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FOG INHIBITOR FOR PHOTOGRAPHIC EMULSIONS

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This invention relates to fog inhibitors for photographic emulsions and to photographic emulsions containing them.

It is known that photographic emulsions particularly ultra-sensitive emulsions, or those containing color sensitizers exhibit a tendency to form a deposit of silver in the emulsion. This deposit extends more or less uniformly over the entire emulsion and is known as fog. Photographic fog is of two types, local and general. Local fog is formed by exposure of the film or plate at undesired points, as by a light leak in the camera. General fog or, as it is sometimes known, chemical fog, is formed in a number of ways. It may be caused by the conditions under which the film or plate is stored, such as conditions of high temperature or unusually long time of storage. The nature of the emulsion, as where emulsions are highly sensitive may also produce chemical fog, as well as the conditions of development of the emulsion, as by development for protracted periods of time or at temperatures above normal. Highly sensitive emulsions are more likely to fog than those of lower sensitivity, owing to the small amount of energy required to make a silver halide grain developable. We are concerned primarily with general or chemical fog.

The primary object of the present invention is to provide anti-fogging or fog inhibiting agents for ultra-sensitive photographic emulsions and to thereby increase the stability of the emulsions. A further object is to provide anti-fogging agents which do not markedly lower the sensitivity of the emulsion.

These objects are accomplished by incorporating in the emulsion an alicyclic amine containing at least two NH_2 groups either or both of which may be unsubstituted or substituted with an alkyl radical or with certain other radicals.

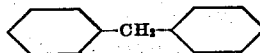
The compounds which we use as fog inhibiting agents are alicyclic amines having two or more NH_2 groups in the same nucleus or in different nuclei. These NH_2 groups may be in either a benzene or in a naphthalene type of ring and they may be unsubstituted or substituted with a single alkyl radical, or aceto radical, or with two alkyl radicals, or with an alkyl radical and an aceto radical.

These compounds are incorporated in a fast negative emulsion, particularly a silver halide emulsion. The emulsion used may be one which is intended to be used directly after emulsification or one which is subjected to ripening by

treatment at a high temperature or by treatment with ammonia.

The compounds used according to our invention may be divided into two classes. The first class includes those compounds in which the amino groups are contained in a single ring of the benzene or the naphthalene type. The second class includes those in which the amino groups are in different rings each of the benzene or naphthalene type joined as in diphenyl. Under the first class of compounds we have used the phenylene diamines and their derivatives. These include para-phenylene diamine, meta-phenylene diamine and ortho-phenylene diamine; amino substituted derivatives, such as para-amino dimethyl aniline (sulfate), para-amino diethylaniline, para-amino dibutyl aniline (hydrochloride), para-amino methyl acetaniline and tetramethyl phenylene diamine; ring substituted derivatives, such as 2:5-diamino toluene (hydrochloride), 2:5-diamino anisole (hydrochloride), 2:4-diamino toluene, 2:4-diamino phenyl (hydrochloride) and 2:4-diamino anisole (hydrochloride). The second class of compounds includes benzidine and its derivatives and diphenyl methane derivatives. These include benzidine, amino substituted derivatives of benzidine, such as tetra-methyl benzidine and diacetyl benzidine; ring substituted derivatives of benzidine, such as ortho-tolidine and dianisidine. The diphenyl methane derivatives include p:p'-diamino diphenyl methane; amino substituted derivatives such as tetra-methyl diamino diphenyl methane; p:p'-tetra-ethyl diamino diphenyl methane; ring substituted derivatives, such as 2:2'-4:4'-tetra-amino 5:5'-dimethyl diphenyl methane (sulfate).

In the diphenyl methane type of compound, which has the following structural formula:



the CH_2 group between the rings may be replaced by other groups, such as $-(\text{CH}_2)_n-$, $-\text{S}-$, $-\text{O}-$.

In these compounds the benzene nucleus may be substituted by a naphthalene nucleus which may contain substituent groups in the ring, as described above for the benzene ring compounds. The compounds described above do not all function equally well as fog inhibitors and different amounts are required to secure the maximum fog inhibiting effect. This effect will depend to some extent on the type of emulsion used. In general, the amount of fog inhibiting agent used in the

emulsion will vary from .01 gram to 5 grams per 1000 ccs. of wet emulsion. The following table will serve to illustrate amounts which we have found to be satisfactory. In each case the amount specified is used with 1000 ccs. of a gelatino-silver halide emulsion.

	Grams
p-Phenylenediamine	.01-1
p-Aminodimethylaniline	.05-1
10 p-Aminodiethylaniline	.05-1
p-Aminodibutylaniline	.05-5
p-Aminomethylacetanilide	1-5
Tetramethylphenylenediamine	.1- 2
2:5-diaminotoluene·2HCl	.01-1
15 2:5-diaminoanisole·2HCl	.05-1
m-Phenylenediamine	.2-5
2:4-diaminotoluene	1-5
2:4-diaminophenol·2HCl	.05-1
2:4-diaminoanisole·2HCl	.05
20 o-Phenylenediamine	1-5
Benzidine	1
Tetra-methylbenzidine	1
Diacetyl benzidine	less than 1
o-Tolidine	do 1
25 Dianisidine	1
p-p'-Diaminodiphenylmethane	1
Tetra-methyldiaminodiphenylmethane	1-5
p - p' - Tetra - ethyldiaminodiphenylmethane	1-5
30 2:2' - 4:4' - tetra - amino - 5:5' - dimethyldiphenylmethane (sulfate)	less than 1-5

It is to be understood that more or less of the anti-fogging agent than the amount stated above may be used. Generally, however, if a greater amount is used in the emulsion, either no increased fog inhibiting effect is obtained, or there is a decrease in the sensitivity of the emulsion. These compounds may be incorporated by mixing them with any suitable solvent which is inert with respect to the sensitive emulsion, such as water, methyl alcohol, ethyl alcohol, acetone and others. The following examples, which are by way of illustration only, indicate methods of incorporating the anti-fogging agents in emulsions according to our invention.

Example I

A gelatino-silver halide negative emulsion which contained sensitizing agent and which had been made in the usual way and had a pH of 7.4, was heated on a water bath sufficiently to melt it. To a 1000 cc. portion of this emulsion there were added 50 ccs. of an ethyl alcohol solution containing the .5 gram of para-phenylene diamine. The resulting solution was thoroughly mixed and was coated on glass plates, dried, and incubated for 7 days at 60° C. to obtain a fog test. The fogging produced at the end of this time was very much less than that produced on a plate coated with the emulsion to which no fog inhibiting agent had been added.

Example II

A gelatino-silver halide negative emulsion which contained sensitizing agent and which had been made in the usual way and had a pH of 7.4, was heated on a water bath sufficiently to melt it. To a 1000 cc. portion of this emulsion there was added 100 ccs. of a water solution of p-aminodibutyl aniline hydrochloride containing 1 gram of this compound. The resulting solution was thoroughly mixed and was coated on glass plates,

dried and incubated for 7 days at 60° C. to obtain a fog test. The fogging produced at the end of this time was very much less than that produced on a plate coated with the emulsion to which no fog inhibiting agent had been added.

Example III

A gelatino-silver halide negative emulsion which contained sensitizing agent and which had been made in the usual way and had a pH of 7.4, was heated on a water bath sufficiently to melt it. To a 1000 cc. portion of this emulsion there were added 100 ccs. of an ethyl alcohol solution containing 1 gram of benzidine. The resulting solution was thoroughly mixed and was coated on glass plates, dried and incubated for 7 days at 60° C. to obtain a fog test. The fogging produced at the end of this time was very much less than that produced on a plate coated with the emulsion to which no fog inhibiting agent had been added.

The fog inhibiting agents which we have described may be used in various kinds of photographic emulsions. In addition to being useful in ordinary non-color sensitized emulsions they may also be used in orthochromatic, panchromatic and X-ray emulsions. They may be used with or without color sensitizing dyes and if used with the sensitizing dyes they may be added to the emulsion before or after the dyes are added. Various silver salts may be used as the sensitive salt, such as silver bromide, silver iodide, silver chloride or mixtures of these. The dispersing agent may be gelatin or other colloids, such as collodion, albumin, or suitable cellulose organic derivatives or artificial resins.

It is to be understood that we contemplate as included within our invention all modifications and equivalents coming within the scope of the appended claims.

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

1. A photographic emulsion comprising gelatin having sensitive silver salts dispersed therein and containing as an anti-foggant 0.2 to 1 gram per 1000 ccs. of wet emulsion of a phenylene diamine.
2. A photographic emulsion comprising gelatin having sensitive silver salts dispersed therein and containing as an anti-foggant 0.2 to 1 gram per 1000 ccs. of wet emulsion of paraphenylene diamine.
3. A photographic emulsion comprising gelatin having sensitive silver salts dispersed therein and containing as an anti-foggant .05 to 1 gram per 1000 ccs. of wet emulsion of an amino dialkyl aniline salt.
4. A photographic emulsion comprising gelatin having sensitive silver salts dispersed therein and containing as an anti-foggant .05 to 1 gram per 1000 ccs. of wet emulsion of p-aminodimethylaniline sulfate.
5. A photographic emulsion comprising gelatin having sensitive silver salts dispersed therein and containing as an anti-foggant .05 to 1 gram per 1000 ccs. of wet emulsion of p-aminodibutylaniline hydrochloride.
6. A gelatino silver halide emulsion containing as an anti-foggant 0.2 to 1 gram per 1000 ccs. of wet emulsion of a phenylene diamine.

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