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DESENSITIZATION OF PHOTOGRAPHIC EMULSIONS

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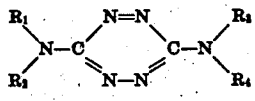
5 Claims. (Cl. 95—7)

This invention relates to photographic baths and particularly to improvements in the desensitization of photographic emulsions by treatment in such baths.

It is known that gelatino-silver halide emulsions can be desensitized with, for example, mercuric cyanide, pinakryptol yellow and pinakryptol green. It has now been found that 3:6-diamino 1.2.4.5.tetrazines are powerful desensitizers for neutral emulsions. Such compounds have the general formula:



where R_1, R_2, R_3, R_4 are hydrogen, alkyl, such as methyl, or ethyl, aryl, such as phenyl or tolyl, aralkyl such as phenylethyl, or acyl such as acetyl, propionyl or benzoyl, or other monovalent organic radicals. The most powerful desensitizing effect appears to be exerted by the simple diamine where R_1, R_2, R_3, and R_4 are all hydrogen atoms. At a concentration as low as .0002 gram per litre simple 3:6-diaminotetrazine lowers the speed of a fast negative emulsion to less than half its original speed.

According to the present invention, therefore, a photographic emulsion, particularly a gelatino-silver halide emulsion, is desensitized by treatment with a substituted or unsubstituted 3:6-diaminotetrazine. The treatment may take place by bathing the emulsion before development in a solution of the free base, or in a solution of a salt of the base, from which the base itself may afterwards be liberated by treatment with alkali, e. g., the alkali of a developer. Alternatively, the desensitizer may be present in a photographic developer so that its action is exerted during development.

Preferably unsubstituted 3:6-diaminotetrazine is used, which is a red crystalline solid stable to air and light and fairly soluble in water. It may be kept in the form of a stock solution of one part in one thousand parts of water and such solution is also quite stable to light and air. It is a reducing agent and will develop a latent image but the salts are water-soluble solids generally yellow in colour and are not reducing agents. The red solution of the free base even at the concentration indicated does not stain the fingers or gelatine or film base and is not poisonous. Although it is a developer, it has no harmful effect on latent images as is shown by the fact that an exposed photographic plate bathed for two minutes in a one-in-five thousand aqueous solution shows no trace of latent image destruction. Its desensitizing power is, like that of pinakryptol yellow, effected by sulphite in the developer but its desensitizing power is comparable with that of mercuric cyanide or pinakryptol green, disregarding the effect of the developer.

The following table shows the desensitizing effect of the free base in three different concentrations compared with three known desensitizers. A panchromatic film was treated for two minutes in the desensitizing solution and exposed for two minutes through a tricolour and neutral balanced step wedge, 1 metre from a 25 watt lamp and then developed in the dark. In the table is shown the light intensity required to give the density of .1 above the fog.

Desensitization	Concentration	Fog	Neutral	Red	Blue	Green
Control		.14	1	1	1	1
II	1:10,000	.16	137	137	137	137
II	1:5,000	.15	137	137	137	220
II	1:2,000	.16	350	220	220	690
$Hg(CN)_2$	1:10,000	.11	110	110	174	137
Pinakryptol yellow	1:2,000	.11	870	------	220	--------
Pinakryptol green	1:5,000	.23	690	1,370	275	--------

In the above table the effect of the developer on the desensitizing agent was neglected.

In the following table we show similar comparative tests in which the film was bathed for two minutes in the desensitizer, then subjected to the developer for two minutes, then exposed for two minutes under the same conditions as above, and finally development was completed for six minutes in the dark. Under these conditions the desensitizing action of the tetrazine was greatly reduced at concentrations of 1 in 10,000 and 1 in 5,000. Concentrations of 1 in 2,000 or 1 in 1,000 still had good desensitizing properties. In the table the ratio of light intensities to give a density of 0.1 above fog is shown. Since the control is treated without first desensitizing it shows only the desensitizing effect due to the developer. Since the developer desensitizes roughly

to one-sixth of the initial speed, the total desensitization is represented by the figure for the desensitization alone multiplied by six.

Desensitization	Concentration	Fog	Neutral	Red	Blue	Green	Total desensitization for green
Control		.21	1	1	1	1	6
II	1:10,000	.21	22	22	22	22	132
II	1:2,000	.16	69	55	55	87	522
Pinakryptol green*	1:10,000	.27	500	500	500	500	
$Hg(CN)_2$	1:10,000	.16	35	35	55	35	210
Do*	1:2,000	.21	350	220	170	550	
Pinakryptol yellow	1:10,000	.14	137	220	55	550	
Do*	1:2,000	.23	550		137		

*High fog density.

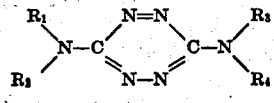
As can be seen the effect of the developer on the desensitizer for at least 4–6 minutes after bathing at 1:2,000 is negligible.

Although the desensitizing power of 3:6-diaminotetrazine is less than that of pinakryptol green, or pinakryptol yellow, it is sufficiently powerful for practical purposes and for the same fog density is practically equal to that of mercuric cyanide. On the other hand, mercuric cyanide brings about a latent image destruction equivalent to reduction in speed of 50% at 1:2,000 and about 30% at 1:10,000, whereas 3:6-diaminotetrazine, as stated above, has no action.

The manufacture of 3:6-diaminotetrazine is given in Gazzetta Chimica Italiana, 43 (2) (1913) at page 162 and 45 (I) at page 182.

I claim:

1. The method of desensitizing a gelatino-silver halide emulsion prepared by the neutral process, which comprises treating it in a bath containing a compound having the following formula:



where R_1, R_2, R_3 and R_4 are selected from the group consisting of hydrogen, alkyl, aryl, aralkyl, and acyl.

2. The method of desensitizing a gelatino-silver halide emulsion prepared by the neutral process, which comprises treating it in a bath containing a 3:6-diaminotetrazine.

3. The method of desensitizing a gelatino-silver halide emulsion prepared by the neutral process, which comprises treating it after exposure in a bath containing a 3:6-diaminotetrazine.

4. The method of desensitizing a gelatino-silver halide emulsion prepared by the neutral process, which comprises treating it after exposure in a bath containing a 3:6-diaminotetrazine in an amount of at least 0.0002 gram per liter.

5. The method of desensitizing a gelatino-silver halide emulsion prepared by the neutral process, which comprises exposing it and developing it in a bath containing a 3:6-diaminotetrazine in an amount of at least 0.0002 gram per liter.

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