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PHOTOGRAPHIC IMAGE TRANSFER PROCESS UTILIZING IMIDAZOLIDINE-2-THIONE

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Int. Cl. G03c 5/54
U.S. Cl. 96—29 7 Claims

ABSTRACT OF THE DISCLOSURE

Imidazolidine-2-thiones are utilized in silver diffusion transfer processes to give positive transfer prints of improved quality over a broad range of processing temperatures.

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 dsirable that such processes operate to give prints of good quality over a wide temperature range. In a diffusion transfer process at elevated temperatures, the reactions of solution, transfer and development which are balanced at 70° F. are accelerated non-uniformly. 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 tend to retard the formation of a silver transfer image to such an extent that a substantial reduction in effective film speed (exposure index) results.

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, without any decrease in effective film speed, positive prints having improved contrast and whiter highlights at processing temperatures ranging 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 particular imidazolidine-2-thiones. Though certain imidazolidines have found utility as toning agents in diffusion transfer processes to provide black rather than brownish or sepia prints, it is quite unexpected that such compounds will materially reduce or substantially eliminate greying of the highlights in the positive and at the same time actually provide an increase in effective film speed.

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.

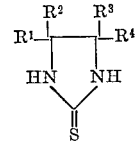
For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is primarily concerned with the processing, in the presence of certain imidazolidine-2-thione(s), of an exposed silver halide emulsion to give directly and, without further exposure, a positive print obtained by the development of the 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 where the silver is precipitated to produce a visible image.

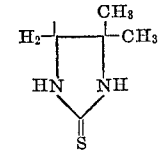
In one form of the process, the development of the latent image and the transfer and precipitation of the silver from the undeveloped areas of the silver halide emulsion occur almost simultaneously. A liquid processing composition is so applied to the surface of a photosensitive silver halide element 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 preferably applied in a thin, uniform, relatively viscous layer, for example, by being spread on the emulsion. In a preferred form of the process, the emulsion and image-receiving layers are in superposed relation, and the liquid processing composition is applied, e.g., as by being spread between the photosensitive and image-receiving layers as described in detail in U.S. Pat. No. 2,647,056 issued July 28, 1953 to Edwin H. Land and numerous other patents.

The class of imidazolidine-2-thiones particularly useful for practicing the present invention may be represented by the following structural formula:

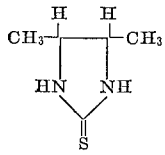


wherein R^1, R^2, R^3 and R^4 each are usually selected from the group consisting of hydrogen, alkyl, phenyl and carboxy (including the ammonium and alkali metal salts thereof). It will be understood that the R components are selected such that the compound will be soluble in the particular processing composition used.

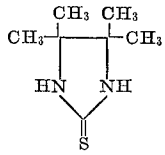
Typical of the imidazolidine-2-thiones that may be used in the present invention are:



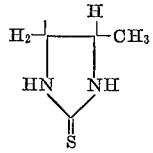
4,4-dimethyl imidazolidine-2-thione



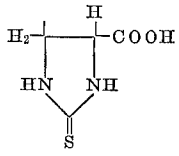
4,5-dimethyl imidazolidine-2-thione



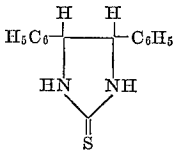
4,4,5,5-tetramethyl imidazolidine-2-thione



4-methyl imidazolidine-2-thione



4-carboxy imidazolidine-2-thione



4,5-diphenyl imidazolidine-2-thione

In carrying out the present process, a single imidazolidine-2-thione may be employed, or a mixture of two or more such compounds may be employed. For achieving the benefits of the present invention most efficiently, they are preferably incorporated in the processing composition.

The imidazolidines may be used advantageously over a relatively wide range of concentrations to give transfer prints of satisfactory pictorial quality at the various processing temperatures. The minimum concentration should be that amount sufficient to decrease D_{min} in the transfer print. The optimum concentration will depend upon the particular emulsion, the processing composition, etc., and can readily be determined in each case. When the imidazolidine is incorporated into the liquid processing composition, it is ordinarily added in amounts ranging between about 0.1 and 5 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 unexposed silver halide a silver complex which is soluble in the particular liquid vehicle used for the processing composition and (c) an imidazolidine(s) as defined above for increasing the effectiveness of the process for producing positive transfer prints of good pictorial quality at processing temperatures up to and in excess 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, t-butyl hydroquinone, p-methyl aminophenol sulfate, triamiophenyl 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 sulphite; 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 hereinbefore, 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 imidazolidine 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 3-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, chloroiodide, chlorobromoiodide and bromoiodide 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 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 aggregation of silver into its most effective form.

To illustrate the efficacy of imidazolidine-2-thiones in producing transfer prints of more uniform quality at both room temperature (72°–74° F.) and elevated temperatures (100°–103° F.), a number of such compounds were evaluated 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 grams
Sodium sulfite—31.1 grams
Sodium hydroxide—50.7 grams
Sodium thiosulfate pentahydrate—88.5 grams
Triaminophenol dihydrochloride—5.9 grams
t-butyl hydroquinone—16.8 grams.

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 10 seconds, the photosensitive and image-receiving elements were separated to uncover the positive transfer prints.

The particular imidazolidines employed and designated A–D were as follows:

(A) 4,4-dimethylimidazolidine-2-thione.
(B) 4-methyl imidazolidine-2-thione.
(C) 4,5-dimethyl imidazolidine-2-thione.
(D) 4,5-diphenyl imidazolidine-2-thione.

Compounds A, B and C were added to the processing composition in an amount of 0.001 gram per 10 cc. (cubic centimeter). Compound D was employed at a concentration of 0.02 gram per 10 cc. of composition.

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 with no imidazolidine 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

Imidazolidine compound	Diffusion transfer exposure index		Maximum density		Minimum density	
	Room	Hot	Room	Hot	Room	Hot
Control	264	368	1.61	1.40	0.23	0.43
A	2,710	1,680	1.59	1.51	0.00	0.07
B	1,450	980	1.68	1.38	0.00	0.11
C	2,640	1,450	1.56	1.47	0.00	0.07
D	920	626	1.61	1.40	0.03	0.13

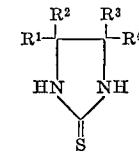
It will be noted from the data set forth in the table that D_{min} of the positive at room and high temperatures is materially reduced, without materially affecting D_{max}, by processing in the presence of the imidazolidine-2-thiones. It will be noted further that the speeds in terms of Diffusion Transfer Exposure Indices obtained in the presence of these compounds are considerably higher at the different processing temperatures as compared to the exposure indices of the control prints. This improvement in minimum density characteristics, together with increased speeds ensures the production of high quality transfer prints at temperatures up to and in excess of 100° F.

It will be apparent that it is within the scope of the present invention to modify the processing composition 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 halide emulsion with a silver halide developing agent and reacting unexposed silver halide of said photosensitive emulsion with a silver halide solvent to form with said unexposed silver halide an imagewise distribution of a soluble silver complex, transferring at least a portion of sadi imagewise distribution of said silver complex by diffusion in alkaline solution to an image-receiving element and reducing said transferred silver complex to provide a silver image, the improvement which comprises conducting said process in the presence of at least one compound selected from those represented by the formula



wherein R^1, R^2, R^3 and R^4 are selected from the group consisting of hydrogen, alkyl, phenyl and carboxy, whereby the minimum density of the transfer image is de-

creased, said compound being soluble in said alkaline solution.

2. A process according to claim 1 wherein said compound is incorporated in said solution.

3. A process according to claim 2 wherein said compound is present at a concentration of between about 0.1 and 5 grams per liter of solution.

4. A process according to claim 1 wherein said compound is 4-methyl imidazolidine-2-thione.

5. A process according to claim 1 wherein said compound is 4,4-dimethyl imidazolidine-2-thione.

6. A process according to claim 1 wherein said compound is 4,5-dimethyl imidazolidine-2-thione.

7. A process according to claim 1 wherein said compound is 4,5-diphenyl imidazolidine-2-thione.

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