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FINE GRAIN DEVELOPERS

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5 Claims. (Cl. 95—88)

This invention relates to addition agents for photographic developers.

A number of compounds have been found which, when added to a developer of moderate or low activity, decrease the graininess produced by that solution. These are mostly solvents for silver halide and include thiocyanates, thiosulfates and thioureas. The common theory attributes their action to the dissolving of the silver halide and its redeposition physically from the solution upon the development centers in a more evenly dispersed state. The use of all of these compounds is accompanied by significant losses in emulsion speed and the speed loss for a given reduction in graininess or, conversely, the reduction in graininess for a given loss in emulsion speed varies widely with the nature of the compound.

Many of the known addition agents produce high dichroic fog and, in addition, they may be unstable in the alkaline developing solutions and, on standing, especially following aeration, decompose to sodium sulfide which not only produces a high fog but also stains or scums on the surface of films.

It is, therefore, an object of the present invention to provide novel addition agents for photographic developers. A further object is to provide addition agents for photographic developers which will produce a reduction in graininess of the image. A still further object is to provide addition agents for photographic developers which will produce a reduction in graininess without a great loss in emulsion speed. A further object is to provide addition agents for developers which will produce a reduction in graininess without the production of high fog. Another object is to provide more stable addition agents which will not decompose when the developer solution is stored or aerated. Other objects will appear from the following description of our invention.

These objects are accomplished by incorporating in a photographic developer a quaternary nitrogen salt of a benzothiazole, especially a quaternary nitrogen salt of an aminobenzothiazole.

During the course of these investigations, the properties of these addition agents have been checked by a number of different methods of exposure, development, and measurement of graininess. Most of the quantitative data were gathered by exposing films carrying a gelatino-silver halide emulsion behind a gray step wedge and developing strips of these for different periods in a special developing machine, using high agitation to produce uniform results. The emulsion speed was usually determined by the minimum useful gradient method, which was checked by threshold and inertia speeds. Graininess was preferably determined by matched enlargements from negatives of equal printing contrast but this method was supplemented by direct microscopic comparison at 20 diameters.

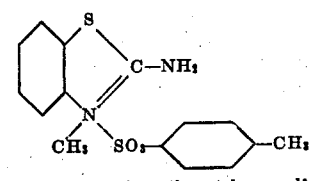
A comparison of graininess was made by assigning numbers to degrees of graininess differing by equal graininess increments as judged visually. By assigning a graininess value to a high speed photographic emulsion developed in a standard developer, the relative graininess values could then be recorded for the same emulsion developed in the same developer with the addition of the various agents used according to our invention.

These addition agents were tested in a number of different formulas but, in addition, all were tested in the following basic developer formula for intercomparison:

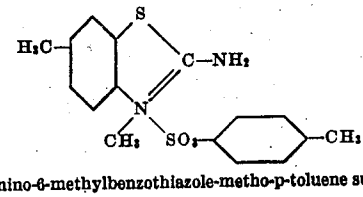
Monomethyl-p-aminophenol sulfate	grams	5
Sodium sulfite (anhydrous)	do	100
Sodium metaborate	do	2
Water to	liter	1

The addition agents were either dissolved directly in the developer or added from stock solutions.

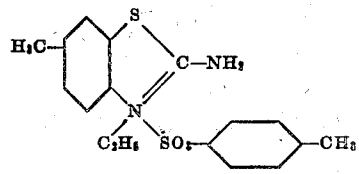
The following compounds were found to be effective for use in photographic developers:



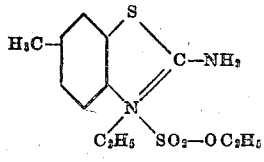
2-aminobenzothiazole-metho-p-toluene sulfonate



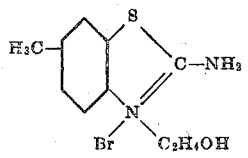
2-amino-6-methylbenzothiazole-metho-p-toluene sulfonate



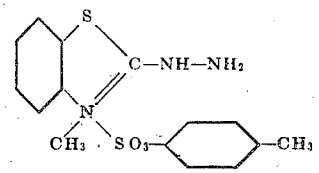
2-amino-6-methyl benzothiazole-etho-p-toluene sulfonate



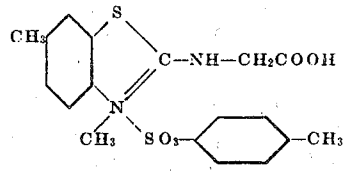
2-amino-6-methyl benzothiazole, etho-ethyl sulfonate



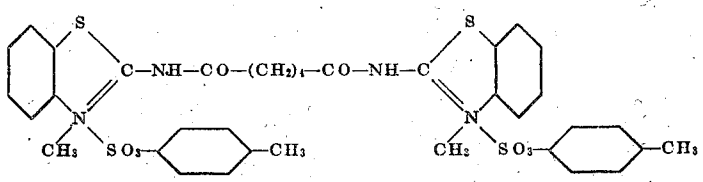
2-amino-6-methyl benzothiazole, β-hydroxyetho bromide



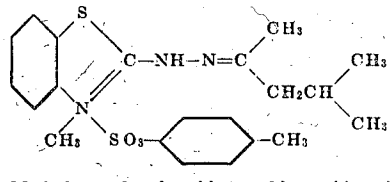
2-hydrazino benzothiazole-metho-p-toluene sulfonate



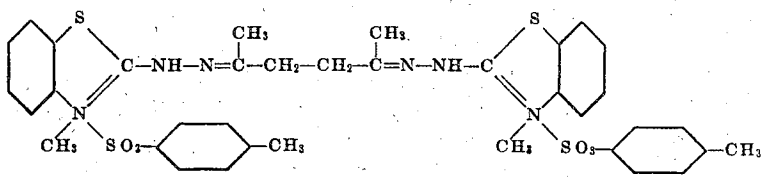
6-methyl-2-benzothiazoyl glycin-metho-p-toluene sulfonate



Adipamide-bis (2-benzothiazole-metho-p-toluene sulfonate)



Methyl-secondary butyl-ketone-2-benzothiazoyl hydrazone-metho-p-toluene-sulfonate



Diacetonyl-di(2-benzothiazoyl-ketone)di-(metho-p-toluene sulfonate)

The amino-benzothiazoles may be prepared by the methods commonly described in the literature, for example from the corresponding thiourea or from the 2-chlorobenzothiazole. When these agents are substituted in the "6" position, they are preferably prepared by direct thiocyanogenation of the corresponding amine (see Kaufmann, Berichte 67B; 944-48, 1934). The glycin is formed by the reaction of the amine with chloracetic acid in acetic acid solution. The quaternary salts may be readily prepared by heating the amine with methyl-p-toluene sulfonate or diethyl sulfate, etc.

These compounds were used in concentrations ranging from 0.10 gram per liter to the solubility limit, which is somewhat less than 5 grams per liter. Quantities of from 0.5 to 2 grams per liter were found to be especially effective.

The following examples illustrate developing solutions containing the addition agents used according to our invention:

Example 1

Monomethyl p-aminophenol sulfate	grams	5.0
Sodium sulfite (anhydrous)	do	100.0
Sodium metaborate	do	2.0
Potassium bromide	do	1.0
2-amino-6-methyl benzothiazole-metho-p-toluene sulfonate	grams	0.5
Water to	liter	1.0

This solution, developing in about 25 minutes at 68° F., gives a greater graininess reduction than that produced by the ordinary p-phenylenediamine developers and is free of staining properties.

Example 2

Monomethyl p-aminophenol sulfate	grams	1.0
Hydroquinone	do	4.0
Sodium sulfite (anhydrous)	do	15.0
Sodium carbonate (anhydrous)	do	22.5
Potassium bromide	do	1.1
2-amino-6-methyl benzothiazole, etho-ethyl sulfonate	grams	0.15
Water to	liter	1.0

This formula possesses a remarkably short development time for a fine grain developer yielding a gamma of about 1.0 in 5 minutes at 68° F. on a high speed roll film.

Example 3

N-(ethyl-3-methyl-4-aminophenyl)glycineamide	grams	5.0
2-amino-6-methyl-benzothiazole-metho-p-toluene sulfonate	grams	0.2
Sodium sulfite (anhydrous)	do	100.0
Sodium metaborate	do	20.0
Water to	liter	1.0

The chemicals are dissolved in the order given in hot water (about 160° F.). This solution requires 30 to 60 minutes development time, depending on the emulsion and degree of agitation at 68° F. It gives especially large reductions in graininess with only moderate losses in emulsion speed, and especially low fog.

Example 4

N-(ethyl-3-methyl-4-aminophenyl glycineamide	grams	5.0
2-amino-6-methyl-benzothiazole-metho-p-toluene sulfonate	grams	0.2
Sodium sulfite (anhydrous)	do	50.0
p-Hydroxy-phenyl-glycin	do	5.0
Sodium metaborate	do	10.0
Water to	liter	1.0

The chemicals are dissolved in the order given in hot water (about 160° F.). This solution requires 15 to 30 minutes development time at 68° F. It gives slightly less graininess reduction than Example 3 but has the advantages of shorter time of development and also gives low fog. (The glycineamide developer used in this formula is described in Dickey and McNally U. S. application Serial No. 301,446, filed October 26, 1939).

In addition to their property of reducing the graininess of the image, we have found that many of the addition agents used according to our invention decrease the fog produced. For example, with 2-aminobenzothiazole metho-p-toluene sulfonate the net fog is only ½ or less that obtained without the addition of the agents used according to our invention. Similarly, with adipamide-bis-(2-benzothiazole metho-p-toluene sulfonate) an appreciable reduction in fog is noted.

The following table illustrates the relative values of graininess, emulsion speed, and fog obtained by using the compounds of our invention in the basic Elon developer formula given above. These values are for a high speed panchromatic roll film.

Addition	Grams per liter	Emulsion speed	Graininess [1]	Net fog
2-aminobenzothiazole-metho-p-toluene sulfonate	0.5	62	28	0.11
	1.0	40	22	0.07
	2.0	27	16	0.02
2-amino-6-methyl-benzothiazole-etho-ethyl sulfate	0.5	52	23-24	0.03
Adipamide-bis (2-benzothiazole-metho-p-toluene sulfonate).	0.7	65	30	0.08
	5.0	30	19	0.03
None		100	40	0.16

[1] Empirical scale based on equal visual increments.

Most of the addition agents producing low graininess usually give a warm or brownish image although a cold tone may be produced. A glossy, sometimes whitish, surface is also a common characteristic.

In addition to the ordinary Elon or Elon-hydroquinone developers, other developing agents may be used with the addition agents of our invention. Elon was found to be as sensitive to addition agents as any of the conventional developers. Developing agents requiring a high pH such as hydroquinone were inefficient. p-Phenylenediamine was very sensitive to the addition agents of our invention when used in weakly alkaline solutions. Certain p-phenylenediamine derivatives were found to be even more sensitive, and to produce lower graininess when the agents of our invention were added to them.

These agents may not only be used in solutions employing only one developing agent but also in solutions employing two or more developing agents such as Elon and hydroquinone; paraphenylenediamine or its derivatives and a p-hydroxyphenyl glycin; or paraphenylenediamine, p-hydroxyphenyl glycin, and Elon.

In addition to the use of quaternary salts of benzothiazoles, the quaternary salts of structurally analogous heterocyclics may be used; for example, the sulfur atom of the benzothiazole ring may be replaced by an ethylene group as in the quinoline ring or by an imino group as in the benzimidazole ring.

It will be understood that the formulas included herein are illustrative only and that our invention is to be taken as limited only by the scope of the appended claims.

We claim:

1. A fine-grain photographic developer comprising a developing agent and a quaternary nitrogen salt of a 2-aminobenzothiazole.

2. A fine-grain photographic developer comprising a developing agent and a 2-aminobenzothiazole alkyl-p-toluene sulfonate.

3. A fine-grain photographic developer comprising a developing agent and a 2-aminobenzothiazole metho-p-toluene sulfonate.

4. A fine-grain photographic developer comprising a developing agent and 2-amino-6-methyl-benzothiazole-metho-p-toluene sulfonate.

5. A fine-grain photographic developer comprising a developing agent and 2-amino-6-methyl benzothiazole, etho-ethyl sulfonate.

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