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NITROSOPYRIMIDINE DESENSITIZING COMPOUNDS AND PHOTOGRAPHIC EMULSIONS CONTAINING THEM

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7 Claims. (Cl. 96—101)

This invention relates to photographic emulsions, and more particularly, to photographic emulsions containing nitrosopyrimidine desensitizing compounds.

It is known that photographic silver halide emulsions can be treated with various chemical compounds which cause desensitization and that the emulsions can be fogged and then used to produce direct positive images. For example, Kendall and Hill U.S. Patent 2,541,472, issued February 13, 1951, describes direct positive photographic silver chloride emulsions containing various heterocyclic compounds having at least one nitro group attached to a benzene nucleus as desensitizers.

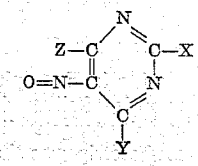
It is also a matter of common knowledge that certain photographic silver halide emulsions can be exposed to blue light and that upon exposure of the emulsions to long wavelength radiation before they are developed, some of the effect of the original exposure is destroyed so that a direct positive image is obtained. This is known as the Herschel effect.

The prior art has also described direct positive photographic emulsions containing various desensitizing dyes. (Mees, "The Theory of the Photographic Process," 1942, pages 280–282). The difficulty accompanying the use of many desensitizing dyes is that they are frequently highly colored and sometimes leave stain in the finished prints. Since some of these desensitizers are rather highly colored, they also sensitize the emulsions to certain regions of the spectrum, causing a negative sensitivity to long wavelengths of light. In order to eliminate this unwanted absorption, it is necessary to use special filters or combinations of filters, thus increasing the exposure time required to produce a photographic reproduction.

It is, therefore, an object of our invention to provide photographic silver halide emulsions containing certain desensitizing compounds. Another object is to provide photographic emulsions which have been fogged and are useful in producing direct positive photographic images. Still another object is to provide compounds for desentizing photographic silver halide emulsions which are only slightly colored and have substantially no absorption in the region of the spectrum to which direct positive photographic emulsions are conventionally exposed. Other objects will become apparent from a consideration of the following description and examples.

According to our invention, we provide photographic silver halide emulsions containing a nitrosopyrimidine compound selected from those represented by the following general formula:

(I)



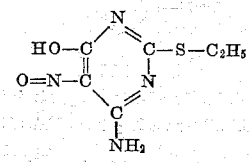
wherein X is an amino group (e.g., amino, methylamino, ethylamino, etc.), a hydroxyl group, a lower alkyl group (e.g., methyl, ethyl, propyl, etc.), a mercapto group or an alkylmercapto group (e.g., methylmercapto, ethylmercapto, etc.), and Y and Z each represents a hydroxyl group or an amino group (e.g., amino, methylamino, ethylamino, etc.).

The nitrosopyrimidine compounds of our invention can be used to desensitize photographic silver halide emulsions intended for the production of direct positive images. For this purpose, the nitrosopyrimidine compounds can be added to the emulsion during any step in the preparation thereof, or the nitrosopyrimidine compounds can be added by bathing the coated emulsion in a solution containing the desired desensitizing compound. For making direct positive photographic emulsions, the nitrosopyrimidine compounds of our invention are advantageously added to the emulsion during the preparation thereof, either before or after the after-ripening. The emulsion can then be fogged by exposure to light or, alternatively, the emulsion can be fogged by treatment with a suitable fogging composition, such as an alkaline solution containing formaldehyde. Other chemical fogging agents can also be employed.

The nitrosopyrimidine compounds represented by Formula I above can also be used to desensitize photographic emulsions which require rather intense light for exposure, and are exposed to subdued light during processing. However, the nitrosopyrimidine compounds of our invention are particularly useful in the preparation of direct positive photographic emulsions.

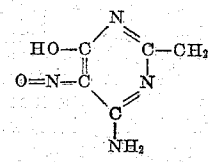
The nitrosopyrimidine compounds of our invention comprise a well-known class of organic compounds, the preparation of which has been previously described in the technical literature. Typical of such compounds are the following:

(1)



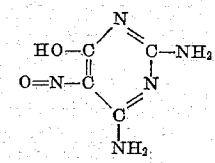
4-amino-6-hydroxy-2-ethylmercapto-5-nitrosopyrimidine
("Bull. Soc. Chem.," vol. 12, pages 78–83 (1945))

(2)



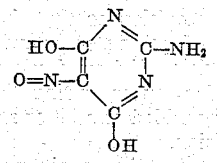
4-amino-6-hydroxy-2-methyl-5-nitrosopyrimidine
("Ann.," vol. 432, page 266 (1923))

(3)



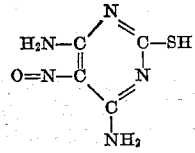
2,4-diamino-6-hydroxy-5-nitrosopyrimidine
("Berichte," vol. 33, page 1371 (1900))

(4)



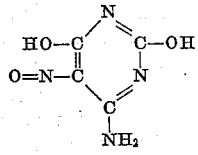
2-amino-4,6-dihydroxy-5-nitrosopyrimidine
("J. Prakt. Chem.," vol. 49, page 35 (1894))

(5)



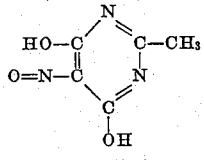
4,6-diamino-2-mercapto-5-nitrosopyrimidine
("J.A.C.S.," vol. 70, p. 3111 (1948))

(6)



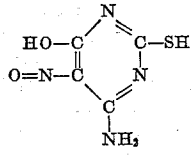
4-amino-2,5-dihydroxy-5-nitrosopyrimidine
("J.A.C.S.," vol. 55, page 1668 (1933))

(7)



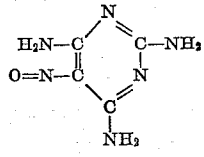
4,6-dihydroxy-2-methyl-5-nitrosopyrimidine
("Ann.," vol. 432, page 286 (1923))

(8)



4-amino-6-hydroxy-2-mercapto-5-nitrosopyrimidine
("Ann.," vol. 331, page 71 (1904))

(9)



2,4,6-triamino-5-nitrosopyrimidine
("J.A.C.S.," vol. 69, page 1814 (1947))

As an example of the preparation of one of the above compounds, ethyl cyanoacetate was reacted with thiourea in the presence of sodium ethoxide to produce 6-amino-4-hydroxy-2-mercaptopyrimidine. This latter compound was then reacted with sodium ethoxide to convert the mercapto group to the ethylmercapto group. The ethylmercapto compound was then nitrosated in the usual manner with nitrous acid to produce 6-amino-2-ethylmercapto-4-hydroxy-5-nitrosopyrimidine.

The above nitrosopyrimidine compounds are either colorless or only slightly colored, and they are readily soluble in processing solutions so that they do not leave stain in the finished prints. Moreover, these compounds do not have unwanted absorptions of the type mentioned above, so that no special filters are required to remove unwanted blue absorption (requiring a deeper filter than the conventional filters used in direct positive work), or green or red absorption, in which case low minimum densities cannot be obtained regardless of the filter used. In some instances, the nitrosopyrimidine compounds of our invention can be used without any filter, further reducing the required time of exposure.

The nitrosopyrimidine compounds of our invention are quite stable in the emulsion so that they can be added before any chemical fogging step or even during the precipitation of the emulsion, if desired, whereas many known desensitizers will decompose during the chemical fogging and can only be added at a latter stage in the preparation of the emulsion.

A further advantage of our nitrosopyrimidine compounds is that their effect increases rapidly up to about

1–2 grams per mole of silver halide, but only very slowly at higher concentrations. The result is that the concentration is not critical when a maximum effect is desired. From a practical standpoint, this is an improvement over some otherwise useful desensitizers which show a decided optimum concentration, below and above which photographic speed is lost.

It appears that the nitrosopyrimidine compounds of our invention are effective because of the strong electron-accepting properties of the nitroso group, which absorbs photolytic electrons, preventing them from combining with ionic silver to produce the elemental silver specks which make the silver developable. However, the pyrimidine ring and the other groups attached to the ring have a strong effect upon the activity of the nitroso group and substitution in the 2-position of the pyrimidine ring is especially important. It has been found that mercapto, alkylmercapto, alkyl or amino groups in the 2-position produce compounds which are more useful than those containing hydroxyl or chloro groups in this position.

The photographic silver halide emulsions useful in our invention contain a predominant amount of silver chloride. The emulsions can contain small amounts of other halides, such as up to about 2% of silver bromide or up to about 1% of silver iodide. Accordingly, it is to be understood that our invention contemplates emulsions containing at least about 95 mole percent of silver chloride. As indicated above, the quantity of desensitizing compound is not critical, although we have found that generally from about 0.1 to 4.0 g. of desensitizer per mole of silver chloride is adequate.

The following examples will serve to illustrate more fully the method of practicing our invention.

Example 1

A gelatino-silver-chloride emulsion was melted at 40° C. and divided into three portions, each portion containing approximately 0.05 mole of silver chloride. Compound 1 above was dissolved in methanol (75 mg./3.75 cc. of methanol) and then added to each aliquot portion of emulsion at concentrations of 0.01, 0.1 and 1.0 g./mole of silver chloride. A portion of the same emulsion containing 0.05 mole of silver chloride emulsion to which 25 cc. of distilled water were added served as a control.

After the addition of Compound 1, the emulsions were held at 40° C. for 30 minutes, and coated on glossy, single-weight, baryta-coated paper stock at a coverage of approximately 850 ft.^{2}/mole of silver chloride. The coatings were then exposed in an Eastman Type I*b* Sensitometer to a standard step-wedge and developed in a developer having the following composition:

	Grams
N-methyl-p-aminophenol sulfate	3.1
Sodium sulfite, desiccated	45.0
Hydroquinone	12.0
Sodium carbonate, desiccated	67.5
Potassium bromide	1.9
Water to make 1.0 liter.	

The coatings were then fixed, washed and dried in the usual manner. As compared with the control coating containing no desensitizing compound, the coating containing 10 mg. of Compound 1 per mole of silver chloride was 0.5 log E slower, the coating containing 100 mg. was about 2.0 log E slower, and the strip containing 1.0 g. was approximately 3.7 log E slower.

Example 2

A strip from the coating in Example 1 containing 0.1 g. of Compound 1 per mole of silver chloride was flashed 4 seconds to a high intensity tungsten light source. Using the same light source, the strip was then exposed for 15 seconds to a calibrated step tablet through a Kodak Wratten No. 4 Filter, i.e., a filter transmitting radiation only beyond about 455 mμ. After development, fixing,

washing and drying as in Example 1, the strip had a density of 1.4 at the end which received the least yellow light exposure and 0.05 at the end which received the most yellow light exposure. When exposed and processed in exactly the same manner, a control strip showed only a uniform black.

Example 3

A sample (3580 g.) of a silver chloride emulsion was melted, fogged at a high pH with formaldehyde, and acidified in the manner of U.S. Patent 2,541,472, Example 2. Then 500 cc. of a 0.2 percent methanol solution of Compound 1 was added per mole of silver. A coating aid and hardener were added and the emulsion was coated on a thin paper and dried. The coating was exposed to the tungsten light source, used in Example 2, through the calibrated step tablet, developed, fixed, washed and dried in the same manner as Example 2. A good quality direct positive print (i.e., density decreased with increasing exposure) having high contrast and low minimum density resulted.

Example 4

Example 3 was repeated using 500 cc. of a 0.2 percent solution of Compound 4 (dissolved in 0.2 percent NaOH) per mole of silver in place of Compound 1. In this test the exposure was made through a Kodak Wratten No. 4 Filter plus the step tablet and again a high contrast, low minimum density direct positive print resulted.

Example 5

An emulsion was prepared in the manner of Example 3 using 1.0 g. of Compound 5 per mole of silver in place of Compound 1. Exposure of the coated paper was through a Kodak Wratten No. 2A Filter (i.e., a filter transmitting only radiation longer than 410 mμ), and again a good quality direct positive print resulted.

Example 6

In the manner of Example 3, 1.0 g. of Compound 6 was added per mole of silver and the coating exposed through a Wratten No. 4 Filter to give a good quality direct positive print.

Example 7

In the manner of Example 3, 5 millimoles of Compound 7 was added per mole of silver and the coating exposed through a Wratten No. 4 Filter to give a good quality direct positive print.

Example 8

In the manner of Example 3, 5 millimoles of Compound 8 was added per mole of silver. In this case, no filter was required during exposure to get a good quality direct positive print.

Example 9

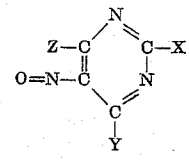
In the manner of Example 3, 5 millimoles of Compound 9 was added per mole of silver, and the coating exposed through a Wratten No. 4 Filter to give a good quality direct positive print.

The nitrosopyrimidine compounds of our invention can be added to the emulsions in methanol solution, as illustrated in the above examples. Other solvents, such as pyridine, ethanol, dioxane, etc., can also be used to dissolve the nitrosopyrimidine compounds of our invention. Mixtures of solvents can also be employed sometimes to advantage.

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.

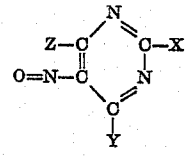
What we claim as our invention and desire secured by Letters Patent of the United States is:

1. A direct positive photographic silver halide emulsion containing at least 95 mole percent, based on the silver halide content of said emulsion, of substantially uniformly, strongly fogged silver chloride grains and a desensitizing amount of a compound selected from the class represented by the following general formula:



wherein X represents a member selected from the class consisting of amino, methylamino, ethylamino, a hydroxyl group, a lower alkyl group, a mercapto group and an alkylmercapto group, and Y and Z each represents a member selected from the class consisting of a hydroxyl group, amino, methylamino and ethylamino.

2. A direct positive photographic gelatino-silver-halide developing-out emulsion comprising at least 95 mole percent, based on the silver halide content of said emulsion, of substantially uniformly, strongly fogged silver chloride grains and a desensitizing amount of a compound selected from the class represented by the following general formula:



wherein X represents a member selected from the class consisting of amino, methylamino, ethylamino, a hydroxyl group, a lower alkyl group, a mercapto group and an alkylmercapto group, and Y and Z each represents a member selected from the class consisting of a hydroxyl group, amino, methylamino and ethylamino.

3. A direct positive photographic emulsion comprising at least 95 mole percent, based on the silver halide content of said emulsion, of substantially uniformly, strongly fogged silver chloride grains and a desensitizing amount of 4 - amino - 6 - hydroxy - 2 - ethylmercapto - 5 - nitrosopyrimidine.

4. A direct positive photographic emulsion comprising at least 95 mole percent, based on the silver halide content of said emulsion, of substantially uniformly, strongly fogged silver chloride grains and a desensitizing amount of 2-amino-4,6-dihydroxy-5-nitrosopyrimidine.

5. A direct positive photographic emulsion comprising at least 95 mole percent, based on the silver halide content of said emulsion, of substantially uniformly, strongly fogged silver chloride grains and a desensitizing amount of 4,6-diamino-2-mercapto-5-nitrosopyrimidine.

6. A direct positive photographic emulsion comprising at least 95 mole percent, based on the silver halide content of said emulsion, of substantially uniformly, strongly fogged silver chloride grains and a desensitizing amount of 4-amino-2,5-dihydroxy-5-nitrosopyrimidine.

7. A direct positive photographic emulsion comprising at least 95 mole percent, based on the silver halide content of said emulsion, of substantially uniformly, strongly fogged silver chloride grains and a desensitizing amount of 4 - amino - 6 - hydroxy - 2 - mercapto - 5 - nitrosopyrimidine.

References Cited in the file of this patent

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2,541,472	Kendall et al.	Feb. 13, 1951
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