

1

3,236,642

**PROCESS FOR PRODUCING DIRECT POSITIVES
BY THE SILVER SALT DIFFUSION PROCESS**

Harald von Rintelen, Cologne-Rodenkirchen, Siegfried Petersen, Leverkusen, and Max Heilmann, Cologne-Flittard, Germany, assignors to Agfa Aktiengesellschaft, Leverkusen, Germany, a corporation of Germany
No Drawing. Filed Sept. 12, 1961, Ser. No. 137,491
Claims priority, application Germany, Sept. 24, 1960,
A 35,652

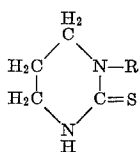
7 Claims. (Cl. 96—29)

This invention relates to direct positives as well as to a process for producing the same.

French Patent No. 879,995 describes a process for the direct production of positives in which the unexposed and, therefore, undevelopable silver halide of an image-wise exposed photographic silver halide emulsion layer is dissolved during or after the development of the negative and is transferred in another image-receiving or transfer layer with which it is in close contact under the catalytic influence of development nuclei that are present in this transfer layer which are capable of precipitating metallic silver from the dissolved silver salt to form a positive image. The terms "negative" and "positive" are in this case used only in a relative sense, since it is possible by the same process to obtain directly a negative from a negative original.

This process, which is known as a silver salt diffusion process, is used inter alia for high-speed copying in business offices, using a developing apparatus suitable for this purpose. The present tendency is to arrange for the entire process to be carried out as quickly as possible, i.e., so that the time of travel through the developing apparatus and thus also the time of contact of the positive with the negative that is required in such a diffusion process should be as short as possible.

It has now been found that the production of direct positives by the silver salt diffusion process can be substantially accelerated and simultaneously black silver images of high density can be obtained, if the process is carried out in the presence of compounds having the general formula



in which R represents a hydrogen atom or an aliphatic radical containing from 1 to 5 carbon atoms such as

2(1H)-tetrahydropyrimidinethione,
1-methyl-2(1H)-tetrahydropyrimidinethione,
1-ethyl-2(1H)-tetrahydropyrimidinethione,
1-propyl-2(1H)-tetrahydropyrimidinethione,
1-n-butyl-2(1H)-tetrahydropyrimidinethione, and
1-n-pentyl-2(1H)-tetrahydropyrimidinethione.

These compounds have also been referred to as 2-hexahydropyrimidinethiones.

These 2(1H)-tetrahydropyrimidinethiones can be prepared from N-alkyl-substituted 1,3-propylenediamines and carbon disulfide in a manner analogous to that described by C. F. H. Allen, C. O. Edens and James Van Allan on pages 34 and 35 of Organic Syntheses, vol. 26, published 1946 by John Wiley & Sons, Inc., New York, for the preparation of ethylene thiourea (2-imidazolidinethione) from ethylenediamine and carbon disulfide. 2(1H)-tetrahydropyrimidinethione was described by Arthus E. Baum, in United States Patent No. 2,544,746; its preparation from 1,3-diaminopropane(1,3-propylenediamine) and car-

2

bon disulfide was described by A. F. McKay and W. G. Hatton, in Journal of the American Chemical Society, vol. 78, page 1619 (1956).

These 2(1H)-tetrahydropyrimidinethiones are soluble in water and alkali and are added to the transfer material and/or to the developer solution in quantities of between 1 and 200 milligrams per square meter of transfer material or per liter of developer.

The deposition of the silver is accelerated by the use of these compounds, i.e., a black silver image of high density is obtained with contact times of as little as a few seconds, whereas when using the same material without addition of one of these compounds, a longer period of contact of the negative with the positive is necessary for obtaining the same density of the silver image. At the same time, these compounds cause a displacement of the image toning towards bluish-black.

These 2(1H)-tetrahydropyrimidinethiones are moreover characterized by their good stability, both in the transfer layers and in the developer. It is especially surprising that they retain their efficacy over a long period in positive layers on paper, without migrating into the baryta coating or into the paper raw material, as is frequently the case with other substances, for example, photographic stabilizers.

Various silver halides and their mixtures, such as silver chloride, silver bromide or silver bromiodide, can be used for the production of the light-sensitive negative material, and the said halides or mixtures can if desired be optically sensitized in the usual manner. All known layer-forming substances are to be considered as layer formers for the negative layer, including gelatin, starch, polyvinyl alcohol, cellulose derivatives and the like.

Paper, and films consisting, for example, of cellulose acetate, cellulose nitrate, polycarbonate, polyethylene terephthalate, polystyrene and others are suitable as the base for the silver halide emulsion layer.

A base or support consisting of paper or a plastic film is also advantageously used for the positive material. However, other supports such as metal, textile fabric and the like can also be used. For the production of such a positive material, a layer which contains development nuclei, such as colloidal noble metals or metal sulfides, and, if necessary, a silver halide solvent may be applied to such a support. As layer former for the positive layer, a hydrophilic colloid is advantageously used, such as gelatin, casein, carboxymethyl cellulose, starch, starch ethers, starch esters, galactomannans polymannuronic acids, polymannuronic acid esters, polymannuronic acid amides, polyvinyl alcohol and its derivatives or the like.

All prior known developer substances which have been used for the development of films and papers can be used in the development process of the present invention. The developer solution can contain a silver halide solvent as well as conventional developer additives, such as preservatives, wetting agents and the like. The developer substance can also be added to the negative layer and/or to the positive layer.

The process is more fully described in the following examples:

Example 1

A support, for example, a sheet of paper, has applied thereto a solution of the following composition:

65 Gelatin	-----g--	70
Ag ₂ S (colloidal)	-----g--	0.03
Formaldehyde solution (30 percent)	-----ml--	10
Water to make 1 liter.		

70 which also contains 0.025 grams per liter of 1-methyl-2(1H)-tetrahydropyrimidinethione (M.P.=123° C.)

A gelatino-silver chloride layer exposed through an

original by reflex copying is developed in a developer having the following composition and brought into contact with the positive:

	G.
Anhydrous sodium sulphite -----	70
Hydroquinone -----	16
1-phenyl-3-pyrazolidone -----	1
Potassium bromide -----	1.5
Sodium hydroxide -----	10
Sodium thiosulphate -----	20
Water to make 1 liter.	

After a contact time of 10 seconds, a dense black silver image of the original is obtained.

Example 2

A sheet of paper is coated as in Example 1 with a layer which contains a white pigment, for example, barium sulfate. To the said layer is then applied a layer having the following composition:

	G.
Carboxymethylcellulose of low viscosity -----	40
Sodium thiosulphate -----	30
1-ethyl-2(1H)-tetrahydropyrimidinethione -----	0.032
Water to make 1 liter.	

After development in a developer having the composition:

	G.
Anhydrous sodium sulphite -----	70
Hydroquinone -----	16
1-phenyl-3-pyrazolidone -----	1
Potassium bromide -----	1.5
Sodium hydroxide -----	10
Water to make 1 liter.	

and after the transfer, results equally as good as those of Example 1 are obtained.

Example 3

Using a developer of the composition:

	G.
Anhydrous sodium sulphite -----	60
Hydroquinone -----	15
1-phenyl-3-pyrazolidone -----	1
Sodium hydroxide -----	7
Sodium carbonate -----	10
Potassium bromide -----	1
1-methyl-2(1H)-tetrahydropyrimidinethione -----	0.022
Water to make 1 liter.	

an exposed negative is developed in contact with a transfer material, which is obtained by application of the following solution to a sheet of paper:

	G.
Gelatin -----	80
Carboxymethyl cellulose -----	20
Ag ₂ S (colloidal) -----	0.03
Sodium thiosulphate -----	35
Water to make 1 liter.	

Using this material, positive images of better density and deeper blacks are obtained than with the same material and developer without addition of 1-methyl-2(1H)-tetrahydropyrimidinethione.

Example 4

To a sheet of paper is applied a solution having the following composition:

	G.
Gelatin -----	150
Carboxymethyl cellulose -----	22
Ag ₂ S (colloidal) -----	0.05
Sodium thiosulphate -----	60
2(1H)-tetrahydropyrimidinethione -----	0.03
Water to make 1 liter.	

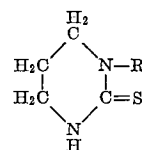
This positive material and an exposed negative are each moistened in a developer as in Example 2 and thereafter

brought into contact with each other. After a contact time of about 12 seconds, a deep black positive image of the original is obtained.

The foregoing examples illustrate methods of using 2(1H)-tetrahydropyrimidinethiones in accordance with the processes and products of the present invention. It is to be understood, however, that these examples are preferred embodiments, and are not to be considered as limiting the invention thereto. It is clear to those skilled in the art that the practice of the invention lends itself readily to a number of useful modifications, especially with regard to the ingredients of the light-sensitive photographic material, the transfer material and the developer composition, for example, as developers, numerous conventional products are useful, e.g., p-methyl aminophenol, p-aminophenol, hydroquinone, diaminophenols, 4-aminopyrazolones and 1-aminophenyl-3-aminopyrazolones, and the developer composition may be alkalized by adding thereto alkali-metal hydroxides, alkali-metal carbonates or tertiary alkali-metal phosphates. The developers may contain any stabilizing agents, anti-fog agents and antioxidants, such as alkali-metal sulphites or salts of hydroxylamine. Chemical compounds which can be used as silver halide solvents include, for example, water-soluble thiosulphates, such as alkali-metal thiosulphate, ammonium thiosulphate and alkaline earth thiosulphates.

What is claimed is:

1. In a process for the production of a direct positive print from an original by developing an imagewise-exposed light-sensitive silver halide emulsion layer in a silver halide developer solution containing a silver halide solvent and contacting the silver halide emulsion layer during the course of the development with an image-receiving layer that is insensitive to light and contains development nuclei, in which developing process the silver halide from the unexposed areas of the silver halide emulsion layer is dissolved and transferred to the said image-receiving layer and is reduced on the said image-receiving layer to a silver image, the improvement of contacting the silver halide emulsion layer with the image-receiving layer in the presence of a 2(1H)-tetrahydropyrimidinethione having the general formula



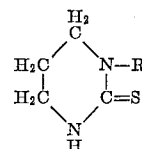
wherein R stands for a radical selected from the group consisting of hydrogen and alkyl radicals containing from 1 to 5 carbon atoms.

2. A process as defined in claim 1 in which the 2(1H)-tetrahydropyrimidinethione is added to the developer.

3. A process as defined in claim 1 in which the 2(1H)-tetrahydropyrimidinethione is added to the image-receiving layer.

4. A process as defined in claim 1 in which the 2(1H)-tetrahydropyrimidinethione is added to both the image-receiving layer and the developer solution.

5. An image-receiving material that is insensitive to light which comprises a paper support coated with a layer of a hydrophilic colloidal substance containing development nuclei and containing an amount between about 1 and 200 milligrams per square meter of surface of a 2(1H)-tetrahydropyrimidinethione having the general formula

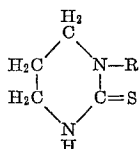


wherein R stands for a radical selected from the group

consisting of hydrogen and alkyl radicals containing 1 to 5 carbon atoms.

6. The image-receiving material according to claim 5 wherein the hydrophilic colloidal substance is selected from the group consisting of gelatin, casein, carboxy methyl cellulose, starch, starch ethers, starch esters, galactomannans, polymannuronic acids, polymannuronic acid esters, polymannuronic acid amides, polyvinyl alcohol and polyvinyl alcohol derivatives.

7. An aqueous alkaline developer solution containing a developer for silver halides and between 1 and 200 milligrams per liter of a 2(1H)-tetrahydropyrimidine-thione having the general formula



in which R is a radical of the group consisting of hydrogen and alkyl radicals containing from 1 to 5 carbon atoms.

References Cited by the Examiner

UNITED STATES PATENTS

2,901,351	8/1959	Van Pee et al.	260—256.5
3,017,270	1/1962	Tregillus	96—29

FOREIGN PATENTS

753,434	7/1956	Great Britain.
783,793	10/1957	Great Britain.
867,174	5/1961	Great Britain.

OTHER REFERENCES

Chemical Abstracts, 46, 3885 (1952).

NORMAN G. TORCHIN, *Primary Examiner*.