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FINE GRAIN PHOTOGRAPHIC DEVELOPER

Paul W. Vittum, Rochester, N. Y., assignor, by mesne assignments, to Eastman Kodak Company, Jersey City, N. J., a corporation of New Jersey

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4 Claims. (Cl. 95—88)

This invention relates to photographic developers and more particularly to developers which produce a fine-grain image.

It is desirable in developing photographic films which are to be used for producing an image by projection either for cinematographic purposes or for still pictures, to have a fine-grain image on the negative. Numerous methods have been suggested for obtaining these fine-grain images on development. Among these methods are the use of a developing agent which produces a fine-grain image, such as paraphenylene-diamine, and the addition of special agents which slow down the speed of development. Many of these methods have the disadvantage of causing fog on development or require the use of poisonous or otherwise undesirable developing agents. In prior Patent Number 2,053,516 granted September 8, 1936 to J. I. Crabtree and myself, the use of ammonium chloride in metol-hydroquinone developers was described. These developers produce a fine-grain image but they possess the undesirable feature of loss of ammonia on aeration.

The principal object of the present invention is to provide a non-fogging photographic developer which is effective in reducing graininess of the image. A further object is to provide a fine-grain photographic developer which is stable toward aeration.

These objects are accomplished in the present invention by adding certain aliphatic amine salts, namely, acid-reacting, aliphatic-substituted ammonium salts, to the developer.

In producing a fine grain photographic developer according to my invention, I add to an ordinary photographic developing solution a salt of a primary, secondary, or tertiary aliphatic amine such as an alkylamine or an alkanolamine or an alkylenediamine. I prefer to use the hydrochloride of these compounds but I may also use the salts formed by reaction with sulphuric acid, nitric acid, or acetic acid. The following compounds may be used in producing effective fine-grain developers:

Primary amine salts

$C_2H_5NH_2 \cdot HCl$ ..... Ethylamine hydrochloride

$(C_2H_4OH)NH_2 \cdot HCl$ ..... Ethanolamine hydrochloride

$CH_2—CH_2$
$NH_2 \quad NH_2 \cdot HCl$ ..... Ethylenediamine hydrochloride

Secondary amine salts

$(C_2H_5)_2NH \cdot HCl$ ..... Diethylamine hydrochloride

$(C_2H_4OH)_2NH \cdot HCl$ ..... Diethanolamine hydrochloride

Tertiary amine salts

$(C_2H_5)_3N \cdot HCl$ ..... Triethylamine hydrochloride

$(C_2H_4OH)_3N \cdot HCl$ ..... Triethanolamine hydrochloride

The following developing solutions containing amine salts, which are given by way of example only, may be used according to my invention.

Example 1

p-Methylaminophenol sulfate	grams	5
Hydroquinone	do	2.5
Sodium sulfite (desiccated)	do	80
Ethanolamine hydrochloride	do	75
Sodium metaborate	do	6
Potassium bromide	do	1
Water to	liter	1

Example 2

p-Methylaminophenol sulfate	grams	2
Hydroquinone	do	5
Sodium sulfite (desiccated)	do	100
Ethanolamine hydrochloride	do	75
Sodium metaborate	do	2
Water to	liter	1

Example 3

p-Methylaminophenol sulfate	grams	5
Hydroquinone	do	2.5
Sodium sulfite (desiccated)	do	80
Ethylenediamine dihydrochloride	do	50
Sodium metaborate	do	6
Potassium bromide	do	1
Water to	liter	1

Example 4

p-Methylaminophenol sulfate	grams	2
Hydroquinone	do	5
Sodium sulfite (desiccated)	do	100
Ethylenediamine dihydrochloride	do	50
Sodium metaborate	do	2
Water to	liter	1

Example 5

Amidol (diaminophenol hydrochloride)	grams	2.5
Ethylenediamine dihydrochloride	do	50
Sodium sulfite (desiccated)	do	50
Potassium bromide	do	0.25
Water to	liter	1

Example 6

p-Aminophenol oxalate	grams	2.5
Sodium sulfite (desiccated)	do	50
Ethylenediamine hydrochloride	do	50
Sodium metaborate	do	10
Potassium bromide	do	0.5
Water to	liter	1

The aliphatic amine salts used in the developing solutions according to my invention may be prepared by neutralizing an aqueous solution of the desired amine with an acid and separating the pure amine salt by evaporation. The preparation of these compounds however, forms no part of my invention. An alternate procedure consists of forming the salt in the developing solution by adding to the developing solution equivalent amounts of the amine and the acid.

While in a number of the above examples I have referred to developers in which the developing agent is paramethylaminophenol sulfate and hydroquinone, usually referred to as "M-Q", it is to be understood that developers may be prepared according to my invention in which other types of developing agents are used. For example, developers containing developing agents such as diaminophenol hydrochloride, paraminophenol oxalate, etc., may be used as fine grain developers upon addition of the aliphatic amine salts which I have disclosed.

In addition to the aliphatic amine salts referred to above I may use salts of other aliphatic amines, for example, salts of methyl, ethyl, propyl, or higher alkyl amines. I may also use salts of substituted alkyl amines such as benzylamine. Other compounds which may be used according to my invention are cycloalkylamines such as cyclohexylamine and unsaturated aliphatic amines as propenylamines. In the case of the alkylene diamine I may use either the mono- or the dihydrochloride.

The compounds which I have described do not function in equal degrees as fine-grain producing agents but all of them will reduce the grain size of the developed image to some extent. I have found that in general the primary amines are better for this purpose than the secondary amines and that the secondary amines are, in turn, better than the tertiary amines. The alkylamines are ordinarily better than the alkanolamines. In each case, however, the grain size on development was found to be much less than when the developer was used alone without the addition of an amine salt.

In using a photographic developer it is frequently necessary to agitate the developing solution in order to secure uniformity of development. This agitation tends to bring the developing solution into contact with the air to a greater extent than if it were not agitated. It has also been proposed to blow air through the developer in order to secure agitation. For this reason it has been found that a fine grain developer containing ammonium chloride loses its activity quite rapidly as a result of loss of ammonia from the solution. When amine salts are used in place of ammonium chloride, the developer is more stable toward aeration and can be used for a longer time without being replenished.

What I desire to claim and secure by Letters Patent of the United States is:

1. A fine-grain photographic developer comprising a developing agent and a strong acid salt of ethylenediamine.

2. A fine-grained photographic developer comprising a developing agent and an ethylenediamine hydrochloride.

3. A fine-grain photographic developer comprising an M-Q developing agent and an ethylenediamine hydrochloride.

4. A fine-grain photographic developer comprising diaminophenol hydrochloride and ethylenediamine dihydrochloride.

PAUL W. VITTUM.