United States Patent Office 3,260,604 Patented July 12, 1966

3,260,604

PHOTOGRAPHIC COLLOID TRANSFER SYSTEM

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No Drawing. Filed Nov. 19, 1963, Ser. No. 324,820
20 Claims. (Cl. 96—101)

This invention relates to colloid transfer photographic materials, more particularly to light-sensitive materials which are suitable for roomlight handling.

In the photographic colloid transfer system, as described in Yutzy et al. U.S. Patents 2,596,756 and 2,716,059, an unhardened silver halide photographic emulsion containing a tanning developer is exposed to an image and after sufficient development, the developing silver halide emulsion is pressed against a surface to transfer a stratum of unexposed, untannned gelatin to the receiving surface. In this way, a positive image is obtained of the exposed image.

In one embodiment of colloid transfer, the silver halide emulsion used for office copying purposes is handled in roomlight so that there is a need for adding a substance to the emulsion which acts to reduce the emulsion speed to a level which will permit roomlight handling in light, such as fluorescent light, rich in blue light. However, it is necessary to preserve the sensitivity of the emulsion to incandescent lamps, sufficiently to permit exposure on the office copying apparatus.

Methylene blue has been proposed for this purpose. However, methylene blue has not been entirely satisfactory since it interferes with certain spectral sensitizers causing a loss in sensitized speed which is reflected in requiring increased exposure. In some instances, the incorporated developer causes the emulsion containing methylene blue to become resensitized both to the printing light and to roomlight. Moreover, there is a limited desensitization possible with methylene blue, since the desensitization approaches a maximum asymptotically as the concentration is increased.

It has been desirable to find an additive for the unhardened colloid transfer type emulsions which contain tanning type silver halide developers, which would overcome the disadvantages of methylene blue. However, such an additive needs to be stable to provide for good keeping. It needs to be inert to the incorporated developers in the emulsion and to be compatible with both methylene blue and the silver halide emulsions. In addition, the additive should not interfere with the tanning action of the developer on the colloid such as gelatin in the exposed non-image areas so that poor transfers result.

I have found that certain lower dialkoxy derivatives of 5-phenyl tetrazole can be used to overcome some of the deficiencies of methylene blue in the colloid transfer emulsions. These tetrazoles increase the desensitization of methylene blue and reduce its interference with the spectral sensitivity of the emulsion.

One object of this invention is to provide an unhardened silver halide emulsion containing a desensitizer which permits roomlight handling of the emulsion without seriously reducing its sensitivity to the printing light. A further object is to provide an additive to a methylene blue desensitized colloid transfer silver halide emulsion which increases the desensitization obtained from methylene blue and decreases its interference with spectral sensitization therein.

The above objects are attained by incorporating into a methylene blue desensitized emulsion at least one lower dialkoxy derivative of 5-phenyl tetrazole. The preferred species are dimethoxyphenyl tetrazole compounds. However, other lower dialkoxy derivatives are, for example, diethoxy, dipropoxy, dibutoxy, etc.

A useful method of incorporating the tetrazole is to dissolve it in a small amount of a water-miscible solvent such as, for example, acetone, methanol, ethanol, etc.

In our preferred embodiment 0.5 to 3 grams of the tetrazole per mole of silver halide are added to a spectrally sensitized, substantially unhardened colloid silver halide emulsion containing a desensitizing amount of methylene blue and a tanning silver halide developer. A useful amount of methylene blue is 15 mg.–250 mg. per mole of silver halide, but a preferred range is from 30 mg.–100 mg./mole.

Although our preferred emulsion is a silver chloride emulsion, other silver halide emulsions can be used, including silver bromide, silver iodide, silver chlorobromide, silver chloroiodide, silver bromoiodide, and silver chlorobromoiodide. Mixtures of these may also be used.

The tanning developers which may be used are those disclosed in the above U.S. patents describing colloid transfer emulsions. In addition, non-tanning silver halide developers may be incorporated in the emulsions as described in the above patents or used in the developing solution to improve the density of the transferred image.

The colloid transfer emulsions of this invention may also be used to prepare lithographic plates, and the emulsions of this invention may be exposed either by the reflex method or through appropriate optical systems, depending upon the speed of the emulsion used, the desired result, etc.

The concentration of the tanning developing agent in the emulsion is dependent in part upon the result desired but can be of the order of 350 grams of tanning developing agents per kilogram of silver nitrate converted to silver halide, used in making the emulsion, to obtain good density or about 250 grams per kilogram of silver nitrate to obtain adequate density and an emulsion having optimum keeping properties.

The photographic emulsion layer used in this process can be a dispersion of silver halide grains in a colloid vehicle such as gelatin or in a resin such as polyvinyl alcohol, polyacrylamide, etc., capable of being differentially tanned.

It is necessary for the successful operation of the invention that the emulsion layer be not harder than would be the case with gelatin containing 0.25 ounce of formaldehyde solution (40 percent diluted 1:3 with water); or 0.7 gram of dry formaldehyde per pound when freshly coated; or 0.1 ounce of the solution per pound for a sample aged 3 to 6 months. By "substantially unhardened" as used herein, and in the appended claims, it is to be understood that this means a hardness of the order obtained with gelatin treated with formaldehyde under the conditions above.

The following examples are intended to illustrate my invention but not to limit it in any way.

A substantially unhardened gelatino-silver halide emulsion containing 1 mole of silver chloride, 300 grams of gelatin and 5700 grams of water is gelled, noodled and washed for one-half hour with water, then melted at 40° C., and the following addition made:

650 grams of 8 percent aqueous saponin, 600 grams of a dispersion of 4-phenylcatechol prepared by dissolving 50 grams of 4-phenylcatechol in 70 grams of dibutyl phthalate at 80° C., and pouring it into a vigorously stirred solution of 50 grams of gelatin in 50 grams of 8 percent aqueous saponin solution and 500 cc. of water at 40° C.

To this emulsion is added a green sensitizing merocyanine dye, methylene blue at a concentration of 30 mg./mole silver halide, and to each sample to be tested, a tetrazole in an amount as shown in the table below. The tetrazole is dissolved in a small amount of methanol. The

emulsion is coated at 190 mg. of silver per square foot on a paper support and dried.

The following tetrazoles were used in the above emulsions:

Tetrazoles

I. 5-phenyltetrazole
II. 5-(4-cyanophenyl)tetrazole
III. 5-(4-carboxyphenyl)tetrazole
IV. 5-dimethylaminotetrazole
V. 5-(3-hydroxyphenyl)tetrazole
VI. 5-(2-cyanophenyl)tetrazole
VII. 1-(2,5-dichlorophenyl)-5-methyltetrazole
VIII. 5-(p-methoxyphenyl)tetrazole
IX. 2-ethyl-1,5-dimethyltetrazolium-p-toluenesulfonate
X. 5-(3,4-dimethoxyphenyl)tetrazole

The results shown in the table below were obtained by testing with light, which simulated blue light, and also with white light in which the light to which the emulsion is inherently sensitive had been removed. The test using the Wratten No. 4 filter (B) indicates the response of the emulsion to white light which has the light to which the emulsion is inherently sensitive, removed therefrom. The test using the Wratten No. 35 and 39A filters (A) shows the response to white light in which all wavelengths of the spectrum have been removed except for the blue light. Each set of samples are grouped under a control containing no tetrazole, indicating the data obtained at the same time as the given control.

Coating No.	Tetrazole (conc., g./mole)	Wratten No. 35 and 38A Filters		Wratten No. 4 Filter		Speed Ratio
		Relative Speed (A)	Fog	Relative Speed (B)	Fog	B:A
50	None	100	.10	151	.12	1.51
51	I (1.0)	33	.08	30	.12	.91
54	II (1.0)	32.5	.13	49	.20	1.45
07	None	100	.09	83	.09	.83
10	III (1.5)	85	.08	55	.08	.65
12	IV (1.5)	85	.08	54	.08	.65
16	V (1.5)	43	.07	16	.08	.37
18	VI (1.5)	39	.07	24	.08	.61
20	VII (1.5)	105	.07	91	.08	.86
22	VIII (1.5)	63	.08	40	.08	.64
24	IX (1.5)	89	.08	38	.08	.43
57	X (1.0)	50	.06	162	.10	3.24

The coatings in each instance were exposed on a Verifax Regent Copier to incandescent light for 20 seconds, immersed for 60 seconds in an activator solution having the folowing composition:

	Grams
$Na_2CO_3 \cdot H_2O$	40
Urea	50
Water to 1 liter.	

held at a temperature of 81° F. and rolled in contact with Verifax matrix paper.

Compounds which show usefulness in the practical tests with the above copier using incandescent lamps have a lower basic speed (A) than the control and a significantly higher ratio of *B:A* than the control.

Coating **57** showed about ⅔ times the printing time of coating **50** and twice the roomlight tolerance. There was no appreciable change in contrast. Compounds I–IX did not improve roomlight handling.

It will be appreciated that other silver halide emulsions used for room copying purposes and the like can also be desensitized according to this invention. These include those employing the diffusion or chemical transfer system, hardened emulsions, those employing binders known in the art other than differentially tannable colloid binders, etc.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can

be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

I claim:

1. A substantially unhardened methylene blue desensitized gelatino-silver halide emulsion containing a gelatin tanning silver halide developer and 5-(3,4-dimethoxyphenyl)tetrazole.

2. A substantially unhardened methylene blue desensitized gelatino-silver halide emulsion containing a gelatin tanning silver halide developer and 0.5 to 3 grams per mole of silver halide of 5-(3,4-dimethoxyphenyl)tetrazole.

3. A process of preparing a methylene blue desensitized substantially unhardened gelatino-silver halide emulsion for roomlight handling containing a gelatin tanning silver halide developer, comprising dissolving 5-(3,4-dimethoxyphenyl)tetrazole in a water-miscible solvent and adding said tetrazole to the substantially unhardened gelatino-silver halide emulsion.

4. A process of preparing a methylene blue desensitized substantially unhardened gelatino-silver halide emulsion for roomlight handling containing a gelatin tanning silver halide developer, comprising dissolving 5-(3,4-dimethoxyphenyl)tetrazole in a water-miscible solvent and adding the said tetrazole to the substantially unhardened gelatino-silver halide emulsion in an amount of 0.5 to 3 grams of said tetrazole per mole of silver halide.

5. A substantially unhardened methylene blue desensitized gelatino-silver halide emulsion containing a gelatin tanning silver halide developer and a 5-(3,4-lower dialkoxyphenyl)tetrazole.

6. A substantially unhardened methylene blue desensitized gelatino-silver halide emulsion containing a gelatin tanning silver halide developer and 0.5 to 3 grams per mole of silver halide of 5-(3,4-lower dialkoxyphenyl)-tetrazole.

7. A process of preparing a methylene blue desensitized substantially unhardened gelatino-silver halide emulsion for roomlight handling containing a gelatin tanning silver halide developer, comprising dissolving a 5-(3,4-lower dialkoxyphenyl) tetrazole in a water-miscible solvent and adding said tetrazole to the substantially unhardened gelatino-silver halide emulsion.

8. A process for preparing a methylene blue desenitized substantially unhardened gelatino-silver halide emulsion for roomlight handling containing a gelatin tanning silver halide developer, comprising dissolving a 5-(3,4-lower dialkoxyphenyl)tetrazole in a water-miscible solvent and adding said tetrazole to the substantially unhardened gelatino-silver halide emulsion in an amount of 0.5 to 3 grams of said tetrazole per mole of silver halide.

9. A substantially unhardened methylene blue denssitized gelatino-silver halide emulsion containing a gelatin tanning silver halide developer and 5-(3,4-diethoxyphenyl)tetrazole.

10. A substantially unhardened methylene blue desensitized gelatino-silver halide emulsion containing a gelatin tanning silver halide developer and 5-(3,4-diethoxyphenyl)tetrazole.

11. A substantially unhardened methylene blue desensitized gelatino-silver halide emulsion containing a gelatin tanning silver halide developer and 5-(3,4-dibutoxyphenyl)tetrazole.

12. A substantially unhardened methylene blue desensitized gelatino-silver halide emulsion containing a gelatin tanning silver halide developer and 0.5 to 3 grams per mole of silver halide of 5-(3,4-diethoxyphenyl)tetrazole.

13. A substantially unhardened methylene blue desensitized gelatino-silver halide emulsion containing a gelatin tanning silver halide developer and 0.5 to 3 grams per mole of silver halide of 5-(3,4-dipropoxyphenyl)tetrazole.

14. A substantially unhardened methylene blue desensitized gelatino-silver halide emulsion containing a gelatin tanning silver halide developer and 0.5 to 3 grams per

mole of silver halide of 5-(3,4-dibutoxyphenyl)tetrazole.

15. A process of preparing a methylene blue desensitized substantially unhardened gelatino-silver halide emulsion for roomlight handling containing a gelatin tanning silver halide developer, comprising dissolving 5-(3,4-diethoxyphenyl)tetrazole in a water-miscible solvent and adding said tetrazole to the substantially unhardened gelatino-silver halide emulsion.

16. A process of preparing a methylene blue desensitized substantially unhardened gelatino-silver halide emulsion for roomlight handling containing a gelatin tanning silver halide developer, comprising dissolving 5-(3,4-dipropoxyphenyl)tetrazole in a water-miscible solvent and adding said tetrazole to the substantially unhardened gelatino-silver halide emulsion.

17. A process of preparing a methylene blue desensitized substantially unhardened gelatino-silver halide emulsion for roomlight handling containing a gelatin tanning silver halide developer, comprising dissolving 5-(3,4-dibutoxyphenyl)tetrazole in a water-miscible solvent and adding said tetrazole to the substantially unhardened gelatino-silver halide emulsion.

18. A process of preparing a methylene blue desensitized substantially unhardened gelatino-silver halide emulsion for roomlight handling containing a gelatin tanning silver halide developer, comprising dissolving 5-(3,4-diethoxyphenyl)tetrazole in a water-miscible solvent and adding the said tetrazole to the substantially unhardened gelatino-silver halide emulsion in an amount

of 0.5 to 3 grams of said tetrazole per mole of silver halide.

19. A process of preparing a methylene blue desensitized substantially unhardened gelatino-silver halide emulsion for roomlight handling containing a gelatin tanning silver halide developer, comprising dissolving 5-(3,4-dipropoxyphenyl)tetrazole in a water-miscible solvent and adding the said tetrazole to the substantially unhardened gelatino-silver halide emulsion in an amount of 0.5 to 3 grams of said tetrazole per mole of silver halide.

20. A process of preparing a methylene blue desensitized substantially unhardened gelatino-silver halide emulsion for roomlight handling containing a gelatin tanning silver halide developer, comprising dissolving 5-(3,4-dibutoxyphenyl)tetrazole in a water-miscible solvent and adding the said tetrazole to the substantially unhardened gelatino-silver halide emulsion in an amount of 0.5 to 3 grams of said tetrazole per mole of silver halide.

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