing at least one free mercapto group attached to a carbon atom. As used herein, "mercapto" is intended to include —SH and the ammonium and alkali metal salts thereof.

In U.S. Pat. No. 2,956,876, mercapto-substituted purines have been disclosed as useful for preventing color fog in conventional color reversal photographic processes which involve a multistep procedure including black and white development followed by reversal exposure, color development, fixing, washing at various intervals, and so forth. It is quite unexpected that such compounds will perform in diffusion transfer processes where there are balanced and competing developing and solution reactions to give prints having improved contrast and improved highlights. Moreover, that these compounds will perform in diffusion transfer processes to give increased and comparable effective film speeds (exposure index ratings) at both high and low temperatures is not only unexpected but unique and permits the production of prints of improved quality over a very broad temperature range.

The invention accordingly comprises the processes involving the several steps and the relation and order of one or more of such steps with respect to each of the others, and to compositions possessing the features and properties which are exemplified in the following detailed disclosure and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description.

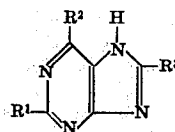
### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is primarily concerned with the processing, in the presence of a mercapto-substituted purine, of an exposed silver halide emulsion to give directly and, without further exposure, a positive print obtained by the development of an exposed emulsion and by the transfer of at least a portion of the silver of the unexposed regions of said emulsion to a suitable image-receiving element, the silver producing a visible image upon precipitation on said element.

In one form of the process, the development of the latent image and the transfer and precipitation of the silver from the undeveloped areas of the silver halide emulsion occur almost simultaneously. A liquid processing composition is so applied to the surface of a photosensitive silver halide element as to be absorbed in part into the emulsion of said element and this single liquid application develops the exposed silver halide and causes the formation of a soluble silver complex with the remaining undeveloped silver halide. The processing composition is best applied in a thin, uniform, relatively viscous layer, for example, by being spread on the emulsion. In a preferred form of the process, the liquid processing composition is spread between the photosensitive and image-receiving elements as described in detail in U.S. Pat. No. 2,647,056 issued July 28, 1953 to Edwin H. Land.

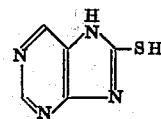
In carrying out the present process of producing diffusion transfer prints of good pictorial quality over a wide temperature range, the purines that may be used contain at least one mercapto group attached to a carbon atom of the purine nucleus. A single mercapto-substituted purine may be employed, or if desired, a mixture of two or more such compounds may be used. For achieving the benefits of the present invention most efficiently, the purine(s) is preferably added to the liquid processing composition.

The class of mercapto-substituted purines particularly useful for practicing the present invention have at least one tautomeric form that may be represented by the following structural formula:



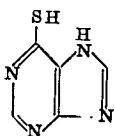
wherein at least one of R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> is —SM and M is hydrogen, ammonium or an alkali metal. By "alkali metal" is meant a metal in Group IA of Mendeleev's Periodic Table, e.g., sodium and potassium. For use in the aqueous alkaline processing compositions commonly used in diffusion transfer processes, R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> each are generally selected from the group consisting of hydrogen, amino, hydroxyl, alkyl, aryl and —SM wherein M is a member selected from the group consisting of hydrogen, ammonium and an alkali metal, at least one of said R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> being —SM. It will be understood that the R substituents are selected such that the compound will be soluble in the particular processing composition employed.

Typical of the purines that may be employed are:

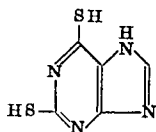


8-mercapto purine

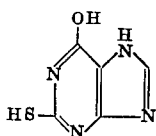
3



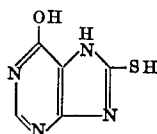
6-mercapto purine



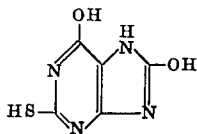
2,6-dimercapto purine



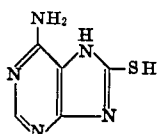
6-hydroxy-2-mercapto purine



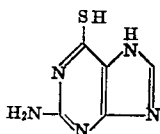
6-hydroxy-8-mercapto purine



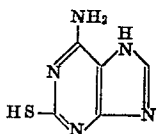
2-mercapto-6,8-dihydroxy purine



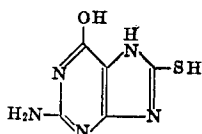
6-amino-8-mercapto purine



2-amino-6-mercapto purine



2-mercapto-6-amino purine



2-amino-6-hydroxy-8-mercapto purine

The purine compounds may be used advantageously over a relatively wide range of concentrations with the minimum concentration being that amount sufficient to give satisfactory prints at both elevated temperatures and in the cold. The optimum concentration will depend upon the particular emulsion, the processing composition, etc., and can readily be determined in each case. When the purine compound is incorporated into the liquid processing composition, it is ordinarily added in amounts ranging between about 1 and 4 grams per liter of composition.

As indicated above, the liquid processing composition contains certain ingredients, some of which may be added wholly or in part to the composition during the spreading thereof as by being dissolved into the composition from the photosensitive and/or image-receiving elements, but which are most conveniently introduced therein prior to spreading. The essential ingredients are (a) a silver halide developing agent(s), i.e., a substance capable of reducing the exposed silver halide of the latent image to silver, (b) a silver halide solvent(s), i.e., a substance capable of forming with the substantially unexposed silver halide a silver complex which is soluble in the particular liquid vehicle used for the processing composition and (c) a mercapto-substituted purine(s) as defined above for increasing the effectiveness of the process for producing positive transfer prints of good pictorial quality at processing temperatures of from slightly above freezing up to temperatures of the order of 100° F.

In the processing composition, any suitable developing agent(s) and silver halide solvent(s) may be employed. Among the developing agents that may be employed are benzene and naphthalene compounds having hydroxyl and amino substituents ortho or para to one another, e.g., hydroquinone, chlorohydroquinone, bromohydroquinone, toluhydroquinone, p-methyl aminophenol sulfate, and pyrogallol.

The silver halide solvent may be selected from any of those known to the art. Particularly useful silver halide solvents include the alkali thiosulfates, e.g., sodium thiosulfate and cyclic imides, e.g., uracil.

Preferably, the processing composition also contains a thickening agent to increase and impart the desired viscosity characteristics. A viscosity of from 1,000 to 200,000 centipoises at a temperature of 20° C. has been found satisfactory for permitting the composition to be readily controlled during and after spreading. Illustrative of suitable thickening agents are carbohydrates, e.g., starch; gums, e.g., gum arabic; and plastic materials, e.g., hydroxyethyl cellulose, sodium carboxymethyl cellulose and the sodium salts of polyacrylic and polymethacrylic acids.

Additionally, the composition contains an alkali, e.g., sodium hydroxide, and may contain a restrainer, e.g., potassium bromide; a preservative, e.g., sodium sulfite; or other adjuvants as conventionally used in diffusion transfer processes. The developing agent, silver halide solvent and any adjuvant employed, such as a thickener, are used in conventional amounts to achieve the desired effects.

As mentioned hereinabove, in a preferred embodiment of the present invention the processing composition is spread in a uniformly thin layer between the superposed surfaces of a photoexposed silver halide emulsion and an image-receiving element, which procedure may be accomplished, for instance, by advancing the elements between a pair of pressure-applying rollers. In such a process, the liquid processing composition, including the developing agent, the silver halide solvent and the mercapto-substituted purine may be conveniently provided in a rupturable container attached to either the photosensitive element and/or image-receiving element such that when the elements are superposed the container is so positioned as to be capable upon rupture of releasing its contents in a substantially uniform layer between and in contact with the surfaces of each of the elements.

Such containers are preferably inexpensive and disposable, and so constructed as to be capable of retaining the processing composition therein for relatively long periods of time without

vapor loss or oxidation. Examples of containers that may be used for this purpose are described in U.S. Pat. No. 2,634,886 issued to Edwin H. Land. Generally, the containers are fabricated from a blank comprising a three-ply sheet material including respectively an outer lamina of a strong deformable sheet material, e.g., kraft paper; an intermediate lamina impervious to the vapor of the processing composition, e.g., a metal foil; and an inner lamina inert and impervious to the processing composition, e.g., a thermoplastic resin layer. The container blank is folded upon itself and sealed in such a manner as to provide a container having a fluid-containing capacity and a sealed marginal edge which may be substantially unsealed throughout a predetermined portion of its length upon application of stress to the container.

The photosensitive element may comprise any of the commercially available silver halide emulsions such as gelatino silver chloride, chlorobromide, chloriodide, chlorobromiodide and bromiodide emulsions which may be coated on any suitable support, for example, glass, paper and plastic film base. The present compositions and processes, however, are particularly useful for improving the results obtained with the higher-speed photosensitive emulsions.

The emulsions may be chemically sensitized with sulphur compounds such as thiourea; with reducing substances such as stannous chloride; with noble metals such as gold or platinum; with amines and with quaternary ammonium compounds. Also, the emulsion may contain accelerators, coating aids and other such addenda where desired.

The image-receiving element may be any of those conventionally used in diffusion transfer processes and comprises a suitable support, such as baryta paper, which may have an outer layer formed of a natural or synthetic resin or a mixture thereof, which layer comes into contact with the processing composition. The image-receiving element preferably contains silver precipitating agents or nuclei since the presence of such materials during the diffusion transfer process has a desirable effect on the amount and nature of the silver precipitated in the formation of the positive print. Examples of materials suitable for this purpose are the metallic sulphides and selenides, thiooxalates, thioacetamides and colloidal metals disclosed in U.S. Pat. No. 2,698,237 issued Dec. 28, 1954 to Edwin H. Land. Also, as disclosed in this patent, it is desirable to provide on the support a continuous film consisting of submacroscopic agglomerates of minute siliceous particles as a vehicle for the silver precipitating agents or nuclei to enhance the aggregation of silver into its most effective form.

To illustrate the efficacy of mercapto-substituted purines in producing transfer prints of more uniform quality at different temperatures, a number of such compounds were evaluated in the hot, in the cold and at room temperature in the same silver halide diffusion transfer process using the same processing composition, the same photosensitive element (silver iodobromide emulsion carried on a paper base) and the same image-receiving element (colloidal silica containing silver precipitating nuclei carried on a paper base in accordance with the teachings of the aforementioned U.S. Pat. No. 2,698,237).

The alkaline processing composition employed comprised the following ingredients:

Water	1000 cc.
Hydroxyethyl cellulose	43.7 g.
Sodium sulfite	31.1 g.
Sodium hydroxide	50.7 g.
Sodium thiosulfate pentahydrate	88.5 g.
Triaminophenol dihydrochloride	5.9 g.
t-butyl hydroquinone	16.8 g.

In formulating the above, the hydroxyethyl cellulose was dissolved in water with stirring at room temperature. Thereafter, the remaining ingredients except for the developing agents were stirred into the solution and finally, the triaminophenol and hydroquinone were dissolved therein.

A series of the above-described photosensitive elements were exposed to the same subject matter under identical conditions and then advanced in superposed relationship with the aforementioned image-receiving elements between a pair of pressure-applying rollers to spread the liquid processing composition between the elements in a layer about 1.8 mils thick. After an imbibition period of 60 seconds in the cold and 10 seconds at both room temperature and in the hot, the photosensitive and image-receiving elements were separated to uncover the positive transfer prints.

The particular purine compounds employed and designated A-K were as follows:

- A 8-mercapto purine
- B 6-mercapto purine
- C 2,6-dimercapto purine
- D 2,6,8-trimercapto purine
- E 6-hydroxy-2-mercapto purine
- F 6-hydroxy-8-mercapto purine
- G 2-mercapto-6,8-dihydroxy purine
- H 6-amino-8-mercapto purine
- I 2-amino-6-mercapto purine
- J 2-mercapto-6-amino purine
- K 2-amino-6-hydroxy-8-mercapto purine

The concentration of purine compound used together with the exposure rating and density characteristics of the prints produced with each compound are given in the following table. The control consisted of the above processing composition without a mercapto-purine present.

Exposure rating is given in terms of "Diffusion Transfer Exposure Index." This term as used herein refers to the exposure index to which an A.S.A. calibrated exposure meter should be set to determine the proper exposure to which a negative for use in a silver diffusion transfer process must be subjected in order to obtain a satisfactory positive print and may be based on a curve relating original exposure of the negative to the density in the resultant positive. Conventionally, the Diffusion Transfer Exposure Index of a silver halide transfer process is determined by plotting a characteristic curve of the reflection density of the positive as a function of the log exposure of the negative, determining the exposure in meter-candle-seconds at the point on this curve corresponding to a density of 0.50, and dividing the constant, 4.0, by the exposure so determined.

TABLE I

Purine compound	Concentration, gms./10 cc.	Diffusion transfer exposure index			Maximum density			Minimum density		
		Cold <sup>a</sup>	Room <sup>b</sup>	Hot <sup>c</sup>	Cold <sup>a</sup>	Room <sup>b</sup>	Hot <sup>c</sup>	Cold <sup>a</sup>	Room <sup>b</sup>	Hot <sup>c</sup>
Control		960	264	368	1.50	1.61	1.40	0.01	0.23	0.43
A	.04	1,300	2,350	1,760	1.55	1.53	1.47	0.00	0.00	0.00
B	.04	2,250	2,400	1,880	1.35	1.44	1.32	0.00	0.00	0.01
C	.04	2,050	2,640	2,100	1.47	1.47	1.45	0.00	0.00	0.01
D	.02	1,680	1,680	1,240	1.46	1.49	1.42	0.00	0.01	0.00
E	.04	1,640	2,500	2,150	1.44	1.58	1.46	0.01	0.01	0.00
F	.04	1,760	2,780	2,100	1.36	1.60	1.40	0.01	0.00	0.01
G	.02	1,450	1,480	1,240	1.39	1.50	1.46	0.01	0.01	0.02
H	.02	720	880	800	1.57	1.50	1.48	0.01	0.02	0.02
I	.02	1,210	1,300	1,180	1.44	1.54	1.48	0.02	0.03	0.02
J	.03	1,360	1,510	1,240	1.50	1.59	1.52	0.01	0.01	0.06
K	.04	1,210	960	1,360	1.50	1.52	1.39	0.00	0.00	0.06
					1.49	1.53	1.50	0.02	0.04	0.02

<sup>a</sup> = 34-38° F.

<sup>b</sup> = 72-74° F.

<sup>c</sup> = 100-103° F.

It will be noted from the data set forth in the table that transfer prints produced in the presence of a mercapto-substituted purine exhibited low minimum densities at all three temperatures and showed a substantial decrease in maximum density loss between room and high temperature processing. It will be noted further that the Diffusion Transfer Exposure Indices obtained in the presence of each purine compound are very similar at the various processing temperatures as compared to the exposure indices of the control prints, wherein the exposure index in the cold is more than 3½ times that at room temperature and more than 2½ times that at elevated temperatures. This improvement in high-temperature density characteristics, together with the uniformity in exposure ratings over the entire temperature range is an unusual combination of properties which ensures the production of high quality transfer prints at low temperatures as well as at high temperatures.

U.S. Pat. No. 2,704,721, issued to Edwin H. Land on Mar. 22, 1955, proposes to improve high-temperature performance of diffusion transfer processes by using certain five-membered heterocyclic compounds, of which 5-nitrobenzimidazole nitrate may be considered illustrative. For comparison purposes, 5-nitrobenzimidazole nitrate was added to the above processing composition at a concentration of 0.04 grams per 10 cc. (cubic centimeters). The resulting composition was used to prepare a series of prints at the three different temperatures given above according to the same procedure and using the same photosensitive and image-receiving elements. The exposure indices obtained in the cold, at room temperature and in the hot were 1075, 740 and 596, respectively. The maximum and minimum densities at the different temperatures (34°-38° F.; 72°-74° F.; 100°-103° F.) were 1.10, 1.56, 1.43 and 0.01, 0.14, 0.21, respectively. From these results, it is readily apparent that the purines of the present invention perform much better over the entire temperature range and especially in the cold than those previously proposed compounds represented by the above benzimidazole. Though previous compounds, such as 5-nitrobenzimidazole nitrate, give improved results at the higher temperatures, it is customary to use other additives in combination with such compounds for obtaining improved results in the cold. In contrast, the mercapto purines perform well at both high and low temperatures in the absence of additives.

In another test, 2-amino-6-hydroxy-8-mercapto purine (compound K) was added in an amount of 0.03 grams per 10 cc. to an alkaline processing composition which comprised the following:

Potassium hydroxide	156.5 g.
Uracil	80.0 g.
Natrosol 250 (trade name of Hercules Corp. for hydroxyethyl cellulose, high viscosity)	50.0 g.
Zinc acetate	15.0 g.
N,N-dimethoxyethyl-hydroxylamine	50.0 cc.
Water	1000.0 cc.

Using this composition, a series of prints were prepared at the three different temperatures given above using the same procedure except that the imbibition time was 45 seconds at room temperature and in the hot and 120 seconds in the cold. The photosensitive element used comprised a gelatino silver iodobromide emulsion on a paper base, and the image-receiving element comprised a cellulose diacetate layer containing a nickel sulfide precipitant coated on a paper base and hydrolyzed to a depth of 0.00005 inch.

The exposure index and maximum and minimum densities for the prints obtained are given in Table II wherein the control represents prints prepared with the processing composition without mercapto-purine present.

TABLE II

Sample	Diffusion transfer exposure index			Maximum density			Minimum density		
	Cold	Room	Hot	Cold	Room	Hot	Cold	Room	Hot
Control	1, 120	800	1,760	1.47	1.56	1.46	0.01	0.14	0.16
Compound K	3, 120	3, 200	3, 600	1.61	1.49	1.55	0.01	0.02	0.02

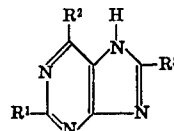
The results set forth in Table II, like those presented in Table I, clearly show that in the presence of a mercapto-purine, improved film speeds are obtained over the entire temperature range and further, that the speeds are relatively uniform at all three temperatures. Also, it is readily apparent that prints of improved highlights are obtained at the higher temperatures in the presence of a mercapto-purine as reflected by the substantial reduction in minimum densities at both room temperature and elevated temperatures.

It will be apparent that it is within the scope of the present invention to modify the processing compositions described above by altering the relative proportions of the ingredients and/or by the substitution of developing agents, silver halide solvents, alkalis and so forth.

Since certain changes may be made in the above processes and compositions without departing from the scope of the present invention, it is intended that all matter contained in the above description be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. In a diffusion transfer process which comprises the steps of developing exposed silver halide of a photosensitive silver halide element with a silver halide developing agent and forming an imagewise distribution of a soluble silver complex by reacting unexposed silver halide of said photosensitive element with a silver halide solvent, transferring at least a portion of said imagewise distribution of said silver complex by diffusion in alkaline solution to an image-receiving element and forming an image incorporating silver from said transferred silver complex in said image-receiving element, the improvement which comprises conducting said process in the presence of at least one purine soluble in said alkaline solution selected from those represented by the formula:



wherein R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are each selected from the group consisting of hydrogen, amino, hydroxyl, alkyl, aryl and —SM wherein M is selected from the group consisting of hydrogen, ammonium and an alkali metal, at least one of said R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> being —SM, whereby a transfer image having improved contrast and whiter highlights is produced at processing temperatures ranging from about 34° F. up to and in excess of 100° F.

2. A process according to claim 1 wherein said purine is 8-mercapto purine.

3. A process according to claim 1 wherein said purine is 6-mercapto purine.

4. A process according to claim 1 wherein said purine is 2,6-dimercapto purine.

5. A process according to claim 1 wherein said purine is 2,6,8-trimercapto purine.

6. A process according to claim 1 wherein said purine is 6-hydroxy-2-mercapto purine.

7. A process according to claim 1 wherein said purine is 6-hydroxy-8-mercapto purine.

8. A process according to claim 1 wherein said purine is 2-mercapto-6,8-dihydroxy purine.

9. A process according to claim 1 wherein said purine is 6-amino-8-mercapto purine.

10. A process according to claim 1 wherein said purine is 2-amino-6-mercapto purine.

11. A process according to claim 1 wherein said purine is 2-mercapto-6-amino purine.

12. A process according to claim 1 wherein said purine is 2-amino-6-hydroxy-8-mercapto purine.